Editorial corner – a personal view Trends in composite materials: the challenge of single-polymer composites

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An important contribution to environment preservation and energy saving may come from our ability to recover, recycle and/or reuse the materials. Consumer consciousness, waste management regulations and environmental legislation are all pushing the manufacturers of raw-materials and end-products to carefully consider the environmental impact of their products at all stages of the life cycle, including ultimate disposal.

This scenario obviously involves also composite materials, increasingly used in several industrial sectors. In fact, there is a marked interest to improve the methods for recycling and reusing the existing composites, or to develop new ones intrinsically more suitable to be recycled and reused. In this framework, a great deal of efforts has been expended for the development of the so called 'single-polymer' composite (SPC) materials, in which both the reinforcing and the continuous phases are polymers with the same chemical composition. These materials have been also denoted as onepolymer composites, homocomposites, all-(the same) polymer composites, or homogeneity composites. The main advantage of SPCs is that, unlike traditional heterogeneous composites (such as glass- or carbon reinforced polymer composites), they can be entirely melted down at the end of the product life for recycling.

The first example of this kind of composites was reported by Capiati and Porter in 1975, who introduced the concept of single-polymer composites by successfully preparing polyethylene/polyethylene

*Corresponding author, e-mail: alessandro.pegoretti@ing.unitn.it © BME-PT and GTE composites. More recently, the preparation of polypropylene, poly(ethylene-terephthalate), poly-(ethylene-naphthalate), and liquid-crystalline copolyesters single-polymer composites has been extensively studied.

In most cases, SPCs have been obtained through the so called 'hot compaction' technique. The use of temperature and pressure to control the melting of the outer surface layer of polymeric fibres implies that the processing window for the hotcompaction process is quite narrow. Other processing techniques include film or fibres stacking, powder impregnation, solution impregnation, etc.

An intriguing challenge for materials scientists and engineers is to explore new materials combinations to extend the processing window and to develop processing techniques sufficiently versatile to be scaled up at an industrial level.



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Preparation, electrical properties and thermal stability of conductive polyaniline:nylon-6,6 composite films

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Abstract. The polyaniline:nylon-6,6 (PANI:Ny-6,6) composite films were prepared by diffusion process and the oxidative polymerization of aniline within the nylon-6,6 matrix. The composite films were characterized by fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) as well as for their electrical properties. The surface electrical conductivity of the HCl (1 M) doped composite films increases with increase in the polyaniline content of the films. The study of electrical properties under isothermal conditions in the temperature range of 50–130°C showed that the composite films were stable under ambient conditions below 90°C in terms of DC electrical conductivity retention.

Keywords: polymer composites, electrical properties, thermal stability

1. Introduction

There is an explosive increase in the demand for composite materials in the last two decades, which are now available as materials with unique combination of properties. The electronic and optical properties of conducting polymer and insulating polymer matrix combined with attractive mechanical properties and processing advantages of the polymers has now attained a level of maturity consistent with a new set of opportunities to develop a wide range of application based conducting polymer composites. Thus, the composites based on conducting polymers and insulating polymers have been studied as materials for industrial products, such as rechargeable batteries, conductive coatings, light emitting diodes, gas sensors and antistatic materials [1].

Polyaniline has been widely investigated due to its low cost, easy synthesis and high as well as tailorable electrical conductivity depending upon the level of doping, environmental stability and interesting redox properties [2–5]. In spite of its several desirable properties, the insolubility in conventional solvents for processing [6] and poor mechanical strength limit its application [7].

One of the ways to overcome these demerits is to prepare conducting composites of polyaniline by chemical or electrochemical polymerization within an insulating polymer matrix [8, 9]. It is easy to control the chemical polymerization of aniline within the insulating polymer matrix to prepare conducting composites of required electrical properties while retaining the mechanical strength of insulating polymer matrix [10–12]. In this paper, we have reported a simple chemical route to prepare polyaniline:nylon-6,6 composite films. Nylon-6,6 is one of the most popular materials used as fibers and thermoplastics.

2. Experimental

2.1. Reagents and chemicals

The main chemicals used, for the preparation of composite films were: aniline, 99% (CDH, India),

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| Sample ID | Temp | Time | Weight of | Amount of | Weight of film | Weight of films after |
|------------------|------|------|---------------------|--------------------|-------------------|-----------------------|
| Sample ID | [°C] | [h] | nylon-6,6 films [g] | aniline soaked [g] | after soaking [g] | polymerization [g] |
| PANI:Ny-6,6-(1) | 80 | 10 | 0.2658 | 0.0225 | 0.2883 | 0.2984 |
| PANI:Ny-6,6-(2) | 80 | 15 | 0.2658 | 0.0450 | 0.3108 | 0.3217 |
| PANI:Ny-6,6-(3) | 80 | 20 | 0.2658 | 0.0675 | 0.3323 | 0.3450 |
| PANI:Ny-6,6-(4) | 80 | 25 | 0.2658 | 0.0910 | 0.3558 | 0.3682 |
| PANI:Ny-6,6-(5) | 80 | 30 | 0.2658 | 0.1125 | 0.3783 | 0,3916 |
| PANI:Ny-6,6-(5a) | 80 | 30 | 0.1627 | 0.0138 | 0.1765 | 0.2396 |
| PANI:Ny-6,6-(5b) | 80 | 30 | 0.1694 | 0.0148 | 0.1842 | 0.2416 |
| PANI:Ny-6,6-(5c) | 80 | 30 | 0.1794 | 0.0156 | 0.1960 | 0.2643 |

Table 1. Preparation details of polyaniline:nylon-6,6 composites

nylon-6,6 (from Research, Design and Standard Organization), hydrochloric acid, 35% (E. Merck, India), potassium persulphate, 98% (CDH, India).

2.2. Preparation of polyaniline:nylon-6,6 composite films

Square shaped pieces of 0.265 g each were cut from nylon-6,6 sheet and then pressed into thin films by applying pressure of 10 tons in an Electrically Operated Automatic Pressure Machine maintained at a temperature of 220°C. The thickness of films varied in the range of 0.40 to 0.50 mm. Each film was kept for soaking in 30 ml of doubly distilled aniline for different periods of time in an air oven at 80°C to allow aniline diffuse into nylon-6,6 matrix. Aniline soaked films were treated with 0.1 M potassium persulphate in 1 M HCl solution and left for 24 hours at ice temperature in order to polymerize aniline within the nylon-6,6 matrix. Thus prepared polyaniline:nylon-6,6 composite films were washed with doubly distilled water up to acid neutralization and undoped by treatment with excess of aqueous ammonia (1 M) followed by washing with distilled water until the filtrate became neutral. The composite films were dried for 24 hours at 40°C in a dry box and then stored in desiccators for experiments. Polyaniline:nylon-6,6 composite films were doped by treating with 1 M HCl solution at room temperature for 24 hours. The preparation details are given in Table 1.

2.3. Testing methods

For the study of the difference in surface morphology between the parent materials and their composites, SEM micrographs were taken by LEO-435 VP SEM instrument. FTIR spectra of polyaniline: nylon-6,6 composites were recorded by Nicolette-Protégé 460. DC electrical conductivity of the doped composites films was measured with increasing temperature by using a four-in-line probe technique. DC electrical conductivity (σ) was calculated using Equations (1) and (2):

$$\rho = \frac{\rho_0}{G_7 \left(W \,/\, S \right)} \tag{1}$$

$$\sigma = \left(\frac{1}{\rho}\right) \tag{2}$$

where σ , ρ , ρ_0 , W and S electrical conductivity [S/cm], corrected resistivity [$\Omega \cdot cm$], uncorrected resistivity $[\Omega \cdot cm]$, thickness of the film [cm] and probe spacing [cm] respectively [13]. $G_7(W/S)$ is a correction divisor, which is a function of thickness of the sample as well as probe spacing. The sample to be tested is placed on the base plate of four-probe arrangement and the probes were allowed to rest in the middle of the sample. A very gentle pressure is applied on the probes and then it was tightened in this position so as to avoid piercing of the probes into the samples. The arrangement was placed in electrically controlled oven. The current was passed through the outer probes and the floating potential across the inner pair of probes was measured. The power supply of the oven was then switched on, the temperature was allowed to increase gradually. The current and voltage were recorded simultaneously with a rise in the temperature.

The thermal stability of composite samples in terms of DC electrical conductivity retention was studied under isothermal conditions by using four-in-line DC electrical conductivity measuring instrument. This study was carried out at 50, 70, 90, 110 and 130°C on the selected composite films. The electrical conductivity measurements were done at an interval of 10 min.

3. Results and discussion

3.1. Preparation of conducting polymer composite films

The preparation of polyaniline:nylon-6,6 composite films was done by diffusing of aniline into nylon-6,6 matrix. During this process, some amount of nylon-6.6 was dissolved in aniline producing jelly like precipitate above 80°C as well as if kept in aniline for more than 30 hours at 80°C. Therefore, the temperature and duration of soaking of aniline within the nylon-6,6 matrix were selected at 30 hours and 80°C respectively. The composition of composite films for the determination of variation in electrical conductivity of the composite films, due to the change in amount of nylon-6,6, four different samples were prepared as same temperature and time. Hence, a number of HCl doped polyaniline:nylon-6,6 composite film samples were prepared as detailed in Table 2.

When aniline is oxidized with 0.1 M potassium persulphate ($K_2S_2O_8$) in acidic media (HCl), the protonated conducting form of polyaniline (emeraldine salt) is produced with black color [14].

Schöllhörn and Zagefka [15] have suggested a redox reaction for ammonia or amine intercalation into layered metal chalcogenides, which has been further supported by the work of Foot and Shaker [16]. On the basis of disproportionation reaction of ammonia as suggested by Mohammad [17] for the undoping of polythiophene (PTH) by water. The overall chemical reactions are given in Equations (3)–(7):

$$8NH_3 \longrightarrow 6NH_4^+ + 6e^- + N_2 \tag{3}$$

$$PTH^{+}-BF_{4}^{-}+NH_{4}^{+}+e^{-} \longrightarrow PTH+NH_{4}BF_{4} \quad (4)$$

$$6H_2O \longrightarrow 4H_3O^+ + 4e^- + O_2$$
 (5)

$$PTH^{+}-BF_{4}^{-}+H_{3}O^{+}+e^{-} \longrightarrow PTH + HBF_{4} + H_{2}O$$
(6)

$$HBF_4 \longrightarrow HF + BF_3 \tag{7}$$

The charge neutralization reaction depends on the rate of chemical reaction between the doped polymer and undoping agent, which depends upon the reactivity of the polymer chain and basic strength of undoping agent [17]. The basic strength of water is very low, hence, it does not act as an effective undoping agent in the case of polyaniline, however, an analogous neutralization reaction for the undoping of the polyaniline component of the composites by ammonia solution may be suggested as shown by Equations (8) and (9):

 $NH_3 + H_2O \longrightarrow NH_4OH$ (8)

$$[(PANI-nH^{+} (Ny-6,6)][(nCl^{-})] + nNH_4OH$$

$$\longrightarrow PANI(Ny-6,6) + nNH_4Cl + nH_2O \quad (9)$$

Recently, it has been reported that PANI:Ny-6 composite film consisted of layers, the outer layers were conducting composite layers and the inner layer was pristine nylon-6 [18]. In a similar way, it seems that polyaniline is mainly polymerized in the outer layer of the composite film (PANI:Ny-6,6) and this layers retards the diffusion of the oxidant solution to the interior side and prohibits polyaniline from being polymerized inside the film or aniline does not diffuse deep inside the polymer matrix as observed in the cross-sectional view of the films.

3.2. Characterization

3.2.1. SEM studies

Figure 1 shows the SEM photographs of polyaniline, nylon-6,6 and polyaniline:nylon-6,6 compos-

Table 2. Preparation details of HCl doped polianiline:nylon-6,6-(5) composite films

| Comula ID | Amount of | Co | G [S/am] | |
|------------------|--------------------|-------------|-------------|------------|
| Sample ID | aniline soaked [%] | As-prepared | HCl doped | 0 [8/cm] |
| PANI:Ny-6,6-(1) | 08.4 | light green | light brown | very low |
| PANI:Ny-6,6-(2) | 16.9 | light green | light brown | very low |
| PANI:Ny-6,6-(3) | 25.3 | green | dark brown | ~10-5 |
| PANI:Ny-6,6-(4) | 33.8 | green | black | ~10-3 |
| PANI:Ny-6,6-(5) | 42.3 | dark green | black | ~10-1 |
| PANI:Ny-6,6-(5a) | 42.3 | dark green | black | 0.121.10-1 |
| PANI:Ny-6,6-(5b) | 42.3 | dark green | black | 0.262.10-1 |
| PANI:Ny-6,6-(5c) | 42.3 | dark green | black | 0.134.10-1 |

ite at different magnifications. Evidently, the homogeneous formation of composites of polyaniline in the nylon-6,6 matrix is observed. The surface morphology of chemically prepared PANI showed a cloudy structure while that of nylon-6,6 is somewhat granular and the morphology of composite film is totally different from their parent compounds i. e. PANI and nylon-6,6. The difference in surface morphology of composite indicates the binding of the parent component consequently, the formation of a composite.







Figure 1. SEM photograph of a) polyaniline, b) nylon-6,6 and c) of PANI:Ny-6,6-(5) composite film

3.2.2. FTIR studies

The FTIR spectra of polyaniline:nylon-6,6 composites are presented in Figure 2. The band corresponding to out of plane bending vibration of C-H bond of p-disubstituted benzene rings appears at 824 cm⁻¹. The bands corresponding to stretching vibration of N-B-N and N=Q=N structures appear at 1497 cm₋₁ and 1587 cm⁻¹ respectively where -B- and =Q= stand for benzenoid and quinoid moieties in the polymer. The bands corresponding to vibration mode of N=Q=N ring and stretching mode of C–N bond appear at 1143 and 1302 cm⁻¹. The band close to 1130 cm⁻¹ is described as being characteristic of the conducting polymer due to the delocalization of electrical charges caused by deprotonation. The FTIR spectrum supports the presence of benzenoid as well as quinoid moieties in the polyaniline. The characteristic bands at around 688, 1642, 3303 cm⁻¹ attributed to nylon-6,6 are present in all the composites. As-prepared polyaniline: nylon-6,6 composite showed a strong



Figure 2. FTIR spectra of polyaniline:nylon-6,6 composite films. a) PANI:Ny-6,6-(3), b) PANI:Ny-6,6-(4) and c) PANI:Ny-6,6-(5)

band around 1650 cm⁻¹ corresponding to carbonyl group of nylon-6,6. For polyaniline, the band corresponding to out of plane bending vibration of C-H bond of p-disubstituted benzene ring appears around 824 cm⁻¹. The bands corresponding to stretching vibration of N-B-N and N=Q=N structure appear around 1377 cm^{-1} and 1500 cm^{-1} respectively (where -B- and =Q= stand for benznoid and quinoid moieties in the polymer). The band corresponding to stretching mode of C-N bond appears at 1504 cm⁻¹ [19]. The gradual increase in the intensities of the bands corresponding to polyaniline and decrease in the intensities of bands corresponding to nylon-6,6 support the gradual change in the composition of the composite samples.

3.2.3. Stability in terms of DC electrical conductivity retention

Three samples, PANI:Ny-6,6-(3), PANI:Ny-6,6-(4) and PANI:Ny-6,6-(5) were selected for the study of thermal stability in terms of DC electrical conductivity retention. It was observed that the electrical conductivity of PANI:Ny-6,6 composites increased on exposure to HCl, due to doping of polyaniline component of the composite films, as evident from Equation (10) [20, 21]:

$$PANI(Ny-6,6) + nHCl \longrightarrow [(PANI-nH^{+}(Ny-6,6)][(nCl^{-})]$$
(10)

The isothermal stability testing of the HCl doped films in terms of DC electrical conductivity retention was carried out at 50, 70, 90, 110 and 130°C in an air oven. The electrical conductivity measurements were done at an interval of 10 minutes in the accelerated ageing experiments. The electrical conductivity measured with respect to time of accelerated ageing is presented in Figure 3. The thermal stability was also studied by repeatedly measuring DC electrical conductivity with increasing temperature from 30 to 130°C for five times at an interval of 40 minutes.

The electrical conductivity of the polyaniline: nylon-6,6 films was measured from 30 to 130°C and found to be in the semi-conducting region. All the composite films followed the Arhenius equation for the temperature dependence of the electrical conductivity from 30 to 115°C. After that a deviation in electrical conductivity was observed. A combination of all or some of the following factors could be responsible for the decrease in electrical conductivity beyond 130°C such as the loss of dopant and degradation, the chemical reaction of dopant with polyaniline or nylon-6,6, the semi-conductor to metal transition and the approaching of T_g . The studies on the stability of electrical conductivity under isothermal conditions at 50, 70, 90, 110 and 130°C showed that the electrical conductivity is stable at 50, 70 and 90°C supporting the fact that all the composite films were sufficiently stable in term of DC electrical conductivity retention under ambient conditions below 90°C and the electrical conductivity decreases with respect to time at 110 and 130°C may be attributed to the loss of dopant. The stability in terms of DC electrical conductivity retention was observed to be fairly good as studied



Figure 3. Stability in terms of DC electrical conductivity retention under isothermal conditions at 50, 70, 90, 110 and 130°C. a) PANI:Nylon-6,6-(3), b) PANI:Nylon-6,6-(4) and c) PANI:Nylon-6,6-(5)

by isothermal technique. The polyaniline:nylon-6,6 composite films were found to be suitable for use in electrical and electronic applications below 90°C under ambient conditions.

4. Conclusions

The preparation of conductive polyaniline:nylon-6,6 composite films is very successfully demonstrated by diffusion of aniline monomer in to the nylon-6,6 matrix followed by oxidative polymerization of aniline within the nylon-6,6 matrix technique. Thus prepared polyaniline:nylon-6,6 composite films possess high electrical conductivities at higher doping levels. It is also observed that the electrical conductivity of polyaniline:nylon-6,6 films increases with increase in polyaniline content of the composite. The composite material was successfully characterized for their electrical properties, FTIR and SEM. Thermal stability in term of DC electrical conductivity retention is fairly good as studied by several experimental techniques. Most of the formulations of the composites so prepared are suitable for use in electrical and electronic applications below 90°C under ambient conditions.

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Rubber curing chemistry governing the orientation of layered silicate

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Abstract. The effect of curing systems on the orientation and the dispersion of the layered silicates in acrylonitrile butadiene rubber nanocomposite is reported. Significant differences in X-ray diffraction pattern between peroxide curing and sulfur curing was observed. Intense X-ray scattering values in the XRD experiments from peroxide cured vulcanizates indicate an orientation of the layers in a preferred direction as evinced by transmission electron micrographs. However, sulfur cured vulcanizates show no preferential orientation of the silicate particles. Nevertheless, a closer inspection of transmission electron microscopy (TEM) images of peroxide and sulfur cured samples shows exfoliated silicate layers in the acrylonitrile butadiene rubber (NBR) matrix. It was revealed in the prevailing study that the use of an excess amount of stearic acid in the formulation of the sulfur curing package leads to almost exfoliated type X-ray scattering pattern.

Keywords: nanocomposites, acrylonitrile butadiene rubber, montmorillonite, orientation, exfoliation

1. Introduction

Recently, there has been considerable interest in forming nanocomposites as a means to improve several properties of polymers. For this purpose layered silicates are now widely being used. These layered silicates are a class of inorganic materials that are naturally layered in structure. Layered silicate refers both to natural clays like smectite and to synthetic layered silicates such as magadite and mica. Among natural clays, both montmorillonite and hectorite belong to the smectite family and are the most commonly used layered silicates in nanocomposites due to their high cation exchange capacities, large surface area, good surface reactivity and surface adsorptive properties [1].

A considerable number of elastomer nanocomposites consisting of various rubbers and layered silicates have been reported. Different methods of intercalation of layered silicates, such as melt intercalation [2–6], latex coagulation [7–9] and reactive mixing intercalation [10] method have been adopted to prepare rubber nanocomposites.

Acrylonitrile butadiene rubber (NBR) is commonly considered the workhorse of the several industrial and automotive rubber products. This rubber is manufactured by copolymerization of butadiene and acrylonitrile. By selecting appropriate acrylonitrile content one can tailor the different properties in order to use it in different application areas like roll covers, hydraulic hoses, conveyor belting, graphic arts, oil field packers, seals for all kinds of plumbing and appliance applications and also oil, fuel, and chemical resistance materials. It has also excellent temperature resistance properties with wider short-and long-term operating temperature range as much as -40°C to +125°C. Like most unsaturated thermoset elastomers, NBR requires formulating with added ingredients, and further processing to make useful articles. Additional ingredients typically include reinforcement fillers,

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plasticizers, weather protectants, and vulcanization packages.

During the course of rubber curing different types of intermediate chemical species are formed in the rubber matrix. It is expected that vulcanization ingredients can further interact with the organoclay during the vulcanization of rubber at higher temperatures and pressure [11]. These unavoidable interactions could be reflected on the final microstructure of layered silicates.

There is no report stating and comparing the effect of peroxide or sulfur crosslinking on the exfoliation and intercalation process. A group of researchers from Toyota, Japan, reported that ethylene propylene diene monomer (EPDM)-clay nanocomposite can be formed successfully when thiuram sulfide and dithiocarbamate were selected as vulcanization ingredients [4]. They assumed that use of these types of vulcanization accelerators leads to sulfur crosslinking by free radial fashion, which ultimately enhances the gallery gap between two adjacent layers of silicates, and, as a result, the vulcanizates get superior physical properties. On the other hand, use of sulfenamide type accelerator does not bring any positive effect on the exfoliation intercalation process. Recently, Karger-Kocsis et al. reported that primary amine, present as a modifier in the clay, is taking part in the sulfur vulcanization process, and this sulfur vulcanization leads to confined and deintercalated (gallery collapsing) structures of the layered silicate in the hydrogenated nitrile butadiene rubber matrix [12]. In the case of peroxide curing systems they found a passive nature of the primary amine, and finally highly intercalated structures were achieved [13]. However, in their study they have used an organic sulfur compound in peroxide curing formulations which is somewhat surprising. It is expected that zinc oxide along with sulfur containing compound could promote some sort of sulfur crosslinking to the HNBR (hydrogenated acrylonitrile butadiene rubber) matrix though the amount of double bonds is less than 1%. In our present study, quaternary ammonium modified layered silicate has been used as a reinforcing filler in the NBR matrix, and the masterbatch comprised with this filler and NBR was produced by melt mixing method. Attention was given to see the effect of curing chemistry on the intercalation and exfoliation process of the layered silicate. The anisotropic behavior of the filler in the rubber matrix was also investigated by comparing peroxide and sulfur cured systems. Finally, the excess dose of stearic acid in a sulfur vulcanization formulation was used to investigate the role of this fatty acid on the reinforcement process of layered particles.

2. Experimental

Acrylonitrile butadiene rubber (NBR) used in this study was obtained from Lanxess, Leverkusen, Germany (Perbunan 4456 F, Acrylonitrile content [%] 44.0±1.5, Mooney viscosity (ML (1+4) 100°C) 55±5). Zinc oxide, stearic acid, and soluble sulfur employed in this study were obtained from Continental AG (Hannover, Germany). Zinc dimethyldithiocarbamate (ZDMC-80) was collected from RheinChemie Rheinau GmbH, Mannheim, Germany. Dicumyl peroxide (synthesis grade) was purchased from Merck, Hohenbrunn Germany. Organomodified montmorillonite (Nanofil 15), was supplied by Süd-Chemie AG, Moosburg, Germany. This clay contains quaternary ammonium salt as organic modifier and the basal spacing of this organoclay is 2.98 nm.

The NBR masterbatch containing 5 phr (parts per hundred of rubber) organoclay was prepared by an internal mixer (Haake PolyLab-System with Banbury type rotor, Thermo Electron GmbH, Karlsruhe, Germany) with 50 rpm rotor speed and 160°C initial temperature. This mixing step was done during 10 min. After taking out this masterbatch, it was then cooled in the air and other crosslinking agent/vulcanization ingredients were mixed on a two roll open mixing mill with the friction ratio of 1:1.2 rotating at 40°C using 10 min compounding cycle. The curing study was carried out with the help of a moving die rheometer (Scarabaeus V-50, Langgöns, Germany) at 160°C. The stocks were cured under pressure at 160°C to optimum cure (t₉₀). Philips XRD-6000 wide-angle X-ray instrument (WAXD) with Cu-K $_{\alpha}$ radiation (30 kV and 40 mA) and a wavelength of 1.542 Å was used for XRD studies. For this experiment round shaped samples were used with diameter of 25 mm and thickness of about 2 mm. The scanning 2θ angle ranged between 2° and 15° with a step scanning rate of 2 deg/min. Tensile tests have been done with Zwick 1456 (model 1456, Z010, Ulm Germany) with a cross-head speed of 200 mm·min⁻¹ (ISO 527). For TEM experiments ultra-thin sections were cut by a microtome at about -100° C, and the images were taken by JEM 2010 with an acceleration voltage of 200 kV.

3. Results and discussion

3.1. Effect of vulcanization type

The combined cure package in a typical rubber compound comprises the cure agent itself (sulfur or peroxide), together with accelerator, antioxidant, activator and retarding agents. Generally, sulfur curing packages are used if more dynamically elastic and flexible properties are desired, like, for example, in tire tread formulations. The peroxide curing system is useful when several other properties are desirable like compression set, abrasion etc. In our present study these two types of curing packages were used in NBR clay composite in order to find the suitability of those on the reinforcement process by layered silicates. The detailed formulations and processing methods are given in Table 1. Mix I is cured with sulfur vulcanization ingredients and Mix II is crosslinked by peroxide. The XRD scans of organoclay and other rubber vulcanizates are shown in Figure 1. The peak corresponding to d_{001} plane of pure organoclay appears at the spacing gap 2.98 nm. The masterbatch containing 5 phr of organoclay shows the peak position at 3.57 nm which corresponds to the d_{001} plane of the layered silicate. This observation indicates that during mixing at 160°C in the internal mixer further increment in the gallery gap is taking place. This means that some sort of intercalation appears by penetration of macromolecular chains into the gallery of the layered silicates. After curing of this masterbatch by a sulfur system the d_{001} plane shows the peak value at 4.35 nm, but also others broad peaks appear for other higher order reflections. This observation reveals the advanced intercalation process of during sulfur vulcanization. In the pattern of peroxide cured NBR containing 5 phr organoclay, the reflection peak corresponding to a basal spacing (d_{001}) at 3.69 nm is relatively more intense compared to the uncured masterbatch compound. Moreover, also the peak intensity is very pronounced as compared with the sulfur cured system. Higher peak intensity means in this case higher orientations in a particular direction of the layered structure [14]. Such type of orientation of the layer silicate in the rubber matrix is expected in the direction of flow during the processing of the rubber compound [2]. The type of crosslinking (sulfur or peroxide) not only influences the degree of intercalation but also significantly affects the order or coherence nature of the layered particles in the amorphous rubber matrix. Though the degree of intercalation of peroxide cured system is less as compared with sulfur system, in peroxide cured system the clay layers are oriented [2]. TEM pictures are giving a direct visual evidence about this orientation and distribution of the layered silicate in the rubber matrix. Figure 2 shows the sulfur vulcanized NBR matrix filled with 5 phr organoclay, mixed at 160°C initial temperature and cured at 160°C. There are lot of small dark lines which indicate the organoclay particles. These silicate particles are finely and uniformly distributed in the whole region of the rubber sample under visual area. The silicate layers in the rubber matrix are oriented randomly in this sulfur cured NBR vulcanized sheet. However, the peroxide cured vulcanizates show that most of the silicates particles are oriented in a particular direction (Figure 3). It is important to note here that both Mix I and Mix II are coming from the same masterbatch, and the same processing procedures were followed to pre-

organoclay in the NBR matrix which takes place

| Table 1. | Formulations | for the | curing | of NBR |
|-----------|---------------|---------|--------|-----------|
| I HOIC II | 1 ormanations | ioi uie | caring | OI I (DIC |

| Stop I | Mat | Material | | | | |
|-----------------------------------|-------------------------------|-----------|------------|--|--|--|
| (Internal mixer) | NBR | 20 | 0 g | | | |
| (Internar mixer) | Organoclay | 1 | 0 g | | | |
| Masterbatch | | 21 | 0 g | | | |
| | | Mix I [g] | Mix II [g] | | | |
| | Masterbatch* | 105 | 105 | | | |
| Stop II | Zinc oxide | 5 | 0 | | | |
| Step II (Two-roll mixing mill) | Stearic acid | 2 | 0 | | | |
| (1 wo-ron mixing min) | Zinc dimethyl dithiocarbamate | 7 | 0 | | | |
| | Sulfur | 0.5 | 0 | | | |
| | Dicumyl peroxide | 0 | 2 | | | |

*All the weight of the curatives are taken in phr



Figure 1. WAXD patterns of (a) cured NBR gum, (b) organoclay, (c) sulfur cured NBR filled with 5 phr organoclay, (d) peroxide cured NBR filled with 5 phr organoclay and (e) NBR masterbatch filled with 5 phr organoclay

pare the vulcanizates. The rubber samples are prepared in the internal mixer and then by two roll mill



Figure 2. TEM image of sulfur cured NBR matrix filled with 5 phr organoclay



Figure 3. TEM image of peroxide cured NBR matrix filled with 5 phr organoclay

mixing and, finally, hot pressing in a mould. So, it is likely expected that silicate particles are oriented during those processing steps. Since the XRD peak intensity of masterbatch is lower than that of peroxide cured NBR vulcanizate, it can be assumed that most of orientation is likely taking place during mixing by two roll mill. This anisotropic behavior is quite common for layered silicate rubber nanocomposites cured by a peroxide system [2]. So, it can be said at least that in opposite to peroxide curing, sulfur cured vulcanizates show a non-oriented isotropy of the layered silicates. It is assumed that during sulfur curing the conformational rearrangement of the macromolecular chains takes place for providing the sulfur crosslinking sites close together, and in this way the silicate particles are forced to move along with rubber chain in different directions. In the other case of peroxide cured system the rubber chains, more or less, do not sustain further rearrangement in conformations because there a lot of crosslinking sites are available to each other for



Figure 4. TEM image of sulfur cured NBR filled with 5 phr organoclay



Figure 5. TEM image of peroxide cured NBR matrix filled with 5 phr organoclay

covalent bond formation (C-C). By a more precise inspection of the TEM pictures, one finds intercalated and exfoliated structures simultaneously. Figure 4 and Figure 5 show magnifications selected from sulfur and peroxide cured vulcanizates, respectively. Here, most of the visible silicate layer thickness is around few nanometers and length is about multiple of hundred nanometers. Single exfoliated layers can also be found from both of them. Therefore, it could be assumed that most of the silicate layers are monolayers, but sometimes couples of layers are also attached together in the intercalated form. Despite all these facts discussed above, intercalation and exfoliation are the common process during the vulcanization reaction irrespective of the curing chemistry in the NBR matrix.

3.2. Effect of stearic acid

Zinc oxide, stearic acid, organic accelerators and sulfur are the very common ingredients in curing packages of a diene rubber like polybutadiene rubber (BR), styrene butadiene rubber (SBR) natural rubber (NR), etc. The ingredients vulcanize the rubber matrix by sulfur crosslinking under estimated optimum temperature and pressure conditions. Stearic acid in this process plays an important role in the vulcanization mechanism. It dissolves zinc oxide and forms a kind of zinc organic complex with the help of sulfur accelerators. Ultimately, this intermediate reactive sulfur metal complex promotes sulfur crosslinking to the unsaturated rubbers under the vulcanization condition. In our present case we have used different amounts of stearic acid to see the effect of this long chain organic acid on the intercalation/exfoliation process. The XRD pattern of those vulcanizates is shown in Figure 6. It is again remembered that the masterbatch containing 5 phr organoclay leads to a XRD pattern with a basal spacing of the d_{001} plane at 3.57 nm. There are also other higher order reflections corresponding to d_{002} and d_{003} plane. So, after high temperature internal mixing the organoclay obviously remains in a well ordered intercalated form. However, after curing with the addition of vulcanization ingredients with 1 phr stearic acid the basal spacing of d_{001} plane shifts to lower angles corresponding a d_{001} plane gap of 4.12 nm. Obviously, during the sulfur vulcanization further intercalation is taking place. It is also observed that at higher angles at around 9.5° and 12° two sharp peaks arise. It should be noted here that these two peaks are also present even from the gum and they are absent in peroxide cured vulcanizates. So it may be speculated that these peaks may be due to the presence of Zn-sulfur-organic accelerators complex, with crystalline character, which are produced in-situ during the vulcanization reaction.

After addition of 2 phr stearic acid the basal peak corresponding to d_{001} was further shifted toward more lower angles, and the value of corresponding d_{001} spacing is 4.35 nm. A very interesting XRD scattering was found when using 4 phr stearic acid in the vulcanization process. The curve obtained from the corresponding vulcanizate shows almost exfoliated type structures of the layered silicates. However, there are also some very broad peaks with very low intensity which signifies the existence of some intercalated layers with uneven space gap of the silicate layers.

For a better understanding of the enhancement of physical properties with variations of stearic acid



Figure 6. WAXD patterns of NBR filled (5 phr organoclay) vulcanizates formulated with(a) 1 phr stearic acid, (b) 2 phr stearic acid, (c) 4 phr stearic acid and (e) without stearic acid



Figure 7. Stress-Strain diagrams of organoclay filled NBR formulated with different amount of stearic acid

the stress-strain plots from tensile experiments are displayed in Figure 7. The curve obtained from gum rubber without any filler and with 1 phr stearic acid shows a very low tensile strength, and an elongation at break of around 650%. With increasing amount of stearic acid up to 2 phr in the filled NBRs the curves become stronger and steeper. Elongation at break values do not change significantly in comparison to the gum rubber. However, at 4 phr stearic acid content the tensile strength and elongation at break increase considerably. We presume that stearic acid promotes the silicate layers to disperse uniformly with a sufficient degree of exfoliation and intercalation, and therefore the rubber matrix becomes strongly reinforced.

4. Conclusions

Both sulfur and peroxide vulcanizations of NBR filled with organoclay lead to intercalated-exfoli-

ated structures of the layered silicate. Peroxide vulcanization brings the silicate layers into well ordered arrangements in a particular direction. This kind of alignment of the layered silicates in the rubber matrix could be of advantage for a more effective hindering of gas permeability. However, peroxide curing also promotes exfoliated structures as evinced from TEM and reflected by the XRD experiments. We demonstrated that the use of excess stearic acid could be a way for getting better exfoliation of the layered silicate in the rubber matrix when sulfur vulcanization will be selected for curing the rubber matrix. Keeping the layered silicate arrangement in mind, it can be envisaged that the choice of peroxide curing packages might have a beneficial effect on the reduction of gas permeability of a rubber nanocomposite. Excess use of stearic acid in the vulcanization ingredients does not affect the curing properties of NBR, but in turn increases the tensile and modulus of the vulcanizates. The detailed physical properties will be shown in our forthcoming publications.

We finally note that after completing the manuscript a similar effect of stearic acid in EPDMorganoclay nanocomposites has been reported in reference [15]. The tensile strength of the corresponding nanocomposites could be improved with increasing amount of stearic acid, whereas the stresses at low strain were almost the same.

Acknowledgements

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Blends of L-tyrosine based polyurethanes for biomaterial applications

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Abstract. Three polyurethane blends were made from segmented polyurethanes synthesized from desaminotyrosyl tyrosine hexyl ester (DTH), an L-tyrosine based diphenolic dipeptide, as chain extender. The soft segment of these polyurethanes is either polyethylene glycol (PEG) or polycaprolactone diol (PCL) and the diisocyanate is hexamethylene diisocyanate (HDI). The blends were developed to investigate the effect of varying composition on the overall physical, thermal, mechanical, surface and degradation properties of the material. The characterization results show that the properties of these blended materials can be controlled by adjusting the composition. Blends with increased PEG based polyurethane exhibited more water absorption and higher degradation characteristics. With increasing PCL based polyurethane, the mechanical properties of the blends were improved although the blends were relatively more amorphous in nature. The L-tyrosine based polyurethane blends hold the potential for use in different biomaterial applications.

Keywords: polymer blends and alloys, L-tyrosine, polyurethane, poly(caprolactone), poly(ethylene glycol)

1. Introduction

Polyurethanes are an important class of biomaterials due to their excellent physical properties and relatively good biocompatibility [1]. Segmented polyurethanes synthesized from various polyols, diisocyanates and chain extenders can be structurally manipulated to achieve a wide range of properties suitable for various biomaterial applications [2]. The properties of segmented polyurethanes are determined by both the soft segment comprised of polyol and the hard segment comprised of diisocyanate and chain extender with the main contribution coming from the soft segment. The use of polyurethanes as tissue engineering material has received a great deal of attention due to its unique combination of physicomechanical properties and degradability [3]. Polyurethanes with polyester soft segment e.g. polycaprolactone (PCL) and polyether soft segment e.g. polyethylene glycol (PEG) are mainly used for tissue engineering applications [3–5]. PCL based polyurethanes are relatively hydrophobic and have slow degradation rates whereas PEG based polyurethanes are highly hydrophilic and therefore show enhanced rates of degradation [3]. But in terms of mechanical properties, PEG based polyurethanes possess poorer moduli and ultimate stress compared to PCL based polyurethanes [5]. Thus PEG based polyurethanes lack the structural integrity required for tissue engineering scaffold formation. Blending and copolymerization are the most commonly used techniques to combine the properties of individual polymers [6, 7]. However, blending is easier than the preparation of copolymers to obtain the advantageous properties of the constituent polymers [5]. Recently, we developed polyurethanes for biomaterial applications from an L-tyrosine based chain extender, desaminotyrosyl tyrosine hexyl ester (DTH) [8]. The polyols used for these poly-

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Figure 1. Structure of L-tyrosine based polyurethanes with PEG or PCL soft segment, HDI as diisocyanate and DTH as chain extender

urethanes are either PEG or PCL and the diisocyanate is hexamethylene diisocyanate (HDI). These polyurethanes have a wide range of physicomechanical properties that are suitable for tissue engineering applications. The structures of the polyurethanes are shown in Figure 1. The polyurethanes synthesized from PEG exhibit poor mechanical properties and a high rate of degradation whereas PCL based polyurethanes have better mechanical properties but very slow degradation rates.

In this work, three blends of L-tyrosine based polyurethanes were fabricated by using different compositions of the two polyurethanes. Structural and morphological characterization of the blends was carried out by spectroscopic, thermal and microscopic techniques. In addition, contact angle, water absorption and hydrolytic degradation studies were done to investigate the applicability of the systems for biomaterial applications.

2. Experimental

2.1. Materials

L-tyrosine, desaminotyrosine, Ethyl-N'-dimethylaminopropyl carbodiimide (EDC.HCl), polyethylene glycol(PEG), poly caprolactone diol(PCL), hexamethylene diisocyanate (HDI) were obtained from Sigma Aldrich, St. Louis(MO) USA. *n*-Hexanol, tetrahydrofuran, N-N'dimethylformamide (DMF), and chloroform were obtained from Fisher Scientific, Pittsburgh(PA) USA. The solvents were analytical grade and were used as received, unless otherwise mentioned. De-ionized water was used for all purposes.

Two different L-tyrosine based polyurethanes were synthesized from either polycaprolactone diol (PCL, $M_w = 1250$ g/mol) or polyethylene glycol (PEG, $M_w = 1000$ g/mol), as the polyol and hexamethylene diisocyanate (HDI) as the diisocyanate. The chain extender was desaminotyrosyl tyrosine hexyl ester (DTH), a diphenolic dipeptide derived from L-tyrosine and its metabolite desaminotyrosine. PEG and PCL were dried in vacuum at 40°C for two days to remove water prior to the polymerization. The solvent N-N'dimethylformamide (DMF) was dried with calcium hydride and stored with molecular sieves for the polymerization reaction. All other chemicals were used as received. The detailed synthesis and characterization of the individual polyurethanes are described elsewhere [8].

Briefly, the chain extender DTH was synthesized by carbodiimide (EDC) mediated coupling of desaminotyrosine with *n*-hexyl ester of L-tyrosine in tetrahydrofuran as solvent at room temperature. The hexyl ester of L-tyrosine was prepared from the esterification of L-tyrosine with n-hexanol at 80°C. The polyurethanes were synthesized by two step condensation polymerization reaction. PEG or PCL was reacted to HDI in the molar ratio of 1:2 at 110°C for three hours in DMF (as solvent) in the first step and was followed by the addition of DTH in the same molar proportion of PEG or PCL. The final step was carried out for 12 hours at 80°C. Finally, the polymers were precipitated in cold concentrated aqueous solution of sodium chloride and were either centrifuged or filtered and dried in vacuum prior to any characterizations. The nomenclature for the polyurethanes used is: PEG-HDI-DTH and PCL-HDI-DTH, where PEG or PCL represents the soft segment and HDI and DTH represent the hard segment. The structures of the polyurethanes are shown in Figure 1. The polyurethanes were blended in three different weight ratios using chloroform as the solvent and films were cast by solvent evaporation. Typically 5% (w/v) solutions of the polyurethanes were prepared in 10 ml of chloro-

| Code | Composition (PEG-HDI-DTH/PCL-HDI-DTH) [wt%] | Weight (PEG-HDI-DTH + PCL-HDI-DTH) [mg] | Volume of solvent (chloroform) [ml] |
|------|--|--|--|
| PU1 | 100/0 | 500 | 10 |
| PU2 | 67/33 | 500 | 10 |
| PU3 | 50/50 | 500 | 10 |
| PU4 | 33/67 | 500 | 10 |
| PU5 | 0/100 | 500 | 10 |

Table 1. Formulation of blends

form. Accurately weighed polymers (500 mg) were dissolved in 10 ml of solvent and allowed to form a homogeneous solution through constant stirring at room temperature for 24 hours. The polymer solutions were filtered through Teflon syringe filters to remove undissolved residue and were cast onto poly(tetrafluoroethylene) (PTFE) Perti dishes. The solvents were initially allowed to evaporate at room temperature followed by vacuum drying at 50°C for another 48 hours to remove the residual solvents. Films of about thickness 0.15 mm were obtained by this method. The nomenclature and summary of the blends are presented in Table 1.

2.2. Measurements

The blends were characterized by ¹H-NMR and FTIR. NMR was carried out in a 300 MHz Varian Gemini instrument with *d*-chloroform ($\delta =$ 7.27 ppm as internal reference) and FT-IR analysis was performed with a Nicolet NEXUS 870 FT spectrometer for neat samples. Differential scanning calorimetry (DSC) was performed with a DSC Q100V7.0 Build 244 (Universal V3. 7A TA) instrument at a scanning rate of 10°C/min from -80 to 250°C. The tensile properties of the films were measured by Instron Tensile Testing Machine with a load cell of 100 N and cross-head speed of 100 mm/min at room temperature. The sample dimension was $20 \text{ mm} \times 6 \text{ mm} \times 0.3 \text{ mm}$ (approximately) with a free length of 10 mm. For contact angle measurement, thin films of polymers were prepared on thoroughly cleaned and dried glass slides by dip coating the slides into the 5 wt% solution of polyurethane for 12 hours. The films were initially dried at room temperature for 24 hours followed by vacuum drying at 50°C for another 48 hours to remove the residual solvents. Static water contact angle was measured by sessile drop method using a Ramé-Hart goniometer at room temperature in an air atmosphere both in advancing and receding modes [4]. To measure water absorption, circular samples were cut from dried films (diameter: 1.5 cm and thickness: 0.15 mm) and immersed in 20 ml of deionized water. At predetermined time intervals the hydrated samples were taken out and weighed after the surface water was blotted with Kimwipes. The water absorption was calculated on the basis of the weight difference of the film before and after swelling. The percentage of water absorption was calculated using Equation (1):

water absorption
$$\left[\%\right] = \frac{w_2 - w_1}{w_1} \cdot 100$$
 (1)

where, w_2 and w_1 are the weight of sample films after and before being immersed in water, respectively. For hydrolytic degradation, similar circular samples (diameter: 1.0 cm and thickness: 0.15 mm) were cut from dried films. The samples were incubated at $37\pm1^{\circ}$ C in 10 ml of phosphate-buffered saline (PBS; 0.1 M, pH 7.4) containing 200 mg·l⁻¹ of sodium azide to inhibit bacterial growth in a sealed vial placed within a constant temperature water bath. Samples were taken at intervals, weighed for mass loss after drying under vacuum at 40°C for 2 days. The hydrolytic degradation was calculated from the weight loss [%] using Equation (2):

weight loss
$$[\%] = \frac{w_1 - w_2}{w_1} \cdot 100$$
 (2)

where, w_2 and w_1 are the weight of sample films after and before degradation, respectively. The SEM images were recorded on silver sputtered samples in Hitachi S2150 (Operating Voltage: 20 kV).

3. Results and discussions

3.1. ¹H-NMR and FT-IR characterizations

The ¹H-NMR spectra for all the blends are very similar due to the similarity in most of the proton

environments. A representative spectrum for the blend (for PU3) is shown in Figure 2. Quantitative estimation by integrating a peak area is difficult due to similar chemical shift of the different protons present in soft and hard segment of the polyurethane [9]. Moreover the results were not



Figure 2. Representative ¹H-NMR of polyurethane blend

reproducible due to sample size and variation. Since the only difference is in the soft segment, two peaks were chosen that were characteristic of the PEG and PCL. The chemical shifts (δ) at 3.65 ppm corresponding to methylene protons $(-CH_2-CH_2-)$ of the PEG soft segment and at 4.06 ppm corresponding to methylene protons $(-CH_2-O-CO-)$ of the PCL soft segment are integrated to estimate the relative contribution of the constituent polyurethane [5, 8]. The interferences due to the peaks present at 4.25 and 3.70 ppm from PCL based polyurethanes were taken into account for the calculation. The results of the integration are shown in Table 2 and indicate that the composition of the blends follows the general trends i. e. PU1 fraction decreases and PU5 fraction increases from PU2 to PU4. However, a significant deviation from the theoretical composition was observed for all the blends. This can be attributed to inhomogeneous



Figure 3. FT-IR spectra and quantitative estimation of absorbance ratio (1730 cm⁻¹/1100 cm⁻¹) of the of pure polyurethanes and blends (error bars represent standard deviation of measurement from 3 samples)

Table 2. Composition of polymer blends from ¹H-NMR

| Sample | Theoretical ratio (PEG-HDI-DTH/PCL-HDI-DTH) | Observed ratio (PEG-HDI-DTH/PCL-HDI-DTH) |
|--------|--|---|
| PU3 | 2:1 | 2.31 : 1 |
| PU4 | 1:1 | 1.61 : 1 |
| PU5 | 1:2 | 1.28 : 2 |

mixing due to incompatibility, variation in sample size and similarity in the proton environment [9]. All the blends show considerably higher fraction of PEG based polyurethanes than the theoretical fraction which indicates some extent of immiscibility between the component polyurethanes.

The FT-IR spectra of the blends are shown with pure polyurethanes in Figure 3. The characteristic peak for PU1 is the absorbance at 1100 cm⁻¹ corresponding to the aliphatic ether linkages (C–O–C) present in the PEG soft segment and that for PU5 is the absorbance at 1730 cm⁻¹ corresponding to the ester carbonyl linkage (C=O) present in the PCL soft segment. In addition, the spectra display characteristic urethane absorbance at 1713 cm⁻¹, aromatic C=C stretch at1620 cm⁻¹ (in DTH) and C=O for amide I bonds at 1640 cm⁻¹. The intensity of the absorbance due to ether linkage around 1100 cm⁻¹ gradually decreases and that for 1730 cm⁻¹ gradually increases from PU1 to PU5. This qualitatively suggests that the content of PEG based polyurethane is gradually decreasing from PU2 to PU4 while the content for PCL based polyurethane is increasing. A quantitative characterization of the blends was attempted by calculating the ratio of the absorbance for 1713 to 1100 cm⁻¹ and the variation of the absorbance ratio is plotted against the composition in the inset of Figure 3. This estimation shows that ratio is least in PU1 and increases for the blends from PU2 to PU4 and is highest in PU5. This estimation qualitatively agrees that PU2 has highest fraction of PEG-HDI-DTH and PU4 has highest fraction of PCL-HDI-DTH.

3.2. Differential scanning calorimetry

The thermal characteristics of the blends were assessed by the differential scanning calorimetry (DSC). The DSC thermograms of the pure polyurethanes and the blends are presented in Figure 4. The glass transition temperature (T_g) of PU1 is -40° C and of PU5 is -35° C. Both PU1 and PU5 exhibit additional endotherms which are assigned as dissociation of ordered hard segment and melting of crystalline hard segment. No hard segment T_g was observed for the pure polymers but PU5 exhibited soft segment melting endotherm at -31° C [8].

 T_g for the blends is in between the range of -40 to -35°C. A shift in the glass transition temperature is



Figure 4. DSC thermograms of pure polyurethanes and blends

indicative of polymer miscibility but any appreciable shift in the T_g for the blends is hard to detect within this small range [10]. However for PU2, which has higher fraction of PU1, the T_g is close to -40°C and for PU4, which has higher fraction of PU5, the T_g is close to -35° C. The T_g for PU3 which has equal fraction of PU1 and PU5 is also close to -40°C, indicating the dominance of PU1 fraction over PU5. The decrease in T_g values with increasing PEG containing polyurethanes in consistent with results observed for blends of phenyl alanine based polyurethanes [9]. All the blends from PU2 to PU4 exhibit an endotherm around 10°C which is due to dissociation of short range order of the hard segment. But the endotherms observed due to dissociation of long range order in PU1 and PU5 around 50°C is only observed in PU2 and is present in PU3 as a broad endothermic transition and is absent in PU4. This indicates that increasing the amount of PU5 inhibits the formation of long range order of the hard segment. This feature is further substantiated by the absence of the hard segment melting endotherm in PU3 and PU4 which indicates that with higher PU5 content the hard segment is more amorphous in nature. Only PU2 with minimum PU5 fraction exhibits a melting endotherm at 152°C. The absence of soft segment melting in PU1 and PU2 indicates that samples with more PEG content are amorphous in nature. The soft segment melting endotherm starts to appear in PU3. This feature shows that relatively crystalline PCL components show a melting endotherm. The soft segment melting endotherm for PU5 appears at 31°C and for PU4 and PU3 at slightly lower temperatures around 25°C. This feature shows that at some concentration, the presence of PEG helps to crystallize the PCL component. This feature is reported for similar systems [11]. In general, the T_g values of the sample show that the polyurethanes are not completely miscible and a possible phase separation occurs due to incompatibility of hydrophilic PEG and hydrophobic PCL soft segment. However due to the chemical similarity of the hard segments, the hard segments of the constituent polyurethanes are likely to form an amorphous one phase domain as evident from the disappearance of hard segment melting endotherm of PU3 and PU4 [12].

3.3. Mechanical properties

The mechanical properties of the blends and the pure polyurethanes are summarized in Table 3. The results show that the blend properties resemble the property of PU1. Even for the blends with comparatively higher PU5 content, i. e. PU3 and PU4, the properties are closer to pure polyurethane PU1. The reason for inferior mechanical properties of the blend PU3 and PU4 is mainly attributed to the distribution of the hard segment fraction of the polyurethane in the blend [13]. In presence of PCL soft segment, it is likely that hard segments do not have any long range order and are more amorphous in nature. The absence of the crystalline melting endotherm of PU3 and PU4 in the DSC analysis indicates that hard segments are not ordered and are random in distribution. The random distribution of the hard segment leads to inferior mechanical properties of the blends PU3 and PU4 in spite of higher content of PU5. Another possible exception is that phase separation between the polyurethanes is likely contributing to lower mechanical properties [13]. The phase separation can be due to several factors, with incompatibility between the hydrophilic PEG and hydrophobic PCL soft segment as the major one. The phase separation between the two phases is likely to constitute a continuous matrix of PU1 in which PU5 is dispersed as discrete domains. This gives a probable explanation for the result that in spite of having higher PU5 fraction, PU3 and PU4 exhibit relatively poorer mechanical properties.

3.4. Contact angle

The contact angle values both in advancing and receding modes are shown in Table 4. The values are average of measurements from 6 readings taken from 3 replicates for each sample. The high contact angle values of the blends indicate that the surfaces are relatively hydrophobic. The hysteresis values of the blends are closer to pure PCL based polyurethane, i. e. PU5, which further supports that the blend surfaces are hydrophobic. The values show that the contact angle of the blend PU2 and PU3 is comparatively closer to PU5 in spite of having higher and equal fraction of PU1 respectively. This indicates a possible phase separation between the components of the polyurethanes with the PCL based polyurethanes migrating from the bulk to the surface [14].

3.5. Water absorption

The water absorption characteristic of the blends is plotted against time and shown in Figure 5 with along with the diagram showing the variation in water absorption (after 17 hours) with the change in

| Sample | Ultimate tensile strength [MPa] | Modulus of elasticity [MPa] | Elongation at break [%] |
|--------|---------------------------------|-----------------------------|-------------------------|
| PU1 | 2.81 ± 0.11 | 3.75 ± 0.21 | 214 ± 9 |
| PU2 | 3.35 ± 0.25 | 5.11 ± 0.73 | 285 ± 57 |
| PU3 | 3.90 ± 0.41 | 6.11 ± 0.95 | 343 ± 21 |
| PU4 | 4.21 ± 0.29 | 6.72 ± 0.91 | 361 ± 64 |
| PU5 | 7.05 ± 0.60 | 17.98 ± 0.68 | 643 ± 87 |

Table 3. Mechanical properties of the samples (mean \pm SD, n = 5)

| Sample | Advancing contact angle (a) | Receding contact angle (r) | Hysteresis (a-r) |
|--------|-----------------------------|----------------------------|------------------|
| PU1 | 33.0° | 21.4° | 11.4° |
| PU2 | 58.7° | 33.7° | 25.0° |
| PU3 | 68.7° | 39.6° | 29.1° |
| PU4 | 72.0° | 42.3° | 29.7° |
| PU5 | 75.0° | 50.5° | 24.5° |

composition of the blends. The water absorption values after 17 hours are not conclusive because of



Figure 5. a) Plot of water absorption of blends against time b) Comparison of water absorption of pure polyurethanes and blends after 17 hours (error bars represent standard deviation of measurement from 3 samples)

weight loss due to degradation of the polymers. The water absorption of the blends increases from PU2 to PU4 with increasing content of PEG based polyurethane, i. e. PU1. As PEG is hydrophilic in nature, blends having higher PU1 content absorb more water. Blends PU4 and PU3 have water absorption characteristics similar to PU5 whereas PU2, having the highest fraction of PU1, has 25% water absorption compared to 73% for PU1. This relatively low water absorption is probably due to the surface characteristics of the PU2 which is predominantly hydrophobic with PCL based polyurethane phase separated and migrating to the surface. This migration is also evident from the contact angle measurements. The results presented follow the general trend that water uptake increases with increasing PU1, i. e. PEG based polyurethane content [5, 9].

3.6. Hydrolytic degradation

The hydrolytic degradation of the samples was measured by the weight loss and is shown in Figure 6. The weight loss is higher with increasing PU1 content, indicating that increased water absorption leads to more hydrolytic degradation. The degradation of the blends decreases from PU2 to PU4 with decreasing PU1 content. Blend PU4,



Figure 6. Weight loss of due to hydrolytic degradation for 30 day (results are average of 3 measurements)

with 33 weight percent of PU1, has almost similar degradation characteristics compared to PU5. PU3 and PU2 have significantly higher degradation compared to PU4 in 30 days.

This indicates that the controlling factor in the degradation of the blends is the soft segment characteristics. The hydrophilic PEG component absorbs more water leading to degradation of the hydrolytically labile urethane, amide and ester linkages present in the polymer leading to more degradation. For all the samples the initial degradation was rapid followed by a significantly slower rate over the 30 day period. This is probably due to rapid and initial degradation of PEG based poly-



Figure 7. SEM images of degraded samples after 30 days of hydrolytic degradation

0000

PU4

20kV

x3.Øk

10,00

urethane, i. e. PU1 followed by the slow degradation of hydrophobic and comparatively crystalline PCL based polyurethane, i. e. PU5.

The degradation pattern was examined for the blends and the pure polyurethanes by SEM and images of representative samples are shown in Figure 7. PU1 shows holes and crevices on a uniformly eroded surface as a result of both surface and bulk degradation while PU5 shows cracked and non-uniform surface structure due to predominantly surface erosion. PU1 is more hydrophilic due to the PEG soft segment while PU5 is hydrophobic due to the PCL soft segment. The SEM images of the blends PU2 and PU3 show that the blends are mainly degraded by surface erosion leading to spherulitic structures which are presumably formed by degradation of the crystalline PCL soft segment after degradation and dissolution of the PEG soft segment [15]. PU4, having a higher fraction of PCL based polyurethane, shows relatively uniform surface degradation.

4. Conclusions

Three blends of L-tyrosine based polyurethanes were fabricated by solvent evaporation from two polyurethanes having PEG and PCL as soft segments. Blending different compositions offers an easy technique to tune the properties of the parent L-tyrosine based polyurethanes. The wide variation in the properties of PEG and PCL based polyurethanes can be adjusted by changing the composition in order to obtain a suitable material for biomaterial applications. The spectral characterization of the blends indicates the relative compositions of these blends are close to theoretical ones. DSC study shows that blends with increasing PCL based polyurethane content are comparatively amorphous while contact angle measurements indicate that surfaces of these blends are mainly hydrophobic probably due to phase separated PCL based polyurethane. Blending of PCL based polyurethane with PEG based polyurethanes slightly enhanced the mechanical properties over the pure PEG material. The water absorption and degradation features along with the other characterization results of the blended polyurethanes show that these material properties can be easily controlled to fabricate a suitable material for different biomedical applications, particularly for fabrication of tissue engineering scaffold. These initial characterizations indicate that blends having lower content of PCL based polyurethane are more stable than blends having equal or higher PCL based polyurethane content. In general, the wide range of material properties of Ltyrosine based polyurethanes was achieved through a relatively simple fabrication technique.

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Chain extension and branching of poly(L-lactic acid) produced by reaction with a DGEBA-based epoxy resin

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Abstract. Dicarboxylated poly(L-lactic acid) (PLLA) was synthesized by reacting succinic anhydride with L-lactic acid prepolymer prepared by melt polycondensation. PLLA and epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) copolymers were prepared by chain extension of dicarboxylated PLLA with DGEBA. Infrared spectra confirmed the formation of dicarboxylated PLLA and PLLA/DGEBA copolymer. Influences of reaction temperature, reaction time, and the amount of DGEBA on the molecular weight and gel content of PLLA/DGEBA copolymer were studied. The viscosity average molecular weight of PLLA/DGEBA copolymer reached 87 900 when reaction temperature, reaction time, and mol ratio of dicarboxylated PLLA to DGEBA is 150°C, 30 min, and 1:1 respectively, while gel content of PLLA/DGEBA copolymer is almost zero.

Keywords: biodegradable polymers, poly(L-lactic acid), epoxy resin, copolymers

1. Introduction

Poly(L-lactic acid) (PLLA) is a completely biodegradable and well biocompatible aliphatic polyester [1]. PLLA has many potential applications in packaging and consumer goods due to its excellent mechanical properties, transparency, compatibility, and biosafety [2, 3].

There are generally two ways to synthesize PLLA, ring-opening polymerization and direct polycondensation [4]. Ring-opening polymerization requires highly purified L-lactid, which makes PLLA rather expensive, hardly competitive with current polymers [5, 6]. Direct melt polycondensation can simplify the synthetic process and reduces the cost of PLLA. However, it is difficult to prepare PLLA with high molecular weight by direct polycondensation because of the complicated equilibrium among lactic acid, H₂O, L-lactid and PLA during the process [7]. The unfavorable reaction equilibrium constant makes the PLLA molecular weight in The low molecular weight PLLA synthesized by direct melt polycondensation has reactive functional groups such as hydroxyl and carboxyl group, and its molecular weight can be improved through chain extension. Woo *et al.* [10] used hexamethylene diisocyanate (HDI) as chain extender, and the average molecular weight of PLLA was improved to 76 000. Kylma and Seppala [11] prepared hydroxyl-terminated PLLA oligomer, used HDI as chain extender, and got the poly(ester-urethane) elastomer. Zhou *et al.* [12] first synthesized telechelic poly(ethylene glycol) (PEG) by reacting PEG with isophorone diisocyanate (IPDI), then

order of only $\sim 10^4$ g/mol. Such low molecular weight PLLA is too brittle to be used as a useful material [8]. PLLA should have at least $\sim 10^5$ g/mol order of molecular weight to exhibit an acceptable level of mechanical properties [9]. Increasing of the molecular weight of PLLA is imperatively demanded [8].

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prepared PLLA/PEG multiblock copolymers by coupling reactions between PEG telechelic oligomer and L-lactic acid prepolymer. The elongation at break of the resulting copolymer can reach 320%. Cohn *et al.* [13] synthesized a series of poly(ethylene oxide)/poly(L-lactic acid) multiblock poly(ether-ester-urethane)s using HDI as extender. It is obvious that isocyanate is widely used as chain extender. However, it has high volatility and toxicity. This will do harm to experiments and pollutes the environment.

Huh *et al.* [14] first synthesized PLLA with carboxylated end-groups by direct polycondensation, then prepared PEG/PLLA copolymer by polycondensation reaction between PEG and PLLA. This is a new method to increase the molecular weight of PLLA. However, the method requires the presence of solvent and further purification of the products. In addition, the chain extension requires long reaction time.

In this paper a DGEBA-based epoxy resin, which has nearly no volatility and toxicity was used to extend the carboxyl-terminated PLLA in short reaction time in melt, and resulting in high molecular weight products. This method avoids the shortages of the previous techniques and has rarely been reported in published articles so far.

2. Experimental

2.1. Materials

L-lactic acid (85 wt%, L-lactic acid content: 98– 99%) was purchased from Purac Biochem Co. (Holland). The impurity was removed before use by distillation under reduced pressure at 130° C for about 2 h.

Stannous octoate (Sn(Otc)₂), succinic anhydride, p-toluenesulfonic acid monohydrate (TSA), tetrahydrofuran (THF), acetone, tetrabutylammonium bromide (TBAB), and DGEBA-based epoxy resin (226.2 g/mol epoxy groups) were obtained from Shanghai Chemicals, and used as received without further treatment.

2.2. Preparation of dicarboxylated PLLA

The melt polycondensation of L-lactic acid was carried out in a rotavapor equipped with a thermostated oil bath. The rotation speed was 120 rpm. 200 g purified L-lactic acid, 0.5 wt% catalyst Sn(Otc)₂ and 0.5 wt% co-catalyst TSA were put into a 500 ml round-bottom flask. The reaction temperature was gradually raised from 150 to 180°C and the pressure was lowered from 5000 to 100 Pa. After a total reaction time of about 12 h the L-lactic acid prepolymer was obtained. Then, the desired amount of succinic anhydride was added to the flask. The reaction of succinic anhydride with L-lactic acid prepolymer was carried out at 180°C and 100 Pa for 1 h. The molten polymer was poured into a stainless steel pan and placed in a desiccator to cool down. The dicarboxylated PLLA, with a viscosity average molecular weight of 10 070, was obtained.

2.3. Chain extension reaction

The chain extension reaction of dicarboxylated PLLA with DGEBA was also carried out in rotava-

| Coming | Dun number | PLLA | DGEBA | ТАВА | Reaction time | Reaction temperature |
|--------|----------------|------|-------|------|---------------|----------------------|
| Series | Kull llulliber | [g] | [g] | [g] | [min] | [°C] |
| | A1 | 73.7 | 12.0 | 0.86 | 30 | 140 |
| | A2 | 73.7 | 12.0 | 0.86 | 30 | 150 |
| А | A3 | 73.7 | 12.0 | 0.86 | 30 | 160 |
| | A4 | 73.7 | 12.0 | 0.86 | 30 | 170 |
| | A5 | 73.7 | 12.0 | 0.86 | 30 | 180 |
| | B1 | 61.4 | 10.0 | 0.71 | 10 | 150 |
| в | B2 | 61.4 | 10.0 | 0.71 | 20 | 150 |
| D | B3 | 61.4 | 10.0 | 0.71 | 30 | 150 |
| | B4 | 61.4 | 10.0 | 0.71 | 40 | 150 |
| | C1 | 70.0 | 5.7 | 0.70 | 30 | 150 |
| C | C2 | 70.0 | 7.6 | 0.70 | 30 | 150 |
| | C3 | 70.0 | 11.4 | 0.70 | 30 | 150 |
| | C4 | 70.0 | 17.1 | 0.70 | 30 | 150 |

Table 1. Experimental conditions for chain extension reaction^a

^aPressure, 100 Pa in series A, B and C

por. The rotation speed was 150 rpm. The predetermined amount of dicarboxylated PLLA, DGEBA and TBAB catalyst were put into a 500 ml roundbottom flask. The reaction was performed at 100 Pa and desired temperature and time. Chain extension reaction conditions for all the series of experiments are summarized in Table 1.

2.4. Analysis and characterization

The amount of carboxyl group in L-lactic acid prepolymer and dicarboxylated PLLA was determined as following steps. 0.20 g sample was dissolved in 40 ml THF, and then titrated by 0.1 mol/l NaOH ethanol solution using phenolphthalein as indicator. The amount of carboxyl group (AC) is given by Equation (1):

$$AC \left[\text{mol/g} \right] = \frac{\left(V_1 - V_0 \right) \cdot 10^{-3} \cdot C}{m}$$
(1)

where V_0 the amount of NaOH consumed by using THF as reference [ml], V_1 is the amount of NaOH consumed by sample [ml], *C* is the mol concentration of titration solution [mol/l], *m* is the weight of sample [g].

The gel content (GC) of PLLA/DGEBA copolymer was determined by extraction. The rough sample was extracted by THF using Soxhlet extractor. The crosslinked copolymer, which remained in extractor, was dried to constant weight in vacuum oven at 80°C. The uncrosslinked copolymer was extracted from the rough sample by THF. The GC is given by Equation (2):

$$GC\left[\%\right] = \frac{m_2}{m_1} \cdot 100\tag{2}$$

where m_1 is the weight of rough sample [g] and m_2 is the weight of crosslinked copolymer [g].

The viscosity average molecular weight of dicarboxylated PLLA and uncrosslinked PLLA/DGEBA copolymer was measured by the intrinsic viscosity method. The viscosity was determined in THF at 30°C by using a viscometer. The intrinsic viscosity was calculated from the equation of Rongshi Cheng [15], given by Equation (3). The Mark-Houwink equation is given by Equation (4) [16]:

$$\left[\eta\right] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{c} \tag{3}$$

$$[\eta] = 1.29 \cdot 10^{-4} \,\overline{M}_V^{0.82} \tag{4}$$

Infrared spectroscopic information of polymers was obtained using Spectrum 100 Fourier Transform Infrared spectrophotometer (PE Corp. USA).

3. Reaction mechanism

The chemical structures of DGEBA and dicarboxylated PLLA are shown in Figure 1. Synthesis of PLLA/DGEBA copolymers involves following steps: (1) Melt polycondensation of L-lactic acid to prepare L-lactic acid prepolymer. (2) L-lactic acid prepolymer reacting with succinic anhydride to prepare dicarboxylated PLLA. (3) Dicarboxylated PLLA reacting with DGEBA to prepare PLLA/ DGEBA copolymers. The epoxy-acid reaction is complex in the presence of TABA [17]. The reaction mechanism of dicarboxylated PLLA reacting with DGEBA may be described as Figure 2. The linear molecule is obtained as reaction I, while the ester formed by the epoxy-acid reaction can react with the OH groups through a transesterification reaction as reaction II. The reaction II leads to chain branching and gel formation.



Dicarboxylated PLLA

Figure 1. Chemical structures of DGEBA and dicarboxylated PLLA



Figure 2. The reaction mechanism of dicarboxylated PLLA reacting with DGEBA



Figure 3. IR spectra of L-lactic acid prepolymer and dicarboxylated PLLA. (a) L-lactic acid prepolymer; (b) dicarboxylated PLLA



Figure 4. IR spectra of dicarboxylated PLLA, DGEBA and PLLA/DGEBA copolymer. (a) DGEBA; (b) dicarboxylated PLLA; (c) PLLA/DGEBA copolymer

4. Results and discussion

4.1. Evidence of reaction

Figure 3 shows the infrared spectra of L-lactic acid prepolymer and dicarboxylated PLLA. The absorbance at 3512 cm⁻¹ in Figure 3 (a) indicates the terminal -OH of L-lactic acid prepolymer. The absence of 3512 cm^{-1} in Figure 3 (b) indicates that the terminal -OH of L-lactic acid prepolymer was transformed to terminal -COOH of dicarboxylated PLLA (3402 cm⁻¹). The amount of carboxyl group of L-lactic acid prepolymer and dicarboxylated PLLA is $3.7 \cdot 10^{-4}$ and $7.2 \cdot 10^{-4}$ mol/g, respectively. The infrared spectra of dicarboxylated PLLA, DGEBA and PLLA/DGEBA copolymer are shown in Figure 4. The absorbance at 914 cm⁻¹ in Figure 4 (a) and 3402 cm⁻¹ in Figure 4 (b) indicates the terminal epoxy group of DGEBA and carboxyl group of dicarboxylated PLLA, respectively. The appearance of new absorbance at 3510 cm⁻¹ and absence of 914 cm⁻¹, 3402 cm⁻¹ in Figure 4 (c) indicates that the epoxy group of DGEBA and carboxyl group of dicarboxylated PLLA was transformed to hydroxyl group of PLLA/DGEBA copolymer.

4.2. Effect of reaction temperature

Figure 5 shows the effect of reaction temperature on the \overline{M}_V of uncrosslinked PLLA/DGEBA copolymer and gel content of PLLA/DGEBA copolymer. The experimental conditions are shown in series *A* of Table 1. The mol ratio of dicarboxylated PLLA



Figure 5. Effect of reaction temperature on chain extension reaction

to DGEBA is 1:1. Figure 5 reveals that the \overline{M}_V of uncrosslinked PLLA/DGEBA copolymer is the highest when the reaction temperature is 150°C. The gel content of PLLA/DGEBA copolymer is almost zero when temperature is lower than 150°C, it increases rapidly with increasing reaction temperature during 150–160°C, and after that it changes indistinctively. The transesterification reaction (reaction II) is more difficult than that of linear reaction (reaction I) in Figure 2, as a result, no gel content was observed at low temperature. The reaction of transesterification reaction increased considerably when reaction temperature increased, so the gel content of PLLA/DGEBA copolymer increased with increasing reaction temperature.

4.3. Effect of reaction time

Figure 6 shows the effect of reaction time on the \overline{M}_V of uncrosslinked PLLA/DGEBA copolymer and gel content of PLLA/DGEBA copolymer. The experimental conditions are shown in series *B* of Table 1. The mol ratio of dicarboxylated PLLA to



Figure 6. Effect of reaction time on chain extension reaction

DGEBA is also 1:1. The $\overline{M_V}$ of copolymer increases steadily with increasing reaction time. However, the gel content is almost zero during the beginning 30 minutes, and after that it increases rapidly with increasing reaction time. When the reaction time reaches 40 min, the gel content of the copolymer is 37.1%. The copolymer will be difficult to process when gel content is high. So, the best reaction time is 30 min.

4.4. Effect of the amount of DGEBA

The effect of the amount of DGEBA on the M_V of PLLA/DGEBA copolymer is shown in Figure 7. The experimental conditions are shown in series *C* of Table 1. No gel content is observed in this reaction system which can be explained by Figure 5 and Figure 6. The $\overline{M_V}$ of PLLA/DGEBA copolymer reaches 87 900, which is the highest, when the amount of DGEBA is 11.4 g. On this point, the feed mole ratio of dicarboxylated PLLA to DGEBA is 1:1. At other points, the amount of carboxyl group and epoxy group is not equal, which causes inadequate reaction of dicarboxylated PLLA with DGEBA.

5. Conclusions

PLLA/DGEBA copolymers were successfully synthesized by chain extension of dicarboxylated PLLA with DGEBA-based epoxy resin. The viscosity average molecular weight of PLLA/DGEBA copolymer reached 87 900 when reaction temperature, reaction time, and mol ratio of dicarboxylated PLLA to DGEBA is 150°C, 30 min, and 1:1, respectively; while gel content of PLLA/DGEBA copolymer is almost zero.



Figure 7. Effect of the amount of DGEBA on chain extension reaction

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Synthesis and characterization of methacrylamidopropyltrimethylammonium chloride and N-substituted acrylamide ionomers

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Abstract. Quaternary ammonium ionomers of Methacrylamidopropyltrimethyl ammonium chloride with N-substituted acrylamides were prepared at $55\pm1^{\circ}$ C using azobiscyanovaleric acid (ACVA) initiator. The monomers and ionomers were characterized by ¹H- and ¹³C-NMR spectroscopy and the copolymer composition was calculated from elemental analysis data. The reduced viscosity of ionomers in methanol behaves as non-polyelectrolytes at lower mole percentage and as polyelectrolyte at higher mole percentage. The molecular weights of ionomers were found to be high and the polydispersity index values indicate termination mainly by disproportionation. The glass transition temperature (T_g) of ionomers were greater than those of the corresponding homopolymers, attributed to a reduction in segmental mobility. The initial decomposition temperature (IDT) showed that the stability of ionomers increases with increasing mole percentage of ionic content.

Keywords: rheology, ionomers, gel permeation chromatography (GPC), thermal properties

1. Introduction

A variety of ion-containing polymers have been developed in the recent past. These polymers are extensively used in paper manufacturing, textile finishes, oil production, plastics, coatings, biomedical applications etc. Cationic quaternary polyelectrolytes have manifold applications. They are used as primary coagulants, flocculants, oil conditioners, hair sprays, shampoo additives, grease thickeners etc. The use of polyelectrolytes based on acrylamide is of increasing interest in the fields of ore separation and waste treatment. The term ionomer is used to denote polymers which contain 0–15% ionic groups and those polymers with higher ionic group contents are classified as polyelectrolytes [1].

The N-substituted acrylamides are used to prepare thermosensitive polymers like poly(N-isopropylacrylamide) and copolymers of N-alkylacrylamide and styrene [2]. Thermosensitive polymers have great potential in applications as drug delivery system [3] human gene vector [4] and biocatalysts [5]. The neutral and strongly basic polyelectrolyte hydrogels are prepared from Methacrylamidopropyltrimethylammonium chloride and N-isopropylacrylamide respectively [6]. A survey of the open literature indicates that much work has been done on the physical properties of ionomers. The preparation and characterization of various quaternary salts from reaction of methyl iodide with dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, N-(3-dimethylaminopropyl) acylamide or N-(3-dimethylaminopropyl) methacryl-

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amide, has been reported by Lee et al. [7]. McCormick and Blackmon [8] studied the copolymers of acrylamide with 2-acrylamido-2-methylpropanedimethylammonium chloride. The molecular weights of copolymers were significantly lower than the molecular weight of the polyacrylamide. Lower degree of polymerization are likely due to increased cross-termination rates in the copolymerisation. Recently, Pazhanisamy et al. [9] have reported the synthesis and characterization of ionomers of Methacrylamidopropyl-N,N'-dimethyl-N-hexadecylammonium iodide (MPDMAC16) or Methacrylamidopropyl-N,N'-dimethyl-N-octadcylammonium iodide (MPDMAC18) with N-substituted acrylamides. The reduced viscosity of ionomers showed non-polyelectrolyte behavior and shear rate dependency of viscosity of ionomers showed viscoplastic behavior. The present study described in this article deals with the preparation, spectral characterization, thermal behavior and solution properties of Methacrylamidopropyltrimethylammonium chloride (MPTMAC) and Nsubstituted acrylamides ionomers.

2. Experimental

2.1. Materials

Methacrylamidopropyltrimethylammonium chloride (MPTMAC) used as a commercial sample (Aldrich Co) is available as an aqueous solution (50% by weight). It was diluted with an equal amount of distilled water and decolourised with activated carbon prior to use. The initiator 4,4'-azobis (4-cyanovaleric acid), (ACVA) was recrystallized from chloroform. Methanol was refluxed along with quick lime (CaO) for 5 h and distilled for use. Benzene was dried overnight using anhydrous CaCl₂ and distilled before use. The monomers N-tert-amylacrylamide (AA), N-tert-butylacrylamide (BA)and N-cyclohexylacrylamide (CA) were prepared by a procedure described in literature [10].

2.2. Copolymerization

A solution containing 2.5 g (0.18 mole) of AA, 1.25 g (0.0057 mole) of MPTMAC and 0.1 g (0.0071 mole) of ACVA in 50 ml of 3:1 methanol/ water medium was placed in a polymerization tube. The solution was flushed with oxygen free dry nitrogen gas for about 30 min and polymerization tube was closed by means of rubber tubings with pinch cock. The tube was then placed in a thermostated water bath at 55±1°C. After 12 h the reaction solution obtained was poured into ice-cold water and the copolymer (ionomer) precipitated by adding 0.1 M NaCl solution. The precipitated polymer was washed with benzene to remove the unreacted monomer and dried for 24 h at 60°C under vacuum (93.4% yield). The monomer feed was varied in order to prepare copolymers having different mol% of MPTMAC, as shown in Table 1. The other ionomers of MPTMAC-BA and MPTMAC-CA were also prepared similarly. In each system, ionomers of different mol% of MPTMAC were prepared by varying the feed composition (Table 1).

2.3. Instrumentation

The ¹H-NMR and ¹³C-NMR spectra of monomers and copolymers were recorded on the GSX-400 spectrometer (JEOL, Tokyo, Japan) operating at 100 MHz and 400 MHz respectively in CDCl₃ or DMSO($-d_6$). Elemental analysis of the copolymers were analysed using Heraeus-CHN–O rapid elemental analyzer. The Ubbelohde suspended level viscometer (Schott Medica GmbH Wertheim/

| Constymore | Mol% of MPTMAC | Elen | nental analysis | data | Mol% of MPTMAC | η _{red} [dl⋅g ⁻¹] ^c |
|------------|----------------|-------|-----------------|------|---------------------------|---|
| Copolymers | in feed | C% | H% | N% | in copolymer ^b | at 0.2 g·dl ⁻¹ |
| | 4 | 59.02 | 10.05 | 9.28 | 10.70 | 0.54 |
| MPTMAC-AA | 10 | 57.21 | 10.34 | 9.14 | 13.15 | 0.74 |
| | 32 | 44.13 | 8.23 | 7.47 | 22.65 | 1.10 |
| МРТМАС-ВА | 4 | 57.04 | 10.02 | 9.20 | 5.51 | 0.27 |
| | 10 | 58.04 | 9.21 | 8.96 | 8.99 | 0.54 |
| | 32 | 46.04 | 8.77 | 8.68 | 25.46 | 1.88 |
| | 4 | 59.25 | 9.08 | 7.77 | 1.31 | 0.34 |
| MPTMAC-CA | 10 | 60.17 | 9.33 | 8.21 | 5.96 | 0.58 |
| | 32 | 54.12 | 8.68 | 8.32 | 21.42 | 0.71 |

Table 1. Copolymerization of MPTMAC with N-substituted acrylamides^a

^aat 55°C using ACVA initiator; ^busing C/N ratio; ^cstudied in methanol at 30°C

Main, Germany) was used to measure the viscosities of copolymers in methanol at 30±0.5°C. Brookfield viscometer (Brookfield Instruments Middleboro, MA) was used to study the effect of shear rate on viscosity of copolymers using a concentration of 1 g per 100 ml in DMF solvent at 30±1°C. The molecular weight analysis was performed using a gel permeation chromatograph (Waters Associates Milford, MA) equipped with a 410 model RI detector. The solvent DMF was stabilized with 0.01% LiBr with a flow rate of 1 ml/min and the columns used were Styragel. Number-average molecular weight (M_n) and Weight-average molecular weight (M_w) were calibrated with polystyrene standards. A Perkin-Elmer DSC-7 Differential scanning calorimeter was used to study the thermal behavior of ionomers at a heating rate of 20°C/min under nitrogen atmosphere. Thermogravimetric analysis was carried out using TGA-7 at a heating rate of 20°C/min under nitrogen atmosphere.

3. Results and discussion

Free radical copolymerization of hydrophilic cationic monomer MPTMAC with N-substituted acrylamides was carried out in aqueous methanol using ACVA as initiator. Since MPTMAC monomer



Figure 1. Copolymerization of MPTMAC with N-substituted acrylamides

was in the form of an aqueous solution (50%) and the N-tertiary alkyl acrylamides are insoluble in water, methanol/water (3:1) medium was used for copolymerization. The schematic representation of ionomer is shown in Figure 1. The copolymerization was carried out by varying the monomer feed composition to get different mol% of cationic monomer in copolymer.

3.1. Characterization

The ¹³C-NMR spectral values of N-tert-butylacrylamide is as follows:

¹³C-NMR (CDCl₃), δ (ppm) : δ 164.9 (CH₂=CH–<u>C</u>O–NH^{····}); δ 132.15 (CH₂=<u>C</u>H–CO–NH^{····}); δ 124.71 (<u>C</u>H₂=CH–CO–NH^{····}); δ 50.86 (^{···}CO–NH–<u>C</u>(CH₃)₃); δ 28.39 (^{···}CO–NH–C(<u>C</u>H₃)₃).

The ¹H-NMR and ¹³C-NMR spectral values of MPTMAC is as follows :

¹H-NMR (CDCl₃), δ (ppm): at 3.1 δ (^{...}N(CH₃)₃); 5.6–5.8 δ (CH₂=CH–); 8.2 (–NH); 3.4–3.5 δ (NH–CH₂–CH₂–CH₂–N⁺–); and 1.6 δ (CH₂=C(<u>CH</u>₃).

¹³C-NMR (CDCl₃), δ (ppm): δ 18.30 (CH₂=C(<u>C</u>H₃)–); δ 22.87 (-NH-CH₂-<u>C</u>H₂-CH₂-N⁺(CH₃)₃); δ 36.58 (-NH-<u>C</u>H₂-CH₂-CH₂-N⁺(CH₃)₃); δ 64.31 (-NH-CH₂-CH₂-<u>C</u>H₂-N⁺(CH₃)₃); δ 121.76 (<u>C</u>H₂=C(CH₃)-CO-NH-); δ 138.89 (CH₂=<u>C</u>(CH₃)-CO-NH-); δ 170.96 (CH₂=C(CH₃)-<u>C</u>O-NH-);

The ¹³C-NMR spectrum of MPTMAC-BA ionomer is shown in Figure 2. The ¹³C-NMR spectrum of MPTMAC-BA ionomer shows the disappearance of vinyl carbon peaks at 121.76 and 138.89 ppm of MPTMAC monomer. The spectrum shows the presence of a peak at 52.1 ppm, due to N–CH₃ group of MPTMAC unit. The peak at 28.37 ppm is due to tert-butyl group of N-tert-butylacrylamide (BA) unit. The carbonyl carbon peaks appears at 163.53 and 174.54 ppm are due to the BA and MPTMAC units respectively. The peak values confirm the occurrence of copolymerization.



Figure 2. ¹³C-NMR spectrum of MPTMAC-BA ionomer (8.99 mol%)

3.2. Determination of mol percentage of MPTMAC

The mol% of cationic monomer, MPTMAC in the MPTMAC-AA copolymers were calculated from elemental analysis data using C/N ratio [8]. Copolymers MPTMAC with N-tert-amylacry-lamide (AA) have the following weight percentages of carbon and nitrogen represented by

%C = 96.08 [AA] + 120.1 [MPTMAC] %N = 14.01 [AA] + 28.02 [MPTMAC]

The mol% of MPTMAC in the copolymer is obtained from the Equation (1):

Mol% of MPTMAC in copolymer =

$$\frac{7 (\%C) - 48 (\%N)}{12 (\%N) - 7 (\%C)} \cdot 100$$
(1)

Similarly for the other ionomers the corresponding equations were derived and the mol% was calculated. The calculated mol% of MPTMAC are given in Table 1. The calculated mol% of MPTMAC in the copolymers indicate the formation of ionomers. In the case of MPTMAC-AA, the content of ionic charge (mol% of MPTMAC) in copolymer is higher than in feed, when the feed mol% is at 4 and 10. But, the mol% of MPTMAC in copolymer is lower than in feed , when the feed mol% is 32. The influence of MPTMAC decreases with increasing the feed mol%. Whereas, in the case of MPTMAC- CA, the influence of MPTMAC increases with increasing the feed mol%. The increasing and decreasing trends of MPTMAC in copolymer depend on the nature of the comonomers.

3.3. Viscosity study

From Table 1 it is clear that the reduced viscosity of ionomers increases with increasing mol% of MPTMAC and it is due to molecular weight of ionomers. The reduced viscosity η_{sp}/C versus concentration C plots of MPTMAC-BA copolymers in methanol are shown in Figure 3. The plots corresponding to mol% of MPTMAC equal to 5.51 and 8.99 do not show an increase of reduced viscosity with the decreasing of concentration, whereas the plot corresponding to 25.46 mol% of MPTMAC shows a steep raise of reduced viscosity with decreasing concentration. So the copolymers with the mol% of 5.51 and 8.99 of MPTMAC possess a behavior close to that of non-polyelectrolyte [11, 12]. The decrease of reduced viscosity for 5.51 mol% of MPTMAC in MPTMAC-BA ionomer at low polymer concentration is due to intramolecular associations at low polymer concentrations. Therefore 'polyelectrolyte behavior' was not observed for this ionomer because of ion-pair interactions [9]. Whereas the copolymer with higher mol% 25.46 of MPTMAC behaves as a polyelectrolyte. This is due to the coil expansion of ionomer chains at extreme dilution [13]. The ionic repulsion of the pendant quaternary ammonium cations



Figure 3. Reduced viscosity plots of MPTMAC-BA ionomer



Figure 4. Reduced viscosity plots of MPTMAC-AA ionomer

attached to the polymer backbone resulting from the dissociation of gegenions like Cl⁻ or I⁻-leads to polymer chain expansion. A similar trend has been observed by other workers in the case of sulphonated polystyrene ionomers [14] and quaternary polymers [11]. The reduced viscosity η_{sp}/C versus concentration C plots of MPTMAC-AA copolymer in methanol are shown in Figure 4. Copolymers having different mol% of MPTMAC content viz., 10.70, 13.15 and 22.65 (Table 1) have been studied. In all these cases the reduced viscosity increases remarkably with decreasing polymer concentration thereby exhibiting polyelectrolyte behavior. The concentration dependency of the reduced viscosity in polar solvents appear to be related to the molecular weight of the polymers. In the case of MPTMAC-CA copolymers (1.31 and 5.96 mol%) the reduced viscosity increases with decrease in polymer concentration upto a concentration of $0.3 \text{ g} \cdot \text{dl}^{-1}$, after which it decreases with decreasing concentration (Figure 5). At lower polymer concentration the mutual attraction between positive and negative charges may cause bending of the polymeric chains and decrease the reduced viscosity. But for copolymer having mol% of MPTMAC equal to 21.42 the reduced viscosity increases with decreasing concentration and hence it behaves as a polyelectrolyte. These ionomers behave as poly-



Figure 5. Reduced viscosity plots of MPTMAC-CA ionomer

| Copolymers | Mol% of MPTMAC in copolymer | M _w ·10-5 | M _n ·10-5 | M_w/M_n |
|------------|-----------------------------|----------------------|----------------------|-----------|
| MPTMAC-BA | 8.99 | 3.95 | 1.90 | 2.08 |
| MPTMAC-AA | 13.15 | 1.52 | 0.97 | 1.57 |
| MPTMAC-CA | 5.96 | 1.51 | 0.70 | 2.17 |

Table 2. GPC analysis of MPTMAC -N-substituted acrylamide Ionomers

electrolyte at higher mol% of ionic content and behave as non-polyelectrolyte at lower mol% of ionic content [9].

3.4. Rheological studies

Viscosity behavior at varying shear rate was studied using a Brookfield viscometer (Brookfield instruments. Middleboro, MA) for MPTMAC-BA (8.99 mol%) and poly BA in DMF at 30°C. The plot of viscosity [cps] versus shear rate [rpm] for ionomer and the homopolymer are shown in Figure 6. The change in the viscosity dependency on shear rate was found to be less in the ionomer than that of hompolymer. The viscoplastic nature of the ionomer less pronounced than that of homopolymer. The sizable content of MPTMAC groups in the ionomer, which produced intramolecular interactions there by reducing that entanglements [15].



Figure 6. Plots of viscosity vs shear rate of MPTMAC-BA (•) and poly BA (0)

3.5. GPC Analysis

The analysis was carried out in the presence of 0.01% Li Br in DMF at 30°C. The molecular weight distribution of hydrophilic ionomers are given in Table 2. The molecular weights are found to be high $(M_w = 3.95 \cdot 10^5)$. The polydispersity index of these ionomers MPTMAC-N-substituted acrylamides range from 1.57 to 2.17 (Table 2) and these value indicates that the termination mainly by disproportionation [16]. The higher molecular weight of ionomers are due to higher degree of polymerization. The steric hindrance caused by the pendant ionic group is less compared with long alkyl moiety [9]. Moreover, the molecular weight of ionomers increases in the order of MPTMAC-CA <MPTMAC-AA<MPTMAC-BA may be due to the influence of N-alkyl substituent of acrylamides (bulkiness of N-alkyl group).

3.6. Thermal analysis

3.6.1. Glass transition temperature

The glass transition temperature (T_g) is the temperature at which the amorphous domain of a polymer takes on the characteristic properties of glassy state. The T_g depends on the morphology of the polymer and the T_g values are presented in Table 3. From the table it is clear that the T_g of poly(N-tert-butylacrylamide) homopolymer is 64.8°C and that of the corresponding ionomer is 79.4°C. The increase in T_g may be attributed to a reduction in segmental mobility due to the electrostatic attraction between the pendent ionic group of the polymer chain and the counterions. The ionomers of N-tert-amylacrylamide and N-cyclohexylacrylamide with MPT-MAC have higher T_g values compared to the corresponding homopolymers of N-substituted acrylamides.

3.6.2. Thermogravimetric analysis

The TGA data for the ionomers of MPTMAC with N-substituted acrylamides are given in Table 3. A

| Copolymers | Mol% of MPTMAC | Mol% of MPTMAC | IDT | T ₁ | T ₂ | Tf | Tg |
|------------|----------------|----------------|-------|----------------|----------------|-------|-------|
| | in feed | in copolymer | [°C] | [°C] | [°C] | [°C] | [°C] |
| MPTMAC-AA | 10 | 13.15 | 242.8 | 265.6 | 445.5 | 463.8 | - |
| MPTMAC-AA | 32 | 22.65 | 328.8 | 349.4 | 444.6 | 468.0 | 112.4 |
| Poly(AA)- | _ | _ | - | - | - | - | 86.2 |
| MPTMAC-BA | 10 | 8.99 | 254.2 | 277.0 | 452.2 | 463.5 | _ |
| MPTMAC-BA | 32 | 25.46 | 330.4 | 357.0 | 448.4 | 471.4 | 79.4 |
| Poly(BA) | - | - | - | - | - | - | 64.8 |
| MPTMAC-CA | 10 | 5.96 | 236.1 | 273.2 | 452.2 | 471.8 | - |
| MPTMAC-CA | 32 | 21.42 | 265.6 | 345.8 | 452.2 | 475.3 | 86.2 |
| Poly(CA)- | - | _ | _ | - | _ | _ | 79.2 |

Table 3. TGA and DSC data for MPTMAC-N-substituted acrylamide ionomers

IDT: Initial Decomposition Temperature; T_1 : decomposition temperature at stage 1; T_2 : decomposition temperature at stage 2; T_f : final decomposition temperature; T_g : glass transition temperature



Figure 7. TGA of MPTMAC-AA ionomer system

typical TGA curves for MPTMAC-AA ionomers are shown in Figure 7. All the ionomers exhibit double stage decomposition. MPTMAC-AA shows an increase in initial decomposition temperature (IDT), with increase in mol% of MPTMAC. Hence the stability of the ionomers increases with the increasing mol% of ionic content. The initial weight loss (8.8%) is observed for these ionomers due to the moisture absorption. For 13.15 mol% ionomer, the weight loss in the stage 1 is about 6.1% corresponding to $T_1 = 265.6^{\circ}$ C and the weight loss in the stage 2 is about 78.4% corresponding $T_2 = 445.5$ °C. The weight loss occurring in the stage 1 may be due to dequaternization at N^+ site of MPTMAC unit. The maximum weight loss occurring in stage 2 may be due to scission in amide linkage of both monomeric units of ionomer. For 22.65 mol% ionomer the $T_1 = 349.4^{\circ}$ C and $T_2 =$ 444.6°C. The decomposition temperature in the stage 1 (T_1) increases with increase of mol% of MPTMAC. A similar trends have been observed in the other ionomer systems.

4. Conclusions

Quaternary ammonium ionomers were prepared by copolymerization of MPTMAC with N-substituted acrylamides at 55±1°C. The monomers and ionomers were characterized by 1H- and 13C-NMR spectroscopy and the mole percentage of cationic monomer in copolymer was calculated from elemental analysis using C/N ratio. The reduced viscosity of ionomers in methanol showed non-polyelectrolyte behavior at lower mole percentage and behaves as polyelectrolyes at higher mole percentage. This is due to coil expansion of ionomer chains at extreme dilution. Shear rate dependency of viscosity of ionomers showed viscoplastic behavior. The molecular weights of ionomers are found to be high due to higher degree of polymerization. Polydispersity index values of ionomers indicate that the termination occurred mainly by disproportionation. The T_g values of ionomers are higher than those of the corresponding homopolymers and the increase in T_g attributed to reduction in segmental mobility. In TGA, all the ionomers showed double stage decomposition. The IDT shows that the stability of ionomers increases with increasing mole percentage of ionic content.

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Photo-oxidation of EPDM/layered double hydroxides composites: Influence of layered hydroxides and stabilizers

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Abstract. The photo-oxidation of ethylene propylene diene monomer (EPDM)/ layered double hydroxide (LDH) composites as well as EPDM/LDH with stabilizers is studied under accelerated UV irradiation ($\lambda \ge 290$ nm) at 60°C for different time intervals. The development of functional groups during oxidation was monitored by FT-IR spectroscopy. The photo-degradation of the pristine polymer and composites take place and the increase in hydroxyl and carbonyl groups with irradiation times, was estimated. EPDM filled LDH showed higher degradation rate than pristine EPDM, while in acidic medium EPDM/LDH showed almost equal degradation as in isolated conditions. These results show the advantages of LDHs as a filler as well as an acid killer. The effect of stabilizers is very less because of their concentration in comparison of LDH.

Keywords: polymer composites, layered double hydroxides, EPDM, photo-oxidation

1. Introduction

Composites of organic and inorganic compounds represent an important class of engineering materials [1, 2]. Amongst the inorganic materials, smectite clays have received considerable attention because their structure exhibits the required stiffness, strength and dimensional stability. In recent years, it has been found that layered double hydroxides (LDHs), also known as hydrotalcite-like compounds (HTlcs), have attracted great attention [3–9], because of their layered structure and high anion-exchange capacity, which enables various technical applications [10, 11]. The structure consists of positively charged brucite (magnesium hydroxide)-like layers with interlayer space containing charge compensating anions and water molecules. The metal cations occupy the centers of octahedra whose vertexes contain hydroxide ions. The octahedra are connected by edge sharing to form an infinite sheet [12, 13]. The general formula of the compounds is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}]A^{n-}_{x/n}mH_{2}O$, where M^{2+} and M^{3+} are divalent $(Mg^{2+}, Zn^{2+}, Ni^{2+},$ etc.) and trivalent cations $(Al^{3+}, Cr^{3+}, etc.), A^{n-}$ is a non-framework charge compensating anion (such as CO_{3}^{2-} , Cl^{-} , SO_{4}^{2-}), and *x* is normally between 0.17 and 0.33. The structure is shown in (Figure 1). Layered double hydroxides and their derivatives are inorganic materials with a positive layer charge in which the interlayer anions can be replaced by ion-exchange processes. Owing to its high anion-



Figure 1. Structure of layered double hydroxide

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exchange capacity, LDHs have found many potential applications, including those in pharmaceuticals, catalyst supports, inorganic fillers and acid killers [14] to prevent the degradation of polymeric materials by effectively scavenging any acid generated during processing as well as during application.

Ethylene propylene diene monomer (EPDM) rubber is widely used due to its good mechanical properties, very low unsaturation and associated resistance to ageing and ozone deterioration [15]. This is due to its saturated hydrocarbon backbone with the presence of double bonds in side chains. It has been extensively used in making automotive tire, side walls, cover strips, wires, cables, hoses, belting, roofing barriers and sporting goods. Due to its outdoor applications, the study of its durability in acidic environment is extremely important for industry as well as academic point of view. Only a few reports have focused on the degradation of EPDM rubbers in specific aggressive acidic environments [16–19].

To the best of our knowledge, the effect of LDHs on the acidic degradation of EPDM/LDHs composites has not yet been reported. In order to derive a more detailed understanding of the various factors influencing the effect of different stabilizers, the filler concentration (composition) was kept constant. This paper deals the degradation of EPDM/ LDH composites in acidic environment in presence of polychromatic irradiation ($\lambda \ge 290$ nm). The effect of commercial stabilizers in composites has also been studied.

2. Experimental

2.1. Materials

The elastomer used was commercial Ethylene Propylene Diene Monomer (EPDM) (ethylene: propylene: diene (5-ethylidene-2-norbornene) 55:41:4.) supplied by M/s. Sediver, France. EPDM rubber was purified by dissolving in toluene solution and precipitating from acetone to remove the additives. The commercial grade thiourea (ethylenethiourea, NPV/C), sulfur, zinc oxide, stearic acid were purchased from S.D. Fine Chemicals Ltd, India. Layered double hydroxide (LDH) was synthesized in our laboratory. The conventional stabilizers (Irganox 1076, Irganox 1010, Tinuvin-P) were obtained from M/s Ciba Geigy India Pvt. Ltd., Mumbai, India.

2.2. Synthesis of layered double hydroxide (acid killer)

For the synthesis of LDH (a Mg/Al double-layered hydroxide) of formula:

 $[Mg_3Al(OH)_8]^+[0.5CO_3] \cdot mH_2O]$, an aqueous solution (250 ml) containing Mg(NO₃)₂·6H₂O and $Al(NO_3)_2 \cdot 9H_2O$ with a ratio of Mg/Al (3:1) were slowly added to a second solution (250 ml) of NaOH (0.675 mol) and NaNO₃ (0.2 mol) under vigorous stirring at 65°C. The addition took nearly 2 hrs. The precipitate formed was filtered and washed thoroughly with 500 ml de-ionised water (at least until the pH of the filtrate was 7) and freeze dried and then aged for 20 hrs at 20°C in their mother liquor and then filtered, washed and dried. The samples were hydrothermally treated using microwave heating (8 hrs with a step-wise increase in temperature from 120 up to 180°C and a corresponding pressure of 2–10 bar). The crystalline phases were characterized by X-ray diffraction [20].

2.3. Preparation of EPDM-layered double hydroxides composites

LDH was mixed with EPDM at 180° C with 70 rpm for 5 minutes by using a twin-screw extruder (DSM, MICRO-5). The screw length was 1365 mm and *L/D* was 45.5, the LDH concentration was kept 5 wt%, vulcanizing agents were added as shown in Table 1. The mixing of EPDM/LDH hybrid and vulcanizing agents (Zinc oxide – 5%, Stearic acid – 1%, Sulfur – 1.8% and Thiourea – 1.5%) were mixed at 90°C for 3–5 minutes. EPDM composites were also filled with stabilizers (Irganox 1076, Irganox 1010 and Tin-P concentration were 0.5 wt%). For comparative study, EPDM samples

Table 1. Composition of the composites

| S.No | LDHs [wt%] | Vulcanization agents*[wt%] | Stabilizers 0.5 [wt%] | Sample code | |
|------|---------------|-------------------------------|--------------------------|----------------|--|
| 1 | - | 9.3 | - | EP-Neat | |
| 2 | 5 | 9.3 | - | EP-H | |
| 3 | 5 | 9.3 | Irganox 1076 | EP-I 76 | |
| 4 | 5 | 9.3 | Irganox 1010 | EP-I 10 | |
| 5 | 5 | 9.3 | Tinuvin-P | EP-Tin P | |

*Zinc oxide -5%, Stearic acid -1%, Sulfur -1.8% and Thiourea -1.5%

were prepared without LDH (only vulcanizers) under same experimental conditions [21]. All composites were molded into films (thickness \approx 100 µm) at 160°C by using the hydraulic press for 10 minutes.

2.4. Photoirradiation

The photo-irradiation experiments were carried out in accelerated weathering chamber SEPAP 12/24 (M/s Material Physico Chimique, Neuilly/Marne, France) at 60°C. The chamber consists of (4·400 W) medium pressure mercury vapor lamps supplying radiation ($\lambda \ge 290$ nm). The instrument is described elsewhere [22]. Nitric acid treated samples were also irradiated in chamber under same conditions. For acidic treatment, the samples were kept in vapour phase in a desicator, containing 5% nitric acid concentration for 3 hrs after every 25 hrs degradation intervals.

2.5. Measurement of photostabilizing efficiency

The photostabilizing efficiency of LDH on EPDM was monitored by the measurement of the carbonyl and hydroxyl group changes by FT-IR spectroscopy. The IR absorption spectral changes of the film upon irradiation with 300 nm UV light were observed for different time intervals. The data obtained were compared with pristine EPDM and EPDM/LDH with and without conventional stabilizers (Irganox 1076, Irganox 1010, Tin-P) under similar accelerated conditions.

2.6. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) observation of EPDM/LDH composites was performed with a Philips CM300 FEG TEM instrument operated under an acceleration voltage of 300 kV. Thin sections (thickness ≈ 200 nm) for TEM observations were cut from the as-prepared composites under cryogenic conditions using a Leica ultramicrotome with a diamond knife (Figure 2).

2.7. Scanning electron microscopy

Surface changes of the irradiated samples were examined by SEM. The stained samples were dried under vacuum for 24 h at 50°C and the gold-coated



Figure 2. TEM image showing LDHs dispersion

samples were examined under electron microscope (Leica Cambridge Stereoscan 440 Model).

3. Results and discussion

3.1. Characterization

The LDH was characterized by XRD according to literature [20]. The XRD data between 2 and 70°, were recorded at 0.5° /min, using CuK_{α} radiation at a generator voltage of 40 kV.

The $[Mg_3Al(OH)_8]^+[0.5CO_3 \cdot mH_2O]^-$ shows a basal 001 reflection at d = 7.9 Å. This reflection corresponds to the interlayer distances.

3.2. Degradation products

FT-IR spectroscopy was successfully used to study the degradation pattern and products in polymers [23, 24]. The rate of photo-oxidation was followed by monitoring the development in carbonyl and hydroxyl region by FT-IR spectra for different time intervals from 0 to 100 hrs. The increase of absorbance in the hydroxyl and carbonyl region was studied as a function of irradiation time. The absorbance of the ethylidene units at 808 cm⁻¹ dramatically decreases and new bands appeared at 910 and 970 cm⁻¹, which can be assigned, respectively, to the vinyl-type unsaturations coming from Norrish II type reactions (Figure 3) and to CH wag of the other double bonds derived from hydrogen abstraction reactions on allylic positions during the photooxidation as already reported in the case of EPDM [25-26] and the photoproducts of composites were same as in the pristine EPDM [22]. Figures 4 and 5 show the IR region for the evolution of carbonyl and hydroxyl regions, respectively, of the composites [EP-H] upon UV irradiation. The



Figure 3. Simplified mechanism of EPDM degradation



Figure 4. Evaluation of carbonyl region of EPDM/LDHs composites during photo-oxidation

increase in these regions may be attributed to the degradation of polymer matrix, which may lead to chain scission. The spectra showed that the induction period is reduced in the presence of LDH. In presence of the stabilizers also, the induction period is less than that of pristine EPDM and it may be due



Figure 5. Evaluation of hydroxyl region of EPDM/LDHs composites during photo-oxidation

to interaction between the phenol groups of stabilizers and LDH. The vibrations at 1780, 1735, 1721 and 1710 cm⁻¹ have been assigned for lactone, ester, ketone and acid groups, respectively. In the hydroxyl region, a large absorption band was observed with a maximum at 3400 cm⁻¹, which is due to oxidized products such as hydroperoxides and alcohols, whereas the rate of formation of these products was higher in composites than neat film. Both, the carbonyl and hydroxyl regions were increased similarly and were faster than in the pristine EPDM where no additional peak could be observed in the present system (Figures 6 and 7). This phenomenon confirms that the presence of filler influences the degradation of EPDM but degradation products remain the same. Transition Metal elements viz., Mn(II), Fe(III), Ru(II), Co(II), etc., play a key role to enhance the rate of hydroperoxide decomposition [27]. The reason to increase the rate of degradation may be due to the presence of metal ions; which may catalyze the decomposition of hydroperoxide to alkoxy or peroxy radicals by the following mechanism and may therefore, accelerate the photo-oxidation of polymers as shown in Figure 8.



Figure 6. Evaluation of carbonyl region as a function of irradiation time duringphoto-oxidation



Figure 7. Evaluation of hydroxyl region as a function of irradiation time duringphoto-oxidation

| R' + O ₂ | \rightarrow | RO ₂ |
|--------------------------|---------------|---------------------------------------|
| RO ₂ ' + RH | \rightarrow | ROOH + R' |
| ROOH + M ^{II} | \rightarrow | RO` + M [⊪] OH |
| M [™] OH + ROOH | \rightarrow | M [™] OOR + H ₂ O |
| M [™] OOR | \rightarrow | M" + ROO' |
| M [⊪] OOR | \rightarrow | MO [.] + RO [.] |
| RO' + RH | \rightarrow | ROH + R' |



The photo-degradation of the same compositions was studied in acidic conditions and was observed that EPDM/LDH composites showed interesting results (Figures 9 and 10). There is not much difference in the degradation rate in acidic and natural environment because of LDHs's acid killer nature, which enhances the LDH importance as filler. The



Figure 9. Evaluation of carbonyl region as a function of irradiation time during photo-oxidation in acidic environment



Figure 10. Evaluation of hydroxyl region as a function of irradiation timeduring photo-oxidation in acidic environment



Figure 11. The acid killer mechanism of LDHs

mechanism of LDHs as an acid killer is described in Figure 11 where $X = CI^-$, NO_3^- , etc. The presence of stabilizers also does not show much effect on stabilization because of very low concentration in comparison to LDH, however, Tinuvin-P shows better stabilization in comparison to Irganox 1076 and Irganox 1010.

3.3. Morphological aspects

SEM is a reliable tool to monitor the surface chances during degradation of polymers and interesting micrographs are shown in Figures 12 and 13. The presence of highly eroded surface with small cavities in the samples, indicates the higher degradation after 100 hrs irradiation. A scattering pattern of small patches was observed after UV irradiation, which must be due to the generation of more oxida-



Figure 12. SEM study of EPDM/LDHs composites after 100 h Photo-degradation



Figure 13. SEM study of pristine EPDM after 100 h Photo-degradation

tion products in Figure 12 than in Figure 13, and this fact again supported the conclusion that presence of LDH enhances the degradation rate in acidic as well as isolated conditions.

4. Conclusions

The comparison of the kinetic curves showed the oxidation for the different samples which reveals an influence of LDH and the stabilisers on the formation of carbonylated photoproducts. It was observed that the photo-oxidative products were not changed after adding the filler, however, the rate of photo-oxidative degradation of EPDM/LDH composites is faster than that of pristine EPDM. LDHs showed good results in acidic conditions, which enhances its importance. The lower efficiency of the stabilizers could result because of high percentage LDH filler. It could be because of the adsorption of the additives onto the LDH, which partially inhibits their stabilizing activity.

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Abaca fibre reinforced PP composites and comparison with jute and flax fibre PP composites

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Abstract. Abaca fibre reinforced PP composites were fabricated with different fibre loadings (20, 30, 40, 50 wt% and in some cases 35 and 45 wt%). Flax and jute fibre reinforced PP composites were also fabricated with 30 wt% fibre loading. The mechanical properties, odour emission and structure properties were investigated for those composites. Tensile, flexural and Charpy impact strengths were found to increase for fibre loadings up to 40 wt% and then decreased. Falling weight impact tests were also carried out and the same tendency was observed. Owing to the addition of coupling agent (maleated polypropylene -MAH-PP), the tensile, flexural and falling weight impact properties were found to increase in between 30 to 80% for different fibre loadings. When comparing jute and flax fibre composites with abaca fibre composites, jute fibre composites provided best tensile properties but abaca fibre polypropylene composites were shown to provide best notch Charpy and falling weight impact properties. Odours released by flax fibre composites were smaller than jute and abaca fibre composites.

Keywords: polymer composites, abaca fibre, adhesion, mechanical properties, odour emission

1. Introduction

Over the last few years, ecological concerns have initiated a considerable interest in natural materials to produce 'green' products. The rapidly increasing environmental awareness, growing global waste problem, geometrically increasing crude oil prices (the raw material of synthetic fibres) and high processing cost trigger the development concepts of sustainability and reconsideration of renewable resources. Natural fibres have already established a record of accomplishment as reinforcing material in automotive parts. Natural fibres like jute, flax, hemp coir and sisal have all proved to be good reinforcement in thermoset and thermoplastic matrices and are being used in automotive applications, construction as well as in packaging industries with few drawbacks [1–5].

Abaca or banana fibre, cellulosic fibres obtained from the pseudo-stem of banana plant (Musa sepientum) is a bast fibre [6]. In tropical countries, agricultural plants like banana plants are available in abundance. Banana fibre is a waste product of banana cultivation and without any further investment banana fibre can be obtained for industrial purposes. Nowadays abaca fibre reinforced composites are coming into in interest due to the innovative application of abaca fibre in under floor protection for passenger cars by Daimler Chrysler [7]. The new combination of polypropylene (PP) thermoplastic with embedded abaca fibre was patented by Daimler Chrysler's researchers, and the manufacturing process (compression moulding process) has been initiated by Rieter Automotive. It is described that abaca fibre has a high tensile

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strength, resistant to rotting and its specific flexural strength is near to that of glass fibre [8]. Abaca is the first natural fibre to meet the stringent quality requirements for components used on the exterior of road vehicles, especially resistance to influences such as stone strike, exposure to the elements and dampness.

Pothan *et al.* [9–12] reported dynamic mechanical properties, effect of hybridization and chemical modification of abaca fibre reinforced polyester composites in compression moulding process. The equilibrium water uptake and diffusion coefficient were found to be minimum for treated fibre composites.

Shibata *et al.* [13, 14] investigated treated abaca fibre and non treated abaca fibre reinforced biodegradable polyesters in injection moulding process. The improvement of mechanical properties is possible by abaca fibre reinforcement regardless of the fibre treatment and kind of matrix polymer used in this study.

In our previous studies [15] different moulding processes, latest applications, innovations and properties of abaca fibre reinforced plastic have been elaborately described. Due to innovation of Rieter Automotive [16] and other motivating properties and the progressively expanding performance of technical and standard plastics, the application of natural fibres came nearer. Among the resourceful natural fibre composite engineering, abaca fibre reinforced polypropylene composite has got remarkable and outstanding interest in the automobile industries owing to low cost availability, high flexural and tensile strength, good abrasion and acoustic resistance, relatively better resistance to mould and rot and very good resistance to UV rays [17].

On the other hand jute is one of the most common agricultural fibres which exhibit moderately higher mechanical properties and are cultivated almost exclusively in Bangladesh, India, Thailand and in some parts of Latin America. The total annual world production of jute is about 2500 thousand tones [18]. In addition, flax is the most important and demandable bast fibres in Europe. About 80% of the total world flax crop is grown in France, Belgium, Spain, UK and Holland. Flax fibre is relatively stronger, crisper and stiffer to handle [19]. During the last decade jute and flax fibre gained remarkable attention as reinforcing materials of composites. The aim of this work is to optimize fibre loading for abaca fibre reinforced composites and compare jute and flax with abaca fibre reinforced PP composites in terms of their mechanical properties, structural and odour emission properties.

2. Experimental

2.1. Materials

2.1.1. Polymeric matrix

Polypropylene (Sabic PP 575P) was provided as granules by Sabic Deutschland GmbH & Co.KG, Duesseldorf, Germany. Its melting temperature was 173°C and melt flow index was 10.5 g/10 min at 230°C. Its density at room temperature was 0.905 g/cm³.

2.1.2. Abaca fibre

Abaca fibre was obtained from RIETER Automotive Heatshields AG, Sevelen, Switzerland. The abaca fibre diameter was 150–260 µm and chopped into 25 mm fibre length by using an automatic cutter provided by company 'EKOTEX', Namyslow, Poland.

2.1.3. Jute fibre

Jute fibre was collected from J. Schilgen GmbH & Co., Emsdetten, Germany. It was wrapped in cone with twist number Nm 3.6/1. The fibre chopped into 25 mm length to ensure easy blending with polymer matrix. The single fibre diameter was $60-110 \mu m$ and original fibre length was 3 to 3.5 m long.

2.1.4. Flax fibre

Flax fibre was obtained from J. Schilgen GmbH & Co., Emsdetten, Germany. It was wrapped in cone with twist number 3.6/1. The twisted flax fibre cut into 25 mm. The single fibre diameter was $60-110 \ \mu$ m.

2.1.5. Coupling agent

A commercially available maleic anhydride-polypropylene copolymer (Licomont AR 504 FG) with an acid number of 37–43 mg KOH/g was used as a coupling agent. It was obtained from Clariant Corp., Frankfurt, Germany. Its softening point was 153° C and density was 0.89–0.93 gm/cm³. It accounted for 5% of the weight percentage of abaca fibre. In our previous work [20], it was found that the coupling agent MAH-PP showed best performance in the concentration of 5 wt% of the natural fibre and wood fibre-PP composites.

2.2. Processing

2.2.1. Mixer-injection moulding

Abaca fibres with PP were mixed by high speed cascade mixer (Henschel heat-cooling mixer system, type HM40-KM120). Abaca fibres were dried at 80°C in an air circulating oven for 24 hours (moisture content <1%) before mixing. The fibre ad PP at different proportions were placed into hot mixer and heated up to the melting temperature of polypropylene (173°C) and then hot agglomerate granules were transferred to the cool mixer where hot agglomerate granules cooled down to room temperature by the cold water. Then cold agglomerate granules were dried again (80°C, 24 hours) before the sample preparation by injection moulding process. Test samples were prepared from dried agglomerate by injection moulding process at temperature zone 150-180°C, mould temperature of 80°C and under an injection pressure 20 kN/mm². The same procedure was preserved for jute fibre-PP and flax fibre-PP composites.

2.3. Characterization of composites

2.3.1. Mechanical properties

Tensile and flexural tests were performed at a test speed of 2 mm/min according to EN ISO 527 and EN ISO 178 for different natural fibre composites with and without coupling agent on a Zwick UPM 1446 machine. All tests were performed at room temperature (23°C) and at a relative humidity of 50%. Charpy impact test was carried out using 10 notched samples according to EN ISO 179. In each case a standard deviation <15% (drop weight) was used to calculate the Charpy impact strength.

Impact properties were tested by using a low velocity falling weight impact tester at room temperature in non penetration mode. All tests were performed according to EN ISO 6603-2. The impactor's mass was 0.75 kg and the impact energy was 0.96 Joules and 10% standard deviation was taken an account with impact properties. The result of the impact test



Figure1. Typical impact force-deflection curve

can be descried by characteristic values: loss energy (W_v) as a measure of dissipated energy and strain energy (W_s) as a measure of the stored energy which is shown in Figure 1. The figure has been taken from one of the experimental tests. The weight impact test characterized by damping index ($\Lambda^* = W_v/W_s$) which is the ratio of loss energy (W_v) and strain energy (W_s). If the composites bear out strain energy more than loss energy, it means that the composites have the ability to regain more energy than lose. So the damping index (Λ^*) value will be less than one which indicates the quality of composites. Five test samples have been investigated for every category and damping index has been calculated.

2.3.2. Scanning electron microscope

The morphology of the abaca fibre reinforced PP composites with and without MAH-PP were investigated using scanning electron microscope (SEM), MV2300, CamSan Electron Optics, whereas fractured surfaces of flexural test samples were fractured in liquid nitrogen and studied with SEM after being sputter coated with gold.

2.3.3. Odour measurement

The most important method to evaluate odour is olfactometry. It uses the human nose as a sensor. In the principal of olfactometry, the sample gas (odour sample) is diluted with neutral air at defined ratio (1 gm/1 litre). This dilution is represented to the panel lists as smell sample. The panel lists are offered several dilution steps. The odour concentration of the examined sample is the dilution factor at the detection threshold and it is expressed as multiples of one odour unit per cubic meter (OU/m³) at the standard conditions. The odour level (L_{od}) is

observed to describe the intensity of a sensation as a function of the logarithm of the amount of the stimulating quantity. The reference quantity of the odorant concentration at the threshold is 1 OU/m³. The equation can be expressed as (1):

$$L_{od} = 10 \cdot \log\left(\frac{C_{od,cs}}{C_{od}}\right) \quad \text{in } dB_{od} \tag{1}$$

where C_{od} is concentration of neutral air and $C_{od,cs}$ is concentration of neutral air with smell sample. The odour measurements were performed with olfactometer T07 (ECOMA) as prescribed by standard method VDI 3881. The samples were stored for 30 minutes at 60°C in all cases [21].

3. Results and discussion

3.1. Abaca fibre reinforced composites

The tensile and the flexural strength properties of modified and non modified abaca fibre composites with respect to different fibre loads are illustrated in Figure 2. It is essential to find out the optimum fibre loading to achieve maximum property [13]. The tensile and flexural strengths showed increasing tendency up to 40 wt% of fibre loading and then both strengths decreased with increasing fibre load. The highest strength properties observed at around 40 wt% fibre loading can be explained by better fibre distribution in matrix material and less fibre fractures. Therefore the bond between fibre and matrix often dictates whether the fibre will improve the properties of composites by transferring an applied load. The stress transfer between matrix and fibers in a composite is not only determined by the intrinsic properties of the fiber and matrix, but also affected by the geometric parameters and fiber arrangement within the matrix such as fibre distribution [22]. It is observed from SEM micrograph that relatively excess amount of fibre lie down onto



Figure 2. Influence of fibre load on the tensile and flexural strength of abaca fibre-PP composites

each other rather than being mixed with matrix at 50 wt% fibre loads and relatively less amount of fibre and fibre fracture is observed at 30 wt% fibre loads which also leads to reduce stress transfer ability. It was also observed that relatively less fibre fracture and more homogeneous mixing can be observed at 40 wt% fibre loading. So it may be said that 40 wt% is the optimum fibre loading of abaca fibre reinforced polypropylene composites.

Due to the addition of MAH-PP, improved fibrematrix adhesion and relatively less fibre fractures are observed for each fibre loading. The highest property was observed at 50 wt% fibre loading, because an equal amount of fibre and resin resulted in a strong adhesion via MAH-PP by forming ester bond. It may mean that further increase of fibre load of abaca fibre composite preparation is not achievable by hot-cold mixer. With addition of MAH-PP, the strength properties were increased 30 to 80 % with respect to fibre loading at 40 wt% fibre load.

The notched Charpy impact strength of abaca fibre-PP composites with respect to fibre loads are presented in the Figure 3. The Charpy impact test is a standardized high strain-rate test which determines the amount of energy absorbed by a material during fracture. This absorbed energy is a measure of a given material's toughness and acts as a tool to study brittle-ductile transition.It was observed from diagram that the notched Charpy impact showed similar trend like strength properties. The best property was observed at 40 wt% of fibre loading. No significant effect was observed by addition of MAH-PP, moreover impact properties were found to decrease a little bit. This could be explained by brittleness increase of matrix material and local internal deformation in the composite material [23]. The falling weight impact tests of abaca fibre reinforced polypropylene composites with different



Figure 3. Influence of fibre load on the notched charpy strength of abaca fibre-PP composites



Figure 4. Influence of fibre load on the falling flow impact strength of abaca fibre-PP composites

fibre loadings are illustrated in Figure 4. As it was indicated in experimental section that the impact properties characterized by damping index which is ratio of the stored energy and lost energy while the impactor freely strikes the composite surface. Figure 4 showed that the damping index has the unlike influence with respect to fibre loads. The damping index of composites increased at 20 to 30 wt% of fibre loading and decreased at 40 wt% of fibre loading and then further increased. The lowest damping index was observed at 40 wt% of fibre loading. It means that at 40% fibre loading the composites prove to store energy the best from all

fibre loadings. MAH-PP has encouraging and significant effect on the damping index of the composites. The damping index considerably decreased 30 to 120%, leads to the store energy increased by strong adhesion between fibre and matrix.

Scanning electron micrographs (SEM) of abaca fibre reinforced polypropylene composites in the injection moulding process are shown in Figure 5 for the different fibre loads (30, 40, and 50 wt%). It represents fibre and matrix adhesion, fibre fracture or pull out, debonding and micro cracks regarding with different fibre loading. It was observed that the adhesion between fibre and matrix is strong but there are fibre pullouts, debondings and also micro cracks which may be caused by local internal stress for every fibre loading. It is also evident that relatively less fibre pullouts and debondings were observed for 40 wt% fibre loading. Figure 6 represents the influence of coupling agent MAH-PP on the microstructures. Fibre pullout and debonding reduced significantly and the adhesion between fibre and matrix improved strongly due to the addition of MAH-PP for every fibre loading, which was the result of the formation of ester linkages between MAH-PP moieties of PP and OH groups of cellu-







Figure 6. SEM micrographs of abaca fibre-PP composites with different fibre loads with MAH-PP

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Figure 7. Influence of fibre load on the odour emission of abaca fibre-PP composites

lose [24, 25]. Apparently the interfacial adhesion of the treated fibre composites is much better than that of untreated fibre composites. It is also observed that there are less fibre pullouts and fibre debondings at 40 wt% fibre load related to other fibre loads without MAH-PP.

The emitted odour concentration has been measured also for different fibre loading which are shown in Figure 7. The odour emission from the natural fibre composites depends on the fibre's volatile organic contents, process steps, temperature and duration. Volatile organic contents readily release odourants at high temperature (process temperature). In this case the emitted odour concentration increased with fibre load because volatile contents increase in composite materials.

3.2. Comparison of jute and flax composites with abaca fibre composites

The properties comparison of abaca fibre reinforced polypropylene composites with flax-PP and jute-PP composites are illustrated in Figures 8–12. In all cases composites were prepared in mixerinjection moulding process with fibre length of 25 mm and fibre loading of 30 wt%. In previous section, better properties were observed at 40 wt% fibre loading for abaca fibre polypropylene composites whereas in this section 30 wt% fibre loading have been taken as consideration because jute and flax fibre composites are industrially established with 30 wt% fibre loading.

The moduli of abaca-PP, flax-PP and jute-PP composites are illustrated in Figure 8. The Figure 8 is divided into two sub sections. Section 8(a) indicates tensile modulus which shows discrete effect. It was observed that jute-PP composites showed better tensile modulus than abaca-PP and flax-PP



Figure 8. Comparison of tensile and flexural modulus of abaca/jute/flax fibre-PP composites with and without MAH-PP

composites without MAH-PP. The abaca-PP composites showed better tensile modulus than jute-PP and flax-PP composites with using coupling agent MAH-PP. MAH-PP has a significant effect on the modulus properties of abaca-PP composite but very little effect was observed on the modulus properties of jute-PP and flax-PP composites. It may be because of relatively hard and tough abaca fibre bonded with matrix by MAH-PP and improved the modulus properties. Section 8(b) represents flexural modulus; in this section jute-PP composites showed somewhat improved modulus than abaca-PP and flax-PP composites with and without coupling agent MAH-PP. By using coupling agent, tensile modulus of jute-PP and flax-PP composites reduced to some extent but in case of abaca-PP composites some increase was observed.

Figure 9 presents the tensile and flexural strength properties. In Figure 9a, it is observed that jute-PP showed better tensile strength than abaca-PP and flax-PP composites for both cases (with and with-out MAH-PP). MAH-PP has significant effect for all type of composites and strength properties improved 20 to 40%. In Figure 9b, it is also observed that for both cases, abaca-PP composites



Figure 9. Comparison of tensile and flexural strength of abaca/jute/flax fibre-PP composites with and without MAH-PP



Figure 10. Comparison of notch charpy strength of abaca/jute/flax fibre-PP composites with and without MAH-PP

showed better flexural strength than jute-PP and flax-PP. MAH-PP has significant effect on flexural strength for all types of composites and improvement range was 20 to 35%.

Figure 10 illustrates the impact strength by notched Charpy analysis for each fibre composites where abaca-PP composites showed better impact potential than jute and flax fibre composites in both cases (with and without MAH-PP). Fibre geometry could be the reason. It is also observed that MAH-PP has no significant effect on notch charpy impact strength for all types of composites but some improvement is observed for abaca-PP composites. Abaca-PP composite shows better damping properties than jute-PP and flax-PP composite which is shown in Figure 11. Due to the addition of MAH-PP, damping index improve in all types of composites, especially abaca-PP composites showed 60 to 70% improvement on the damping properties.

Figure 12 depicted the comparison of odour emission concentration of abaca-PP, jute-PP and flax-PP composites with and without coupling agent. It represents that abaca-PP composites emitted more odorous gas than jute-PP and flax-PP composites that is why abaca fibre is being used as reinforce-



Figure 11. Comparison of weight impact properties of abaca/jute/flax fibre-PP composites with and without MAH-PP



Figure 12. Comparison of odour emission concentration abaca/jute/flax fibre-PP composites with and without MAH-PP

ment for exterior part of automobile industries. Coupling agent has significant effect on odour emission of abaca fibre composites and odour emission is reduced by about 35%, on the other hand about 10% less odour emission was observed for jute-PP and flax-PP composites. In general aldehydes, ketones, small molecular weight organic components and other substances contained by fibre or produced during processing are responsible for odour emission. These chemicals may interact with coupling agent and could reduce odour emission during processing.

4. Conclusions

This study inspected the effect of different fibre loads of abaca fibre composite and comparison with jute-PP and flax-PP composites, as well as the effect of the addition of a coupling agent on the microstructure and mechanical properties.

The following conclusions could be drawn:

- With considering microstructure and mechanical properties, 40 wt% fibre loading was found to be optimal fibre loading for abaca fibre reinforced polypropylene composites.
- The adhesion between abaca fibre and PP matrix has significantly improved due to addition of MAH-PP, which has influence on mechanical properties. Flexural and tensile strength increased 30 to 80% and the damping properties improved 30 to 120% for different fibre loading.
- Jute fibre-PP composites showed better tensile properties and flexural modulus than abaca-PP and flax-PP composites. But abaca-PP composites showed better flexural strength than jute-PP and flax-PP composites without and with coupling agent.

- Abaca-PP composites showed better damping properties than jute-PP and flax-PP composites in both cases with and without coupling agent.
- Jute-PP and flax-PP composites discharged less odorous gas than abaca-PP composites and coupling agent significantly reduce odour emission for all types of fibre composites.

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The mechanism and kinetics of void formation and growth in particulate filled PE composites

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Abstract. Volume strain measurements were carried out on PE/CaCO₃ composites prepared with three different matrix polymers, containing various amounts of filler. The analysis of the debonding process and the various stages of void formation proved that the model developed for the prediction of the initiation of debonding is valid also for the studied PE/CaCO₃ composites. Debonding stress is determined by the strength of interfacial adhesion, particle size and the stiffness of the matrix. In thermoplastic matrices usually two competitive processes take place: debonding and the plastic deformation of the polymer. The relative magnitude of the two processes strongly influences the number and size of the voids formed. Because of this competition and due to the wide particle size distribution of commercial fillers, only a certain fraction of the particles initiate the formation of voids. The number of voids formed is inversely proportional to the stiffness of the matrix polymer. In stiff matrices almost the entire amount of filler separates from the matrix under the effect of external load, while less than 30% debond in a PE which has an initial modulus of 0.4 GPa. Further decrease of matrix stiffness may lead to the complete absence of debonding and the composite. The size of the voids also depends on the modulus of the matrix. The rate of volume increase considerably exceeds the value predicted for cross-linked rubbers. At the same deformation and filler content the number of voids is smaller and their size is larger in soft matrices than in polymers with larger inherent modulus.

Keywords: polymer composites, particulate filled polymers, debonding, growth of voids, shear yielding

1. Introduction

Particulate filled polymers are used in large quantities in many fields of application. They are extensively applied in the automotive industry as bumpers, various panels and structural components, as well as under hood parts [1]. Garden furniture and household articles are also prepared from them and they are applied in construction as well [1, 2]. One particular application is the production of breathable films, which allow the passage of vapor, but prevent the permeation of liquids. These films are utilized as the back sheets of diapers, in other sanitary applications and as internal roof insulation [2, 4]. In heterogeneous polymer systems, stress concentration develops around the particles under the effect of external load and the actual stress distribution determines the local micromechanical deformation processes [5]. In particulate filled polymers the dominant deformation mechanism is the separation of the matrix/filler interface, i. e. debonding, which leads to a volume increase during deformation [6]. The preparation of

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breathable films is based on and utilizes this process. Films are produced from polyethylene containing a large amount, 40-50 wt% CaCO3 and they are stretched to create the porous structure, which makes breathing possible. However, the size of the voids developing during debonding must be controlled otherwise the film does not fulfill its role. Large holes let also the liquid pass through the film, while the moisture vapor transmission rate (MVTR) of the films is not sufficiently large if very small voids are created. An optimization of component characteristics and process parameters is necessary to achieve films offering maximum performance, i. e. as large MVTR (moisture vapor transmission rate) as possible accompanied by acceptable mechanical properties. Optimization requires the detailed analysis of the debonding process and the factors determining it.

The properties, including vapor transmission, of breathable films are determined by the number and size of the voids formed during their deformation, which, in their turn, depend on the initiation and growth of the voids. The debonding process, which takes place during the deformation of particulate filled polymers, was studied earlier by several authors [7-16]. Models were developed, which predict the conditions for the initiation of debonding [6, 17, 18], attempts were made to predict the number of debonded particles [8, 19] and the growth of voids was also described in a paper [7]. However, a concise analysis of the debonding process has never been carried out in the past. The goal of our work was to analyze the separation of matrix/filler interface in polyethylene composites containing various amounts of CaCO₃ filler. Debonding was determined by the measurement of volume increase during deformation and the results were critically analyzed in view of existing theories. The most important factors governing void formation, as well as the number and size of the created particles are pointed out as a result of the analysis.

2. Background

The most important characteristic of breathable films is MVTR, which depends on the number and size of voids forming during the stretching process. The initiation of debonding is predicted by models [6, 17, 18], but for ideal conditions. In practice, only a part of the particles initiate void formation, their number must be estimated from the results of measurements with the help of appropriate theories. Finally, the created voids increase during further deformation, their size depends on the extent of stretching and on some other factors [7]. In this section a brief account is given about approaches which were developed to predict the three main aspects of the debonding process.

2.1. Initiation

According to our knowledge, two models exist for the prediction of the stress necessary to initiate debonding, those developed by Vollenberg [17, 18] and Vörös [20], respectively. According to both models initiation stress depends on the strength of interfacial interaction, on the size of the particles and on the stiffness of the matrix (Equation (1)) [20]:

$$\sigma_D = -C_1 \sigma_T + C_2 \sqrt{\frac{W_{AB}E}{R}}$$
(1)

where σ_D and σ_T are debonding and thermal stress, respectively, W_{AB} the reversible work of adhesion, *E* the Young's modulus of the matrix, *R* the radius of the particles, while C_1 and C_2 are constants. Accordingly, larger initiation stress is needed for debonding to start with increasing adhesion of the components, with increasing stiffness of the matrix and with decreasing particle size. The effect of particle size and interfacial adhesion on debonding stress was studied extensively in the past and results unambiguously proved the validity of the model [6, 20]. As a consequence, our attention is focused on the influence of matrix modulus on the debonding process in this paper.

2.2. The number of debonded particles

The model leading to Equation (1) was developed by using certain conditions, most of which are not fulfilled in practice. Debonding stress was derived for a single particle embedded in an infinite matrix [17, 18, 20]. However, the particle size distribution of commercial fillers is relatively wide; we cannot expect voids to form around all the particles. According to Equation (1) large particles debond easily, while small ones remain strongly attached to the matrix. The picture is further complicated by the fact that small particles form aggregates [21– 25], which behave as large particles and debond under the effect of external stress forming very large holes [26]. The number of debonded particles can be estimated by model calculations. The approach assumes that a part of the filler particles is strongly bonded to the matrix, carries load and increases stiffness, while the rest debonds and does not contribute to the increase of modulus. Accordingly, the composition dependence of Young's modulus, $E(\phi)$, can be expressed by the Kerner-Nielsen equation (2) [27, 28]:

$$E_c(\varphi) = E_m \frac{1 + A_f B_f \varphi_b}{1 - \Psi_f B_f \varphi_b} \frac{1 - \Psi_d B_d \varphi_d}{1 + A_d B_d \varphi_d}$$
(2)

where E_m is the modulus of the matrix polymer, φ_b and φ_d are the volume fraction of bonded and debonded particles, respectively. In this form the model assumes that voids form around particles in a matrix containing the filler in φ_d volume fraction. A_f and A_d take the Equations (3) and (4):

$$A_f = \frac{7 - 5v_m}{8 - 10v_m}$$
 and $A_d = \frac{8 - 10v_{mf}}{7 - 5v_{mf}}$ (3), (4)

where v_m and v_{mf} are the Poisson's ratio of the neat matrix and that containing the bonded particles, respectively. Parameter B_f and B_d can be calculated from Equations (5) and (6):

$$B_{f} = \frac{\frac{E_{f}}{E_{m}} - 1}{\frac{E_{f}}{E_{m}} + A_{f}} \quad \text{and} \quad B_{d} = \frac{\frac{E_{mf}}{E_{d}} - 1}{\frac{E_{mf}}{E_{d}} + A_{d}} \quad (5), (6)$$

Since the modulus of the voids is zero, B_d assumes the value of 1. Ψ is a correction factor taking into account the maximum packing fraction (φ_{max}) of the inclusion and it takes the same form for bonded and debonded particles (Equation (7)):

$$\Psi_f = 1 + \left(\frac{1 - \varphi_{bmax}}{\varphi_{bmax}^2}\right) \varphi_b \tag{7}$$

Naturally always the appropriate volume fraction and φ_{max} value must be introduced into the equation. Finally, the following correlation can be written for the relation of the various filler volume fractions (Equation (8)):

$$\varphi_b = \varphi_f - \varphi_d \tag{8}$$

where φ_f is total filler content, while φ_d is the volume fraction of debonded particles. If we determine the modulus (*E_c*) of prestrained composite samples and know v_m , the amount of bonded (φ_b) and debonded (φ_d) particles can be calculated from Equation (2).

2.3. Size of the voids

Voids initiated by the separation of the matrix/filler interface grow during further elongation. Farris [7] carried out his analysis for a single particle and assumed that each void formed around it is an ellipsoid of revolution with the two equal minor axes fixed by the diameter of the particle. During deformation the major axis of the void increases linearly with strain at a rate proportional to the size of the contained particle. Accordingly, the rate of volume increase, thus the size of the formed voids, depends on filler content in the following way (Equation (9)):

$$\frac{\mathrm{d}(\Delta V)}{\mathrm{d}\varepsilon} = C\varphi \tag{9}$$

where ΔV is volume increase, ε deformation, φ the volume fraction of the filler and *C* is a constant. Farris [7] carried out his experiments in crosslinked polyurethane rubbers and claimed that parameter *C* is close to 1 for particles with a uniform size. In subsequent sections we analyze our experimental results by using the models presented above and identify the most important factors which determine the debonding process and finally the MVTR of breathable films.

3. Experimental

Three polyethylene grades with different stiffnesses were used in the experiments. The most important characteristics of the polymers are listed in Table 1. The CaCO₃ filler added to the polymers

Table 1. Characteristics of the PE matrix polymers used in the study

| Abbrev. | Trade name | Producer | MFI [g/10 min] | Density [g/cm ³] | Modulus [GPa] |
|---------|----------------|----------|----------------|------------------------------|---------------|
| PE04 | Dowlex 2037 | Dow | 2.5 | 0.935 | 0.4 |
| PE07 | Tipolen FB 472 | TVK | 0.7 | 0.947 | 0.7 |
| PE11 | Tipolen ME 610 | TVK | 6.5 | 0.961 | 1.1 |

was the Omyacarb 2 GU grade, a product of Omya GmbH, Switzerland. The average particle size of the filler is 2.5 μ m and its specific surface area is 3.6 m²/g. The filler was used without any coating. The filler content of the composites changed from 0 to 0.3 volume fraction in 0.05 volume fraction steps.

The composites were homogenized in a Brabender DSK 42/7 twin-screw compounder at 180–190–200°C and 50 rpm. Injection molded tensile bars of 150×10×4 mm dimensions were produced from the pellets using a Battenfeld BA 200 CD machine. The composites were processed at 160–180–200°C, the temperature of the mold was kept at 40°C, while injection pressure was 50 bar, holding pressure 45 bar and holding time 15 sec.

The tensile properties of the composites were derived from force vs. elongation traces recorded by using an Instron 5566 machine with a cross head speed of 50 mm/min. Volume strain was determined by measuring also the change in one lateral dimension of the specimen with a strain transducer. Volume strain measurements were carried out at 5 mm/min cross-head speed. In order to avoid complications in the evaluation of the results possibly caused by the inhomogeneous deformation of the specimens, volume strain measurements were always interrupted at the onset of macroscopic yielding [29, 30]. We assumed that changes in both lateral directions are the same. In order to determine the number of debonded particles, specimens were prestrained to different extents. Strained samples were allowed to relax for 15 min and their Young's modulus was determined at 0.5 mm/min cross-head speed, i. e. 1% deformation rate. All measurements were done at room temperature.

4. Results and discussion

The various stages of void formation, i. e. debonding and growth are discussed separately in this section. First the main factors determining the initiation of the voids are presented briefly, and then the number of debonded particles is estimated as described above. The rate of void growth and the final void content of the composites are discussed in the last subsection.

4.1. Initiation

The main factors determining the initiation of debonding is specified by Equation (1). The validity of the correlation was proved several times both by Vollenberg [17] and Pukánszky et al. [6], who showed that interfacial adhesion and particle size influence debonding stress in the way described by the model [6]. Less attention was paid to the effect of matrix stiffness. Stress vs. strain, as well as volume strain traces of composites with 20 vol% filler content are presented in Figure 1 for the three polyethylene grades investigated in this study. The stiffness of the matrix polymer strongly influences the modulus, yield stress and yield strain of the composites, the first two decreases, while the last increases with decreasing stiffness, as expected. The differences in volume strain are less unambiguous. The largest volume increase is shown by the softest matrix, while the volume strain of the other two composites is very similar to each other. Initiation stress (σ_D) was determined as the intersection of the first, almost horizontal part and the increasing section of the volume strain traces, and it is plotted against the stiffness of the matrix in Figure 2 in the form indicated by Equation (1). Although only three polymers were included into the study, the correlation presented in Figure 2 strongly supports the model; debonding stress increases linearly with the square root of matrix modulus. Figure 2 supplies an additional proof for the validity of the debonding model developed earlier, thus it can be used for the prediction of the number of voids. Unfortunately, commercial fillers



Figure 1. Stress vs. strain and volume strain traces of PE composites containing 20 vol% CaCO₃ filler. —— PE04, - - - PE07, · · · · · PE11



Figure 2. Dependence of debonding stress derived from the volume strain measurements on the stiffness of the matrix (see Equation (1)). Symbols:
(□) 15 vol%, (0) 20 vol% filler

have a wide particle size distribution, which may complicate prediction. Nevertheless, we may assume that besides initiation stress the modulus of the matrix polymer probably influences also the number of debonded particles.

4.2. Extent of debonding

Volume strain traces are presented for the softest matrix containing various amounts of filler in Figure 3. It is obvious from the figure that volume increases both with filler content and with the extent of elongation. At the largest filler loading the samples broke already after limited extension.



Figure 3. Effect of filler content on volume increase in PE04/CaCO₃ composites. Filler content increases from 0.1 to 0.3 volume fraction in 0.05 volume fraction steps from right to left

Although volume increases with filler content, the extent of debonding cannot be estimated from Figure 3. The comparison of the various traces indicates a nonlinear relationship between volume increase and filler content, which may be caused both by the changing number of debonded particles and by the varying rate of volume increase. Very small volume increase occurs at low filler content; in fact volume strain could not be measured reliably at 5 vol%. We can conclude, though, that the recorded volume strain traces do not make possible the estimation of the number of debonded particles, this can be determined only by additional experiments.

The modulus of prestrained composite samples is presented in Figure 4. All three matrices contained the filler in 20 vol%. The shape of the correlation is very similar in all three cases, a horizontal or slightly increasing section is followed by a relatively steep decrease. Modulus seems to reach constant, equilibrium value at large prestrains. The modulus of the three composites differs considerably, and the decrease in stiffness as an effect of prestrain seems to be proportional to the initial modulus of the polymer. The correlations presented in Figure 4 obviously support the validity of the Kerner-Nielsen equation [27, 28] assuming that only bonded particles carry load. Nevertheless, the approach merits somewhat more considerations.

In the investigated composites containing PE and uncoated filler, interfacial interaction is created by secondary, van der Waals forces. These forces can be characterized by the reversible work of adhesion



Figure 4. Dependence of the modulus of PE composites containing 20 vol% filler on the extent of prestrain. Symbols: (□) PE04, (0) PE07, (Δ) PE11

indicating the reversibility of the debonding process. Although the traces presented in Figure 4 clearly indicate the initiation of debonding, which can be defined as the intersection of the upper horizontal and the declining sections of the correlations presented in Figure 4, debonding may occur already at smaller deformations. Before the determination of modulus specimens were allowed to relax for 15 min, during which the interfacial bond could have reformed completely. Several authors, including Vollenberg et al. [17] and Dubnikova et al. [31] claim that initiation occurs in the increasing part of the stress vs. strain curve (see Figure 1), while Pukánszky et al. [6] found that initiation occurs at the maximum of the curve, i.e. at yielding. Although this question cannot be decided here, we may assume that modulus starts to decrease when the specimen was subjected to sufficient prestrain resulting in limited plastic deformation, which prevents the reformation of the original interfacial bonds. As a consequence, in subsequent sections, we identify the initiation of debonding as the strain at which sufficient plastic deformation occurs, which prevents the reformation of these bonds. These results also imply that debonded particles do not carry load, indeed, and the approach Kerner and Nielsen [27, 28] can be used for their estimation.

The amount of debonded filler was calculated from the results of Figure 4 by the approach mentioned above (see Equations (2)–(7)). The results are presented in Figure 5 for the same composites. The correlation clearly shows the existence of an initiation prestrain, which differs for the three polymers; debonding starts earlier in a stiffer matrix than in a soft polymer. Not only initiation strain or stress, but also the maximum amount of debonded filler differs for the three matrices. The correlations presented in Figure 5 clearly show that in softer matrices only a part of the particles initiate voids, the rest remain bonded to the polymer even at considerably larger deformations than the yield strain of the composite. The character of the correlation and the equilibrium value of the amount of debonded particles indicate that two competitive processes take place during the deformation of these composites: debonding and plastic deformation. The relative magnitude of the two determines the number of voids formed and probably also their size. The calculation of relative amounts indicates that more than 80% of the particles debond in the stiffest matrix, while this number is about 50 and 30% for the other two matrices. This shows that the efficiency of void formation is very poor in the softest matrix, less then the half of the particles contribute to the creation of holes. Moreover, since thin films are deformed under plain stress conditions, which results in large plastic deformation, the efficiency of void formation may be even smaller under the conditions of breathable film production. The effect of filler content on the amount of debonded particles is presented in Figure 6 for the softest matrix. At small filler loadings, the determi-



Figure 5. Effect of prestrain and matrix stiffness on the amount (in absolute volume fraction) of debonded filler in PE/CaCO₃ composites containing 20 vol% filler. (□) PE04, (0) PE07, (Δ) PE11



Figure 6. Influence of filler content on the number of debonded particles (in absolute volume fraction) in PE04/CaCO₃ composites. Symbols:
(□) 5 vol%, (Δ) 10 vol%, (0) 15 vol%, (∇) 20 vol% filler

nation of this quantity is very difficult, because of the low modulus of the composites and the small changes in properties during prestraining. In spite of these difficulties, the results allow some interesting observations. Debonding is initiated at almost the same deformation, irrespectively of filler content. Although the absolute amount of debonded particles increases with filler content, the relative amount decreases. This result requires further investigation and analysis. Aggregates may form at larger filler contents, the decrease of effective load bearing cross-section may increase local plastic deformation and the interacting stress fields of neighboring particles might also influence the extent of debonding. We may conclude that matrix stiffness plays a crucial role in the debonding process of particulate filled polymers and the competition between debonding and shear yielding of the matrix determines the actual number of debonded particles. As a consequence, the selection of matrix polymer has a crucial impact on the properties of breathable films, including MVTR and stiffness.

4.3. Size of the voids

The final size of the voids depends on the extent of stretching. According to Farris [7] the rate of volume increase is proportional to the filler content of the composites. He found in his experiments that the proportionality constant, *C*, equals 1. However, he investigated cross-linked rubbers, which do not yield and meet quite well the assumptions of his treatment. Conditions are completely different in thermoplastics, where plastic deformation is considerable. These considerations are strongly supported by Figure 7 showing a SEM micrograph taken from the fracture surface of a composite



Figure 7. Size and shape of voids forming during elongation in PE/CaCO₃ composites; 5ε_ystrain



Figure 8. Effect of filler content and matrix stiffness on the rate of volume increase in PE/CaCO₃ composites. Symbols: (□) PE04, (0) PE07, (Δ) PE11

extended to $5\varepsilon_y$ (yield strain). Most of the voids are not regular ellipsoids of revolution and the smaller diameter of the void does not correspond to that of the particle.

The rate of volume increase, i. e. $d(\Delta V)/d\epsilon$ is plotted against filler content in Figure 8. It was determined by fitting a straight line to the increasing part of the volume strain traces (see Figsures 1 and 3). We must call the attention here to the fact that volume strain traces differed considerably from one specimen to the other and the determination of the rate of volume increase was not always easy. As a consequence, the values plotted in the figure must be treated with care. We obtain three different correlations for the three matrix polymers. We can fit straight lines to all three functions, thus they seem to correspond to the prediction of Farris. However, the slopes of the lines differ from each other and also from the predicted value of 1. The steepest slope was obtained for the softest matrix, while the smallest for PE11. Moreover, the extrapolation of two of the lines would indicate zero volume strain below a certain filler content, which does not agree with the prediction of Farris [7]. Considering the difficulties of determination, the relatively small number of experimental points as well as their considerable scatter, we refrain from further interpretation of the data in order to avoid any unjustified speculation. Further, more detailed experiments must be carried out in order to precisely determine the exact nature of the correlations. However, the tendencies observed are clear and the present results suffice for the purpose of this paper. The



Figure 9. Dependence of parameter *C* on the stiffness of the matrix polymer

correlation between parameter C and the modulus of the matrix polymer is presented in Figure 9. Obviously, deformation proceeds in a different way in polyethylene than in cross-linked rubber. Although three values are not sufficient for drawing unambiguous conclusions, based on Figure 9 we may assume that even further increase in stiffness would not decrease the value of parameter Cto 1. The large C value indicates that much larger voids form in a thermoplastic matrix than in a rubber. This proves again that competitive processes take place during the deformation in the former case and the size of the voids is influenced also by the extent of plastic deformation. Our statement is strongly corroborated by Figure 9, which shows that a C value of 3.4 was obtained for the softest matrix, while only 2.5 for the stiffest. Considering the results presented in the previous subsection we may conclude that less particles initiate voids in a soft matrix, but their size becomes larger during further growth than in a stiffer polymer.

The influence of plastic deformation on the final void content of the polymer and consequently on permeability is demonstrated well by Figure 10, in which volume increase is presented as a function of filler content at various extents of deformation for PE04. At small strains volume does not increase practically at all and at least 0.2 volume fraction of filler is needed to achieve observable volume increase. In accordance with results presented above, only a small fraction of the filler particles debond in the soft matrix and plastic deformation dominates at small filler content. The correlation explains also the uncertainty encountered during



Figure 10. Effect of filler content and strain on volume increase; extensive plastic deformation during the elongation of PE04 composites. Symbols: (□) 5%, (0) 10%, (Δ) 15%, (∇) 20% strain

the estimation of the number of debonded filler particles at small filler loadings. With increasing filler content the stiffness of the composite as well as the number of voids increase, which results in considerable volume increase. Volume strain is plotted against filler content for the PE07 composites in Figure 11. All correlations are linear showing a proportional increase of void content with increasing filler content, which indicates that plastic deformation is less significant in this polymer than in the softest one. These results prove that all stages of void formation are equally important in the determination of the moisture permeation of breathable films and only the proper optimization of component properties (matrix stiffness, particle size of the



Figure 11. Volume increase in PE07 composites at different filler contents and deformation. Symbols:
(□) 5%, (0) 10%, (Δ) 15%, (∇) 20% strain

filler, interfacial adhesion), composition (filler content) and processing technology (extent and conditions of stretching) may lead to films with acceptable properties.

5. Conclusions

The analysis of the debonding process and the various stages of void formation in particulate filled composites proved that the model developed for the prediction of the initiation of debonding is valid also for the studied PE/CaCO3 composites. Accordingly, debonding stress is determined by the strength of interfacial adhesion, particle size and the stiffness of the matrix. However, in thermoplastic matrices usually two competitive processes take place: debonding and the plastic deformation of the polymer. The relative magnitude of the two processes strongly influences the number and size of the voids formed. Because of this competition and due to the wide particle size distribution of commercial fillers, only a fraction of the particles initiate the formation of voids. The number of voids formed is inversely proportional to the stiffness of the matrix polymer. In stiff matrices almost the entire amount of filler separates from the matrix under the effect of external load, while less then 30% debond in a PE which has an initial modulus of 0.4 GPa. Further decrease of matrix stiffness may lead to the complete absence of debonding and the composite would deform exclusively by shear yielding. Voids initiated by debonding grow during the further deformation of the composite. The size of the voids also depends on the modulus of the matrix. The rate of volume increase considerably exceeds the value predicted for cross-linked rubbers. The results clearly prove that in soft matrices the number of voids is smaller and their size is larger at the same deformation and filler content than in polymers with larger inherent modulus. In order to achieve sufficiently large vapor transmission in breathable films, all parameters of the process must be optimized.

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Effect of bar sealing parameters on OPP/MCPP heat seal strength

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Abstract. The effect of bar sealing parameters on the heat seal strength of oriented polypropylene (OPP)/metallic cast polypropylene (MCPP) laminate film was investigated. Based on the results obtained from the parametric study, a bar sealing process window was developed. All points drop within the process window are combinations of platen temperature and dwell time that produce acceptable heat seal. Optimum combinations are indicated by the lower border of the window. The plateau initiation temperature, T_{pi} of OPP/MCPP laminate film used in the present study occurred before the final melting temperature, T_{mf} of the sealant material. The highest achievable heat seal strength was at the plateau region, and the corresponding failure modes were delaminating, tearing or combine failure modes (delaminating and tearing). Minimum pressure level of 1.25 bars is necessary to bring the laminate interface into intimate contact in order to effect sealing.

Keywords: mechanical properties, heat sealing, OPP, MCPP, process window

1. Introduction

There are a number of heat sealing techniques which are used to produce flexible pouch or bag using the laminate films, i. e. bar sealers, rotary sealers, impulse sealer, bead sealers, hot knife or side weld sealers, etc. Compared to the others, bar sealing uses the least expensive equipment, hence, it is the most preferred technique [1].

Heat seal is formed by bonding together two polymer surfaces in the way that the surfaces are forced into intimate contact while they are in at least a partially molten state. Therefore, proper control of process parameters such as platen temperature, dwell time and pressure based on the characteristics of each laminate film is important to ensure that the pouch is leak-free and can withstand maximum loading during handlings.

In packaging, the term 'acceptable heat seal' refers to the heat seal that when subjected to loading, will

*Corresponding author, e-mail: azmanh@fkkksa.utm.my © BME-PT and GTE break at the laminate film instead of at the heat seal [2]. In other words, the strength of the heat seal is greater than the strength of the laminate film. This corresponds to the delaminating or tearing mode failures in the peel test specimens, where damage occurred on the laminate film rather than on the heat seal.

Several studies concerning effect of sealing parameters on the performance of heat seal are found in the literature. Theller [3] was the pioneer researcher in this area when a precision laboratory heat sealer was made available in 1989. He studied the heatsealability of plastic film in bar sealing applications. He reported that the interfacial temperature and dwell time are the primary factors which control the heat-seal strength. Pressure normal to the seal surface had little effect above the level required to flatten the web for good contact. Meka and Stehling [4, 5] have conducted a series of studies concerning heat sealing process. The effect of heat sealing process variables on seal properties of polyethylene films was quantitatively determined. They also estimated the required platen temperature for the highest possible heat seal strength of a semicrystalline polymer with the given dwell time and interfacial temperature by finite element model. Further more, they reported that the heat seal strength is primarily controlled by sealing temperature and dwell time, rather than pressure. Heat seal strength versus platen temperature plot has been established in their study. Tetsuya et al. [6] had investigated the effect of heat sealing temperature on the mechanical properties and morphology of oriented polypropylene (OPP)/cast polypropylene (CPP) laminate films. They reported that tensile strength of the seal was affected by the orientation of the films. Whilst, Hashimoto et al. [7] had carried out investigation on the failure criteria of the heat sealed part of OPP/CPP heat seals made by impulse type heat sealing machine. They reported that heat seals were stronger in the transverse direction as compared to the machine direction.

In the present study, the effect of bar sealing parameters on heat seal strength of OPP/MCPP laminate film was investigated. The effects of various combination of platen temperature and dwell time to the process window of the laminate films are also studied in view of to provide a guideline to the bar sealing users when setting up their machine.

2. Experimental

2.1. Laminate films

The plastic film used in the present study was a commercial OPP/MCPP laminate film. The films were laminated through dry-bond process using a urethane adhesive. The thickness of OPP and MCPP films were 23 and 25 micrometers, respectively. The final melting temperature, T_{mf} of the sealant layer (i. e. MCPP film) was 139.4°C as determined by differential scanning calorimeter at 10°C/min scan rate starting at 25 to 300°C under a helium purge gas.

2.2. Making of heat-seals

In the present study, the laminate film was sealed together in the sealant interface (i. e. MCPP film) to simulate fin seal formed in practice. The laminate films were first cut into 15 mm wide strips by Lorentzen & Wettre cutter, made in Sweden. This cutter ensured that clean-cut edges are produced to prevent premature failures in T-peel test.

Heat seals were made in the laboratory using a model HSG/ETK heat sealer, made in Germany. This device clamps two pieces of filmstrips between flat, 10 mm wide heated metal bars. The temperature, pressure and dwell time of the sealing bars are adjustable. Microprocessor programmed controllers maintained and digitally indicated set temperature for each bar. Both bars were operated at the same temperature, and kept close between sealing to minimize heat loss and temperature fluctuations. After the heat seal was made, the sandwich structure was allowed to cool at ambient conditions.

2.3. Testing of heat-seals

The heat seals were allowed to age at room temperature for at least 48 hours to achieve chemical stabilization. Aging of heat-seal was necessary as the strength of seal may change in time, which may due to the memory of polymer, or thermophysical properties of polymer as the heat seal samples undergo melting and cooling processes. The sample was then peeled apart at room temperature in tensile tester of model MICRO 350, using a 100 N load cell. Each leg of the test specimen was clamped in the tensile tester. The heat seal area of each specimen was placed at approximately equidistant between the clamps. The specimen was aligned in the clamps so that the seal line is perpendicular to the direction of pull. The constant rate of loading 300 mm/min with initial jaws separation of 25 mm was chosen as recommended by ASTM F88-85 [8]. The maximum force required to tears apart the seal, and failure mode of each pull was recorded.

3. Results and discussion

3.1. Heat-seal strength and failure modes

Heat-seal strength is defined as the maximum force per width required to separate a heat seal. This value is obtained in a peeling test after the heat seal has been aged in a room temperature for at least 48 hours. All representative values in this paper are the average of six. In addition, failure modes at each pulled was carefully examined for the purpose of identifying the level of acceptance of each heat seals. It was found that the strength of the heat seals and its failure modes are closely related. Similar to the results reported by previous researchers [3, 5], the heat seal failures of OPP/MCPP laminate film occurred in three stages, which are discussed as follows:

When sealing was made at temperature substantially lower then the melting point of the sealant material (i. e. MCPP film), all samples failed in peeling mode failure (Figure 1). Heat seal strength of all samples reported under this failure mode was the lowest compared to the values reported under other failure modes.

In peeling mode failure, disentanglement of polymer molecules occurred which caused the bond to peel apart. This failure mode occurred when the strength of seal is below the strength of the laminate film.

The heat seal strength increases with platen temperature. This can be explained by the micro-Brownian movement of chain segments theory that thermal motion of the polymer increases with platen temperature as suggested by Stehling and Meka [5]. Consequently, the original zone of diffusion between the seal layer is deeper, and causes a greater peeling force required to separate the heat seal.

After the seal initiation temperature, the strength of the heat seal increased sharply before reaching the maximum value. In this range, samples failed in either one of the three failure modes: peeling, delaminating or tearing, or the combination of delaminating and tearing mode failures. This is the transition region in which failure mode was then changed from peeling to delaminating or tearing mode failure, or combination of these two failure modes.



Figure 2. Breaking of sealant layer at the edge of the heat seal and simultaneous separation of laminate layers with heat seal intact

Delaminating mode failure (see Figure 2) involves a tensile break of the sealant layer, and followed by separation of the interlaminar bond. This occurred when the strength of heat seal exceeded the strength of the interlaminar bond. Consequently, separation occurred between the laminate layers (which is weaker) instead of at the heat seal (which is now stronger), and leaving the heat seal portion with the other laminate film intact. Hence, heat seal strength reported in delaminating mode failure was relatively higher than the heat seal strength reported under peeling mode failure.

On the other hand, tearing mode failure (see Figure 3) may be attributed to the strengthening of the interlaminar bond at relatively high platen temperature. Thus when the strength of the laminate structure is lower than both the strength of the interlaminar bond and the strength of the heat seal, failure occurred at the laminate structure during peeling test. Thus the strength of heat seal failed under this failure mode is the highest compared to values reported under other failure modes.



Figure 1. Sealant interface torn apart



Figure 3. Breaking of the laminate film at the edge of the heat-seal



Figure 4. Combination of delaminating and tearing modes

The occurrence of combine failure mode (delaminating and tearing) (see Figure 4) could be attributed to the increased of interlaminar bond strength with platen temperature. It is conjectured that under marginal conditions, uneven strengthening of the interlaminar bond on the heat seal area occurred. Thus under the application of peel force, the laminate film first separated into monolayer structures at the peel line, and followed by tearing on the film where there existed weak points due to irregular tensile stress distribution attributed to the uneven strengthening of the interlaminar bond.

3.2. Heat sealing curve

The plot of heat seal strength versus platen temperature curves at 0.1 and 1 sec dwell time is as shown in Figure 5. From the plot, sealing began at temperature substantially lower than the melting point of the sealant material (i. e. MCPP). This temperature is termed seal initiation temperature, T_{si} where a measurable but low level of heat seal strength was achieved [5]. After the T_{si} , heat seal strength increased sharply with platen temperature. It was then leveled off at about 0.9 N/mm and formed a



Figure 5. Plot of heat seal strength versus platen temperature curves at 0.1 and 1 sec dwell time

plateau to the heat sealing curve. The platen temperature of 122°C at which the plateau region began is termed plateau initiation temperature, T_{pi} [5]. The highest achievable heat seal strength of OPP/MCPP laminate film was at the plateau region, and the corresponding failure modes were delaminating, tearing or combine failure modes.

The trend that OPP/MCPP laminate film achieved its plateau seal strength before the sealant material completely melts, i. e. T_{pi} lower than T_{mf} , is in close agreement with the results reported by Tsujii *et al.* [6]. In their study, laminate film of similar group (i. e. OPP/CPP) was used to study the effect of heat sealing temperature on the properties of heat seal. The T_{mf} of CPP film (in their study) was 146.1°C while the T_{pi} was 120°C.

However, for laminate films using other sealant materials, e.g. LDPE, LLDPE, etc., the T_{pi} could be equaled to, or higher than the T_{mf} of the respective sealant materials. For instance, Stehling and Meka [5] reported that the T_{pi} value correspond closely to the T_{mf} for all the unsupported polyolefins films investigated in their study. Whilst, Morris [9] reported that the T_{pi} of ionomer films begin after the T_{mf} value.

Hence, it can be deduced that laminate films using different sealant materials produces different $T_{pi}-T_{mf}$ trends. Perhaps, more investigations are required to discern this dissimilarity.

3.3. Effect of platen temperature and dwell time

The effects of dwell time on heat seal strength at various platen temperature settings are shown in Figure 6. At the temperature substantially lower than the melting point of the sealant material, i. e. 120°C, no effects of dwell time on heat seal strength was detected. However, when the platen temperature was increased to 122°C, which is the plateau initiation temperature, the plateau seal strength was obtained at 0.7 sec. The same heat seal strength can be achieved at shorter dwell time of 0.2 sec, when the temperature was further increased to 124°C. Moreover, for each platen temperature setting, no effect of dwell time on heat seal strength was detected after achieving the plateau seal strength.

Distortion on the heat seal area appeared when the platen temperature was set at 138°C (which is at



Figure 6. Plot of heat seal strength versus dwell time at various platen temperatures

one degree Celsius below the final melting point of the MCPP film), in both 0.1 and 1 sec dwell time cases. Thus the maximum platen temperature for this laminate structure should be lower than this value.

These results show that the platen temperature and dwell time are interrelated in obtaining the heat seal strength. However, platen temperature plays a more important role as compared to dwell time. It can be seen that, to effect sealing, the lowest activated temperature must be reached at the sealing interface. And in a heat sealing process, the interfacial temperature is primarily controlled by the platen temperature, while dwell time has to be sufficiently long to ensure that enough heat is transfer to the sealing interface in order to melt the sealant material.

Previous researchers have also confirmed that the main factor affecting heat seal strength is the platen temperature. The results of Theller [3], who looked at the effect of dwell time at constant platen temperature, indicated that the heat seal strength is a strong function of platen temperature and is not dependent on dwell time beyond 0.4 sec for low density polyethylene film sealed at 106 and 110°C. Meka and Stehling [4] also reported that heat seal strength depends primarily on plated temperature and secondary on dwell time. In addition, Morris [9] has confirmed the inverse proportionality relation between platen temperature and dwell time, and has stated that they are influenced by film thickness according to heat transfer theorem.

The study of heat seal strength beyond 1 sec dwell time is only of theoretical interest. In practice, the



Figure 7. Plot of heat seal strength versus sealing pressure

setting of dwell time is below 1 sec as packaging machines are usually operated at very high speed in order to achieve the desired production rate.

3.4. Effect of platen pressure

The plot of heat seal strength versus plated pressure is as shown in Figure 7. No seal was produced at pressure of 1 bar. With slight increased of pressure (to 1.25 bar), sealing began, and the reported heat seal strength was indeed at the plateau level. At higher pressure setting after this point, no significant change of heat seal strength with pressure was detected. These results confirmed the results reported by previous researchers [4] that platen pressure has no measurable effect on heat seal strength.

3.5. Process window of bar sealing application

The process window of OPP/MCPP laminate film is as shown in Figure 8. The process window can be described by several parameter illustrated in the figure; The vertical line through AD is the left vertical border which indicates the shortest dwell time, which was determined by the minimum possible time setting of the sealing machine. The vertical line through BC is the right vertical border which indicates the longest dwell time suggested in the process window. Longest dwell time of 1 sec was selected because all samples exhibited approximately a constant value of heat seal strength after 1 sec (Figure 6). In practice, dwell time required for commercial production rate is usually within the range of 0.3 to 0.7 sec, thus 1 sec of longest dwell time in the process window should provides adequate reference for practical usage. CD is the lower border; a lowest activated platen temperature



Figure 8. Process window of OPP/MCPP film at 2 bars

setting for each respective dwell time is reveal in the lower border. Settings fall on this border are optimum combinations of platen temperature and dwell time, because no excessive temperature (energy) was used. The lower border fixed at 122°C indicates that acceptable heat seals can be obtained by setting the platen temperature at this value or above.

As may be seen, the lower border of the process window was constructed by a horizontal line. This indicates that the acceptable heat seal can be obtained at any dwell time settings within the effective temperature range.

AB is the upper horizontal border. Distortion on the heat seal area begins at 138°C. Thus the upper horizontal border must be set lower than this value. In practice, heat seal can be made in a range of platen temperature settings, however, lower sealing temperature uses less energy, allow the package to be handled quicker, and have less potential effect on the contained product [10]. Therefore, the author recommended that the upper boundary be fixed at 130°C such that it provides some flexibility in choosing the platen temperature while ensuring that the setting did not go beyond the limit where seal distortion may result.

All points drop within the shaded area are combinations of platen temperature and dwell time that are capable to produce acceptable heat-seal. In many cases, a form/fill/seal machine will be run at a designed speed, and therefore dwell time is virtually a given. Hence the most suitable platen temperature setting can be found from the process window.

4. Conclusions

Bar sealing process window of OPP/MCPP laminate film was developed. The lower border of the window was fixed at 122°C. Acceptable heat seals can be obtained by setting the platen temperature at this value or above. The lower border of the process window is constructed by a horizontal line. Thus acceptable heat seal can be obtained at any dwell time settings within the effective sealing temperature range (122 to 130°C). The upper boundary of the window was fixed at 130°C. Distortion on the heat seal area can be avoided by setting the platen temperature below this limit. Minimum pressure level of 1.25 bars is necessary to bring the laminate interface into intimate contact in order to affect sealing.

Three failure modes are identified for OPP/MCPP laminate film, namely the peeling, delaminating, and tearing modes. The laminate film may also fail in a combine failure mode (delaminating and tearing). Heat-seal strength achieved under tearing mode failure was the highest, and follow by strength achieved under delaminating mode failure, while the lowest value pertained to peeling mode failure.

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