

IN SITU COMPATIBILIZATION OF LDPE/NYLON-6 BLEND USING LOW MOLECULAR WEIGHT INTERFACIAL AGENT AS A CHEMICAL COMPATIBILIZER

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ABSTRACT

In situ compatibilization of low density polyethylene (LDPE) (30%) and nylon-6 (70%) blends through one-step reactive extrusion using t-BuOOH as an initiator and low molecular weight interfacial agents as compatibilizers was studied. The compatibilizer contained a long chain hydrocarbon, double bond and two polar functional groups which was capable of reacting with both LDPE and nylon-6 in the presence of initiator to form a copolymer at the interface of the two polymer phases. The extruded blends exhibited significant enhancement in their compatibility based on morphological, thermal analysis and mechanical studies. The effect of the hydrocarbon chain length and structure of the functional group of the compatibilizer was also examined. It was found that blends prepared by using the compatibilizer containing longer hydrocarbon chain and amide group had better mechanical properties.

INTRODUCTION

The use of an extruder as a continuous reactor for compatibilization of polymer blends has gained increasing popularity because of its efficiency and economics as compared to conventional operations^[1-3]. Interchain copolymer formation by reactive extrusion is particularly useful for compatibilization of immiscible polymer blends because a product may be obtained with a combination of desirable properties derived from each polymer. Nylon-6 and low density polyethylene (LDPE) are large volume commodity polymers that possess unique properties individually.

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Nylon-6 has a high crystalline melting point and good resistance to hydrocarbons, while LDPE has excellent low temperature flexibility and good resistance to moisture permeation. Hence compatibilization of nylon-6 and LDPE has been extensively studied due to its great commercial potential^[4-9].

In situ compatibilization involves the *in situ* reaction of functionalized components during processing to form block or graft copolymers at the interfaces between the phases. Current effects on the *in situ* compatibilization of LDPE and nylon are focused on the extrusion of nylon with anhydride- or acid-functionalized polyolefin^[10-12]. Polymer containing other types of functionality such as epoxy or benzyl halide groups have been also reported^[13-15]. These polymer usually are functionalized graft copolymers and a separate step is required to produce the blends. In contrast, use of low molecular weight compatibilizer has received little attention. This is probably due to the fact that small molecule compatibilizers do not provide sufficient entanglement couplings to result in the adhesion needed in the solid state. Besides, unreacted short chains can reduce both the melt viscosity and solid-state mechanical properties. On the other hand, small molecule compatibilizers offer some advantages over the block or grafted copolymers currently in use. For example, small molecule compatibilizers are relatively easier to synthesize. In addition, high degree of compatibilization can be achieved because the interfacial reaction is a diffusion control process. Recently, Lambla and Seadan described the use of maleic anhydride and 1-undecenal difunctional monomers to improve the compatibilization of LDPE and polyamide-11 in a single-step process^[16]. Chen and White also showed that the addition of five percent stearic acid in 75/25 polyethylene/polyamide-6 controlled the phase morphology^[17].

In this paper, we wish to report the use of reactive multifunctional monomers as compatibilizers for LDPE and nylon-6 blends through reactive extrusion. These monomers contain long hydrocarbon chains and multifunctional groups, which are similar to low molecular weight emulsifiers. The effect of the structure of the functional groups and hydrocarbon chain length in the monomer was examined with respect to the compatibilization efficiency. The LDPE/nylon-6 blends were characterized by using differential scanning calorimeter (DSC), scanning electron microscopy (SEM) and mechanical measurements.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE) obtained from Sandoz Industrial Chemicals, Hong Kong, had a melt flow index, $MI = 19 \text{ g}/10 \text{ min}$ (2.16 kg, 190° C). Nylon-6

was a general-purpose grade polymer from Du Pont with $MI = 5$ g/10 min (1.05 kg, 235° C).

Maleic anhydride (99% pure), octadecanol (98%), octadecylamine (98%), decylamine (95%), hexylamine (99%), and hexadecane (99%) were purchased from Aldrich Chemical Company. Dicumyl peroxide, benzoylperoxide and cumene hydroperoxide were also obtained from Aldrich Chemical Company while tert-butyl hydroperoxide (80%) and di-tert-butylperoxide (95%) were from Fluka Chemicals. All these chemicals were used as received.

Synthesis of octadecanyle maleic monoester (ODM)

A mixture of octadecanol (135 g, 0.50 mol) and maleic anhydride (54 g, 0.55 mol) was heated to a melt form at 110°C in the presence of 2 ml of concentrated H_2SO_4 , and allowed to further react under stirring for 3 hours. The reaction mixture was then cooled to room temperature to give a white solid. The crude product was recrystallized in acetone and dried under vacuum at room temperature, giving a yield of 88%. The melting point of the octadecanyle maleic monoester was found to be 59–60° C, and the structure was confirmed by FTIR (Nicolet Magna 750 FTIR Spectrometer) and NMR (Jeol Fx-90 MHz NMR Spectrometer).

Synthesis of Alkyl Maleic Monoamide

Maleic anhydride (49 g, 0.5 mol) was first dissolved in 100 ml THF and then 0.5 mol of alkylamine was added. The mixture was refluxed for 2 h and cooled to room temperature. A white solid product was formed which was recrystallized in THF and dried under vacuum at room temperature with a yield of 91–93%. The structure of these compounds was analyzed by IR and ^1H NMR.

Blend preparation

All blends were prepared using a Randcastle single screw microtruder (1/4 inch, $L/D = 24 : 1$). Small granules of nylon-6 (70% by weight) and LDPE powder (30% weight) were physically pre-mixed with initiator and compatibilizer, and melt-blended in the extruder. The temperature inside the mixing zone was controlled at 230° C and the rotation speed of screw was fixed at 40 rpm. To study the effect of hexadecane on the crosslinking of LDPE in peroxide, LDPE powder, t-butyl hydroperoxide and hexadecane were well-mixed prior to extrusion. The temperature and rotation speed of the screw were controlled at 185° C and 30 rpm, respectively.

Thermal characterization

The thermal property of the blends was determined by differential scanning calorimetry (Perkin-Elmer DSC 4). Polymer samples were first kept at 160° C for 6 h and then cooled to room temperature. Samples (10 mg) were then scanned from

50° C to 250° C at the heating rate of 10° C/min.

Scanning electron microscopy

The morphologies of the fracture surfaces were studied by using a Cambridge scanning electron microscope (Stereoscan 250 Mk2). Samples were fractured in liquid nitrogen and the fracture surfaces were coated with gold.

Mechanical properties

Tensile measurements were performed with an Instron model 1122 universal testing machine at room temperature at a crosshead speed of 5 cm/min. The samples used for tensile tests (0.3 mm thick, 12 mm wide, 3 cm long) were cut from a film obtained from extrusion at 230° C (185° C for pure LDPE). All results reported here were averages of at least 4 measurements. They were relative data to the LDPE/Nylon-6 (30:70) blend.

An impact bar (4 × 6 × 50 mm) was prepared by compression molding according to ASTM standard. An impact tester (Ceast code 6545/000) was used to determine the notched Charpy impact strength.

Solvent extraction

The gel content of LDPE after extrusion with peroxide was determined by extraction of the extruded LDPE with xylene for 8 hours in a Soxhlet extractor. The swollen gel material in the thimble was then dried to a constant weight in a vacuum oven. In order to determine the graft degree of compatibilizer (e.g. ODM) onto LDPE after extrusion, the ungrafted compatibilizer in the sample was removed by first dissolving the sample in hot xylene, then precipitating into acetone. The procedure was repeated twice and the solid samples were then dried to constant weight under vacuum. The graft degree was then calculated from the following equation:

$$\text{Percentage of grafting} = \frac{W_0 - (W_1 - W_2)}{W_0} \times 100\%$$

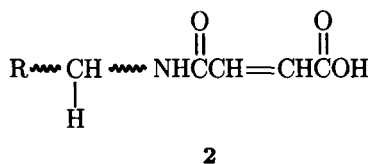
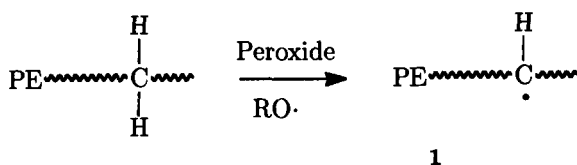
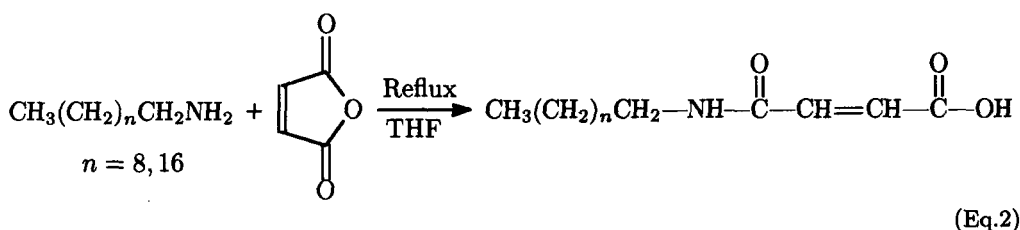
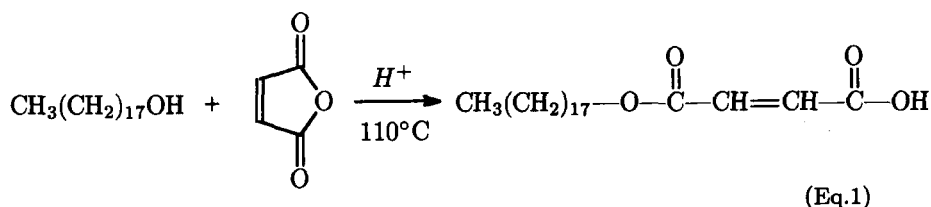
W_0 = weight of compatibilizer added; W_1 = weight of grafted LDPE before purification; and W_2 = weight of grafted LDPE after purification.

RESULTS AND DISCUSSION

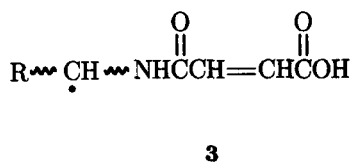
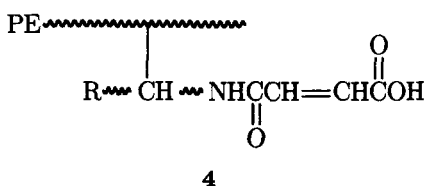
Fundamentals of in situ compatibilization using low molecular weight interfacial agents

Interchain copolymer formation by reactive extrusion is particularly useful for the compatibilization of immiscible polymer blends. A variety of anhydride or acid functionalized polyethylenes produced by free radical grafting with maleic anhydride or other acrylates has been widely employed as compatibilizers for LDPE/nylon

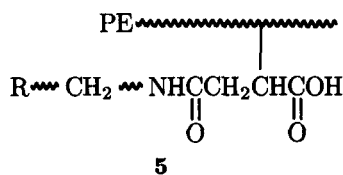
blends through the reactive extrusion. The presence of anhydride or carboxylic acid groups grafted on LDPE leads to the formation of amide or hydrogen bonding with nylon, thereby resulting in better compatibility. In fact, the ability of compatibilizers to locate themselves at the polymer-polymer interface seems to be the key factor in determining how well they perform. In this study, we focused on the use of several low molecular weight compatibilizers containing a long alkyl chain, double bond and functional groups such as carboxylic acid and amide groups prepared according to the equation 1 and 2. These compounds can be regarded as interfacial active agents which tend to distribute in the interface of the immiscible LDPE and



Coupling between 1 and 3



Reaction between 1 and 2



Scheme 1

nylon phases. In addition, these specially designed compatibilizers are conceivably grafted on LDPE through two possible reactive sites: i) radical coupling between the LDPE macroradicals and the long alkyl chain segment. ii) reaction with the double bond (Scheme 1). Consequently, the carboxylic acid, amide or ester groups on the compatibilizer can interact with nylon-6 at the interface, enhancing the compatibility of LDPE/nylon-6.

Effect of organic initiators on the crosslinking of LDPE

During normal extrusion of polyolefins, alkyl radicals are formed thermo-mechanically, but at too low concentration to cause grafting to a desirable extent. Therefore, a source of radicals, organic peroxides, are added in small quantities to the polymer before it is fed to the extruder. At appropriate temperature, the peroxide bond (RO-OR) breaks, generating free radicals which are sufficiently reactive to abstract a hydrogen atom from the polymer backbone. During the reactive extrusion of LDPE in the presence of peroxide, crosslinking of LDPE is a serious problem for its practical applications because it significantly increases the melt viscosity, causing many difficulties during the extrusion process. Some studies on the crosslinking of LDPE in extruder has been reported^[18-22]. Structure of the initiator, initiator concentration and processing temperature were found to influence the degree of crosslinking. Hence selection of an organic peroxide which gives less crosslinking of LDPE during extrusion is desirable. In general, such selection is usually based on the temperature corresponding to a given half-life. Dialkyl peroxides with 1 h half-life temperature ranging from 135–155° C are commonly used. At the typical process temperature

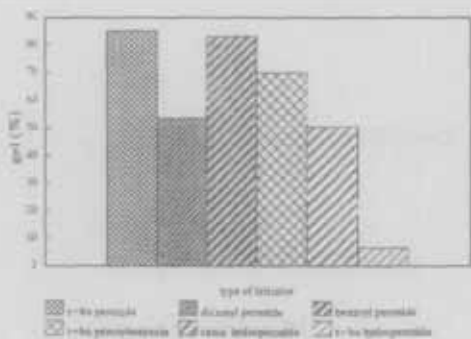


Fig.1 Percentage of gel content of LDPE film after reactive extrusion in the presence of peroxide. Concentration of peroxides used was 0.034 mmol per gram of LDPE, extruded at 180° C

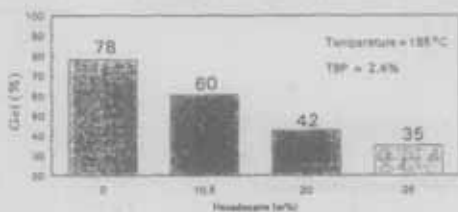


Fig.2 Effect of hexadecane on the crosslinking of LDPE. LDPE was mixed with 2.4 wt% di-*t*-butylperoxide (TBP) and extruded at 180° C

of 180–240°C, these peroxides are capable of generating sufficiently reactive radicals to complete the process within a short residence time. Volatility at process temperature is another important consideration in the peroxide selection because excessive volatility of the peroxide may result in unsafe operation of the extruder. In our current study, various organic peroxides were used as initiator (0.034 mmol per gram of LDPE), and extruded with LDPE at 180°C. The percentage gel content was determined by soxhlet extraction with hot xylene and the results are shown in Fig.1. Among six different peroxides, namely di-*t*-butylperoxide, dicumyl peroxide, benzoyl peroxide, *t*-butyl peroxybenzoate, cumene hydroperoxide and *t*-butyl hydroperoxide (*t*-BuOOH), *t*-BuOOH gave the lowest gel content. This might be due to the fact that the hydroxy radical (HO·) formed from the decomposition of *t*-BuOOH had low solubility in LDPE phase because of its hydrophilic nature.

Effect of hexadecane on crosslinking of LDPE

In order to assume that radical coupling reaction between the LDPE macro-radical and the long alkyl chain of the compatibilizer could take place (Scheme 1, 4), a long chain hydrocarbon, hexadecane (HD), was used to study the crosslinking of LDPE during reactive extrusion in di-*t*-butylperoxide. Fig.2 showed that the percentage gel content decreased with increasing amount of HD, while 2.4 wt% of *t*-di-butylperoxide (TBP) was employed as the initiator. This might be caused by the competitive grafting reaction between LDPE and HD which inhibited the crosslinking between LDPE chains. Hence the presence of a long alkyl chain on the compatibilizer could have dual functions: i) providing reactive site for grafting, ii) reducing the crosslinking of LDPE.

Grafting of octadecyl maleic monoester (ODM) onto LDPE

Similar to maleic anhydride, octadecyl maleic monoester (ODM) could be grafted onto LDPE through free radical reaction on the double bond (Scheme 1, 5). Fig.3 showed that the grafting degree increased with the increased of ODM concentration. The ODM grafted LDPE was isolated by solvent extraction. These results proved that the long alkyl chain on the compatibilizer molecule led to the reduction of crosslinking of LDPE as well as provision of grafting sites. Fig.4 showed the FTIR spectra of pure LDPE and 16% ODM grafted LDPE. The carbonyl bands of the ester and carboxylic acid groups at 1730 cm⁻¹ and 1720 cm⁻¹, respectively, were observed, indicating the presence of ODM grafted on LDPE chains through reactive extrusion.

Thermal analysis

In general, when the compatibility of an immiscible blend system is improved,

the melting temperature of the two polymers will shift closer to each other as a result of the reduction of interfacial tension. Fig.5 showed that T_m of nylon-6 in the blend decreased with increasing concentration of ODM or t-BuOOH. However, the magnitude of the decrease of T_m with the increase of ODM concentration depended on the t-BuOOH concentration. Significant effect of the ODM concentration was found in the t-BuOOH concentration range of 0.5-1.0 wt%. The decrease of T_m of nylon-6 indicated the improvement in compatibility of LDPE/nylon-6 blends.

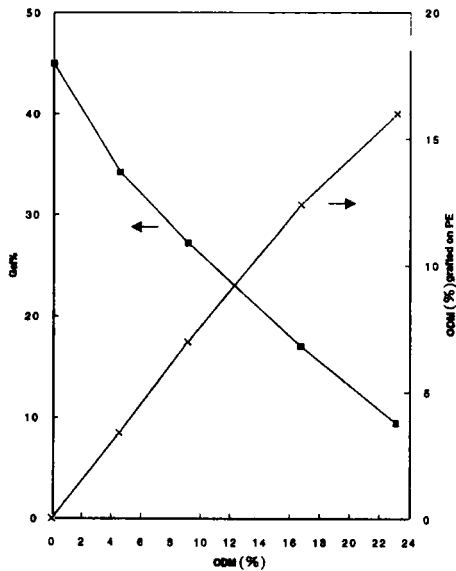


Fig.3 Dependence of percentage gel content and graft degree with the amount of ODM. Reactive extrusion of LDPE with t-di-butylperoxide (1.2 wt%) was carried out at 185° C

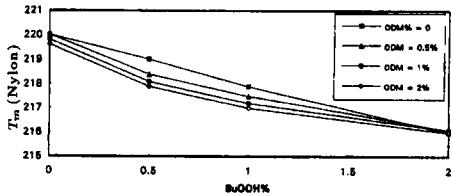


Fig.5 Effect of ODM and t-BuOOH on T_m of nylon of the LDPE/nylon-6 blend

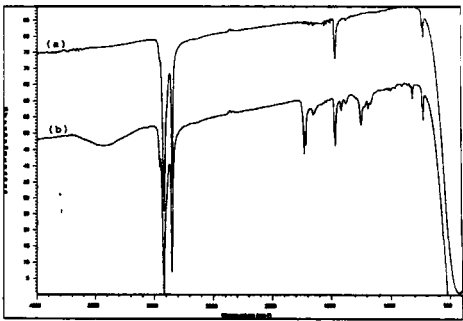


Fig.4 FTIR spectra of LDPE (a), and 16 wt% ODM grafted LDPE (b)

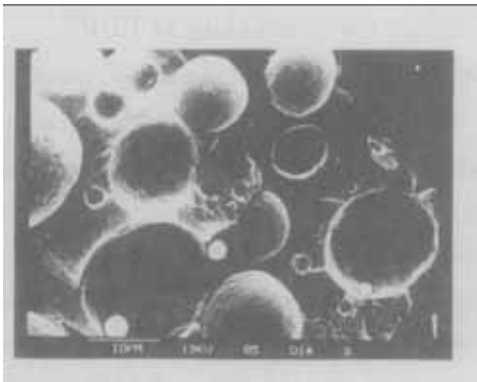


Fig.6 SEM micrograph of LDPE/nylon-6 (3:7) blend

Fracture surface morphology

SEM micrographs of the cryogenic fracture surfaces of the LDPE/nylon-6 (30/70)

blend were studied. With no initiator added, spherical LDPE particles of size 1—10 μm were observed. The large particle size indicated poor compatibility between the two phases (Fig.6). However, the compatibility was improved by the use of 0.5—1 wt% t-BuOOH as a free radical initiator as shown in Fig.7. t-BuOOH decomposed during the extrusion of LDPE/nylon-6, and induced interfacial as well as interpolymeric coupling reactions between the LDPE and nylon-6 phases. Hence their compatibility was enhanced. When 1 wt% ODM was used during the extrusion of LDPE/nylon-6 in the absence of peroxide, the sizes of dispersed LDPE particle were considerably reduced, suggesting a better dispersion of the two phases (Fig.8). A

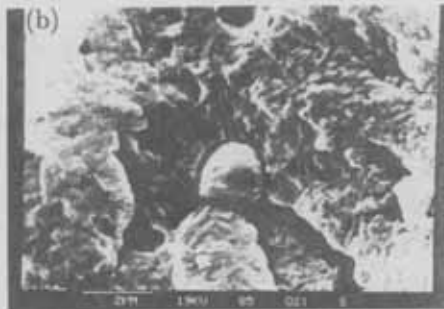
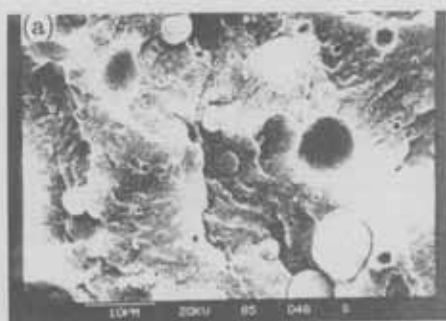


Fig.7 SEM micrographs of LDPE/nylon-6 (3:7) blend extruded with (a) 0.5 wt% t-BuOOH; (b) 1 wt% t-BuOOH

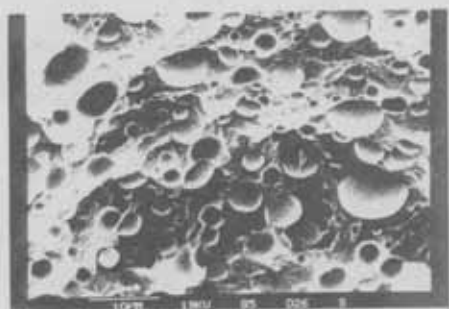


Fig.8 SEM micrograph of LDPE/nylon-6 (3:7) extruded with 1 wt% ODM only

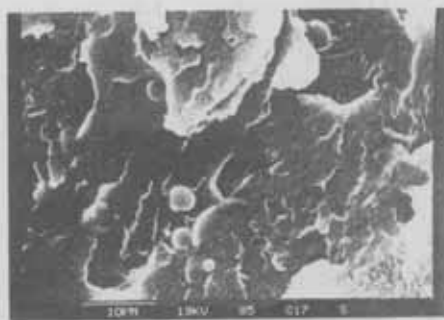


Fig.9 SEM micrograph of LDPE/nylon-6 extruded with a mixture of 0.5 wt% ODM and 0.5 wt% t-BuOOH

combination of these two effects of adding ODM (0.5 wt%) and t-BuOOH (0.5 wt%) into LDPE/nylon-6 blend dramatically changed the fracture surface morphology (Fig.9). Small-size LDPE domains were uniformly dispersed in nylon-6 matrix and there was an excellent adhesion between the two phases. Hence, with the addi-

tion of ODM, improvement of compatibility could be achieved at very low peroxide concentration. These results suggested that a low molecular weight surface-active agent bearing multi-funtional groups and double bond could be used as an effective compatibilizer.

Mechanical properties

A preliminary study of the mechanical properties of LDPE/nylon-6 blends prepared by the reactive extrusion was carried out. These properties included tensile modulus E , tensile strength, elongation at break, and impact strength (Table 1).

Table 1 Mechanical properties of LDPE/nylon-6 blends*

	Material	Additive		Tensile modulus	Tensile strength	Elongation at break	Impact strength
		t-BuOOH (wt%)	Interfacial agent (wt%)				
1	Nylon-6(pure)	—	—	4.3	2.3	3	1.4
2	LDPE/nylon-6 30/70	—	—	1	1	1	1
3	LDPE/nylon-6 30/70	0.5	—	1.1	1.3	5.8	3.3
4	LDPE/nylon-6 30/70	1.0	—	0.9	1.1	1.8	2.2
5	LDPE/nylon-6 30/70	2.0	—	0.8	0.8	0.7	1.3
6	LDPE/nylon-6 30/70	0.5	ODM 0.5	0.9	1.1	4.3	3.6
7	LDPE/nylon-6 30/70	0.5	ODM 1.0	0.7	0.9	3.5	2.5
8	LDPE/nylon-6 30/70	0.5	ODM 2.0	0.5	0.8	1.7	1.2
9	LDPE/nylon-6 30/70	0.5	ODMA 1.0	0.9	1.4	5.5	2.9
10	LDPE/nylon-6 30/70	0.5	DMA** 0.7	0.8	1.2	3.0	2.4

* Above values are relative to those of the LDPE/nylon-6 (30:70) blend

** Mole ratio of the compatibilizers were all the same

All values were given relative to that of LDPE/nylon-6 (30:70) blend. Although pure nylon-6 had high modulus and high tensile strength, the impact strength was quite low. The LDPE/nylon-6 (30:70) blend with no initiator and compatibilizer had mechanical properties inferior to those of nylon-6. By the use of 0.5 wt% of t-BuOOH

as initiator for this system (entry 3), the mechanical properties were significantly improved as a result of the enhancement of interfacial adhesion by coupling reaction between these two polymers. However, when more initiator was used, a substantial decline in mechanical performance was observed (entries 3—5). Although the DSC and SEM results had confirmed that increasing the concentration of peroxide led to better compatibilization of LDPE/nylon-6 blends, the mechanical properties became poorer with the increasing amount of initiator. The blend with 0.5 wt% of ODM and 0.5 wt% of *t*-BuOOH (entry 6) exhibited higher impact strength than the one without ODM. But higher concentration of ODM gave poorer mechanical properties of the blends since it acted as a plasticizer. The effect of the compatibilizer structures was examined. For example, octadecyl maleic monoamide (ODMA) bearing an amide group which could provide extra interaction with nylon through hydrogen bonding showed better mechanical properties than ODM which containing the ester group (entries 7 & 9). On the other hand, decyl maleic monoamide (DMA) (entry 10) was not as effective as ODM or ODMA because the alkyl group contained only 10 carbon atoms which might have less interaction with LDPE.

CONCLUSION

The two phases of a LDPE/nylon-6 (30/70) blend are immiscible and incompatible. This leads to poor interfacial adhesion and large dispersed LDPE domains. The presence of 0.5 wt% of a low molecular weight compatibilizer containing a long hydrocarbon chain, double bond, carboxylic group and either an ester or amide group together with 0.5 wt% of *t*-BuOOH as initiator leads to a significant enhancement of the compatibility of the LDPE/nylon-6 blend as reflected by the improvement of interfacial adhesion and decrease in the size of the dispersed LDPE domains. The elongation at break and impact strength of the compatibilized blends increase particularly at low concentrations of the interfacial agent and initiator, but decrease with further increase in their concentrations. The presence of alkyl maleic monoester or monoamide compatibilizers with peroxide during reactive extrusion can have three functions: 1) it acts as an interfacial active agent to improve the miscibility of LDPE and nylon-6 in the melt state; 2) it provides reactive sites such as alkyl group and double bond which can be grafted onto LDPE through a free radical mechanism. 3) the carboxylic acid groups can react with the amino terminal groups on nylon forming graft copolymer of LDPE and nylon-6, and the ester or amide groups can form hydrogen bonding with the amide groups on nylon. Finally, the interfacial agent with a longer carbon chain was found to be a more effective compatibilizer than that with a shorter carbon chain.

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Keywords:

LDPE; Nylon-6; Reactive extrusion; Compatibilizer

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