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A novel reactive extrusion process for compatibilizing immiscible polymer blends

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Abstract

A novel reactive extrusion process was developed to obtain compatibilized A/B immiscible polymer blends. It consisted of polymerizing a monomer of polymer A in the presence of polymer B. A fraction of polymer B chains bore initiating sites either at the chain end(s) or along the chain backbones, from which polymer A chains could grow. In the process, polymer A and a graft or block copolymer of A and B were formed simultaneously leading to in situ polymerized and in situ compatibilized A/B polymer blends. This paper shows the feasibility of this novel process in a batch mixer using polypropylene (PP) and polyamide 6 (PA 6) blends as an example. Specifically, ε-caprolactam (ε-CL) was polymerized anionically in the presence of PP. A fraction of the PP chains bore 3-isopropenyl-α,α-dimethylbenzene isocyanate (TMI) which acted as growing centers to initiate PA 6 chain growth from the PP chains and to form a graft copolymer of PP and PA 6. © 2001 Published by Elsevier Science Ltd.

Keywords: Reactive extrusion; Compatibilization; Polyamide 6

1. Introduction

It has now been a common practice to blend existing polymers to obtain new materials, instead of searching for new monomers, which are often more costly and time-consuming. However, simply blending different polymers most probably leads necessarily to a material with poor mechanical properties because most polymer pairs are thermodynamically immiscible. Compatibilization is therefore called upon. Its role is to stabilize the morphology and modify the interfacial properties of the blend. This is achieved by adding or creating in situ, during the blending process, a third component, often called an interfacial agent, emulsifier or compatibilizer [1]. The latter can be a graft or block copolymer, which tends to be located at the interfaces between the two components of the blend. As such, the interfacial tension is reduced, the dispersion of one phase in the other improved and the adhesion of the interfaces enhanced. The presence of a copolymer also accelerates the melting of polymer blends [2].

A compatibilizer can be made either separately and then added to a polymer blend or created in situ during the blending process. The first method has the advantage of better controlling the molecular architecture of the compatibilizer. However, it requires specific chemical routes and reaction conditions. More importantly, this method is not suitable for most commercially relevant blends. For example, it is very difficult, if not impossible, to develop a process to synthesize a pure graft or block copolymer of polypropylene (PP) and polyamide 6 (PA 6). Also, it is not always easy for the copolymer to reach and locate at the interfaces where it is most added. The second method, often called reactive blending or reactive compatibilization, allows us to generate the compatibilizer in situ at the interfaces directly during blending. In the case of PP/PA 6 blending system, a graft copolymer can be formed easily during blending if a fraction of the PP chains are functionalized with a functional vinyl monomer such as maleic anhydride. The latter reacts readily with the terminal amine group of PA 6. Moreover, since the compatibilizer is formed in situ at the interfaces, the problem of getting it to the interfaces no long exists. For these reasons, the second method has become very attractive. Nevertheless, since the reaction takes place primarily in the interfaces, it is difficult to control the rate of formation, the amount and the molecular architecture of the compatibilizer.

Not long time ago, a novel reactive extrusion process was reported in the literature to obtain compatibilized immiscible polymer blends using a co-rotating twin screw extruder as a reactor [3]. Instead of blending premade polymers, A and B, the monomer of A was polymerized in the presence

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of B. A fraction of B chains bore initiating sites either at the chain end(s) or along the chains, from which A chains could grow. In the process, polymer A and a graft or block copolymer of A and B were formed simultaneously, leading to in situ polymerized and in situ compatibilized A and B polymer blends. This paper shows the feasibility of the process in an internal batch mixer using PP/PA 6 blends as an example. ε-Caprolactam (ε-CL) was polymerized anionically in PP using a catalyst and a co-catalyst. A fraction of the PP chains bore isocyanate groups, which acted as growing centers to initiate PA 6 chain growth from PP chains. Compatibilized PP/PA 6 blends of varying composition and morphology were then obtained.

2. Strategy

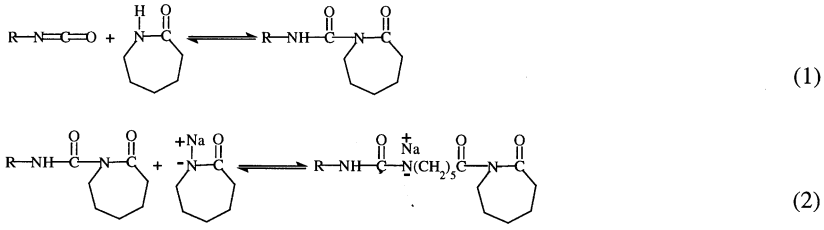
Lactams such as ε-CL can be polymerized anionically in the presence of a catalyst like sodium caprolactam (NaCL) [4–9]. However, the overall polymerization rate is often very slow because of the slow initiation rate and is thus incompatible with reactive extrusion processes. The latter have residence times typically less than 10 min. An activator is thus required to accelerate the initiation rate and consequently the polymerization rate. It can be an isocyanate, an ester or an anhydride [8]. Polymerization of ε-CL in the presence of a catalyst and an activator is called activated anionic polymerization. The activator is incorporated in the starting end of the PA 6 chain, as shown in Fig. 1.

The above chemical process can be explored for two interesting applications. One may synthesize pure copolymers containing polyamide segments. For example, if the activator is a polymer, which bears initiating species like isocyanate along its chain, called macro-activator, a pure graft copolymer will be formed [10,11]. One may also obtain polymer blends by polymerizing lactam like ε-CL in the presence of a polymer. If there is no compatibilizer present in the system, the resulting blend will not be very different from one that is obtained by melt blending a premade polyamide and the polymer. In other words, the morphology of the blend will probably gross and unstable. However, if a fraction of the polymer chains bear initiating sites either at the chain end(s) or along the chains, from which polyamide chains can grow, then formation of the polyamide and a copolymer of the polymer and polyamide will take place simultaneously. In this case, four phenomena are involved in the process: polymerization of the lactam to the corresponding polyamide causes phase separation and eventually phase inversion; formation of a copolymer of the polymer and polyamide that stabilize the system. As such, this process is called in situ polymerization and in situ compatibilization of polymer blends. Conceptually, it should allow us to obtain a variety of morphology including nano-dispersion upon controlling the kinetics of polymerization, phase separation and copolymer formation [3].

If the polymer is PP, it must first be chemically modified in order for it to bear initiating species. The latter must be stable enough under process conditions (high temperature and exposure to air and humidity). In this study, 3-isopropenyl-α,α-dimethylbenzene isocyanate (TMI, see Fig. 2 for its chemical structure) was chosen as a functionalizing monomer and was attached to PP by free radical grafting. In what follows, TMI modified PP will be denoted as PP-*g*-TMI.

The aim of this study was to show the feasibility of making compatibilized PP/PA 6 blends in a batch mixer starting with PP and ε-CL as raw materials using the above concept of in situ polymerization and in situ compatibilization.

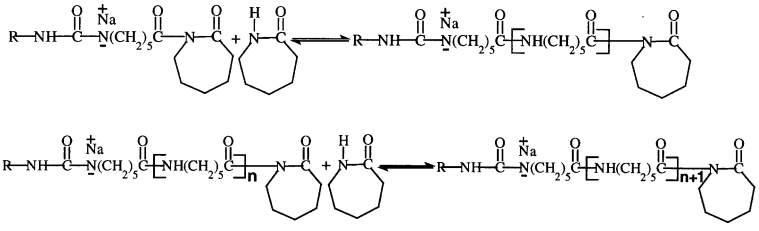
Initiation:



(1)

(2)

Propagation:



(3)

(4)

Fig. 1. Idealized chemical process of the polymerization of ε-CL catalyzed by NaCL and activated by an isocyanate.

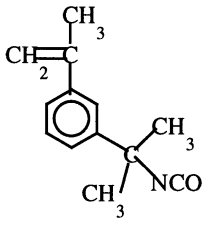


Fig. 2. Molecular structure of 3-isopropenyl-α,α-dimethylbenzene isocyanate (TMI).

The effects of various process parameters such as temperature, composition of the polymerizing system (ε-CL, PP, PP-*g*-TMI and NaCL) and the TMI content in the PP-*g*-TMI were investigated.

3. Experimental

3.1. Materials

The polypropylene used in this study was a commercial grade of Borealis, Norway, in the form of porous pellets. Its number and weight average molecular weights were 62,000 and 280,000 g/mol, respectively. Its melt flow index was 3.5 g/10 min at 230°C under 2.16 kg (ASTM 1238L). The porous PP was able to absorb large amounts of liquid reagents. 3-Isopropenyl-α,α-dimethylbenzene isocyanate (TMI) and styrene (St) were purchased from Aldrich and used without further purification. TMI has a formula weight of 201.27 g/mol and is a liquid at room temperature. Its boiling temperature is about 270°C/760 mmHg. 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-hexane (DHBP) was used as a free radical initiator for the functionalization of PP with TMI. Its half lifetime was reported to be around 6 s at 200°C.

The reagents used for the anionic polymerization of ε-CL were ε-CL (melting point: ~71°C/760 mmHg; boiling point: ~137°C/10 mmHg), a catalyst (NaCL) and an activator (ε-caprolactam blocked hexamethylene diisocyanate). They were kindly supplied by DSM, The Netherlands. The catalyst was in the form of flakes (C-10 katalysator) and contained 1.4 mol sodium per kg ε-CL. The activator (Accelerator V5/C-20 Aktivator) was powdery and contained 2.0 mol isocyanate per kg ε-CL.

3.2. Preparation of PP-g-TMI

PP-*g*-TMI was prepared by free radical grafting. The experimental procedures used were the same as those described elsewhere [12–15]. The reaction was carried out in a Rheocord Haake mixer (50 cm^3) in which two sigma rotors rotated in opposite directions at 64 rpm to ensure mixing. For a typical experimental run, PP pellets (40 g) along with the liquid monomer(s) and peroxide were first mixed in a cup for about 15 min so as for the liquid reagents (TMI, St and DHBP) to be absorbed by the PP pellets. They were then charged to the mixer, which was preheated up to 200°C. TMI modified PP was collected after 10–15 min of reaction. Residual TMI and copolymerized TMI were removed from the PP-*g*-TMI by dissolution in boiling xylene and precipitation in acetone at room temperature. The TMI grafting yield was measured by Fourier transform infrared (FTIR) using purified PP-*g*-TMI films (~100 μm). The grafting of TMI onto PP was characterized by the appearance of a peak at 2255 cm^{-1} corresponding to the isocyanate group of TMI. That peak was thus chosen to quantify the TMI grafting yield. The peak at 2772 cm^{-1} characteristic of PP was chosen as an internal reference. A calibration curve was constructed using mixtures of PP and TMI of known compositions (Fig. 3).

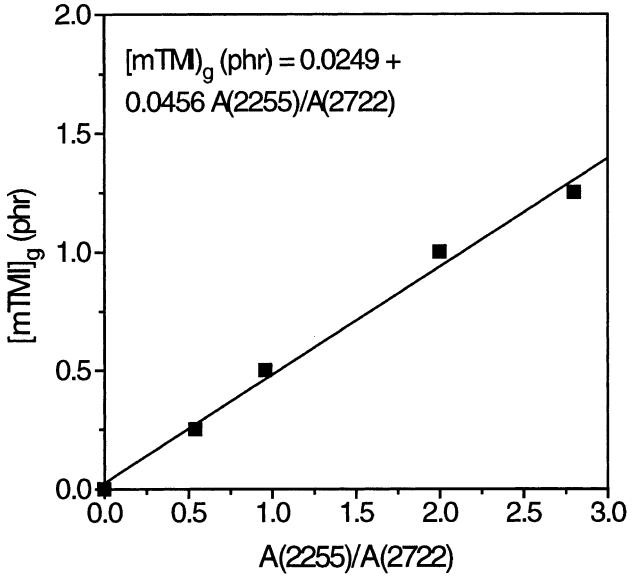


Fig. 3. Calibration curve for the measurement of TMI content in PP-*g*-TMI by FTIR.

3.3. In situ polymerization and in situ compatibilization of PP/PA 6 blends

Different polymerization experiments were carried out in the batch mixer. The rotation speed of the rotors was always 64 rpm. Before the reagents of the polymerization system (ε-CL, NaCL and activator) were charged to the batch mixer which was preheated to a desired temperature, they were ground together to powder. For experiments involving PP or PP + PP-*g*-TMI, the powdery mixture of ε-CL, NaCL, the activator was first mixed with the powder of PP or PP + PP-*g*-TMI. The whole system was then added to the mixing chamber. Samples were taken from the mixing chamber after 10 min of reaction and then quenched quickly in liquid nitrogen to stop the reaction.

3.4. Material characterization

The melting and recrystallization behavior of the materials was examined using differential scanning calorimetry

(DSC). Samples were subjected to the following cycle: they were heated from 50 to 250°C at 10°C/min, maintained at 250°C for 10 min, then cooled down to 50°C at 10°C/min (recrystallization) and heated again to 250°C at 10°C/min (melting).

Morphology of the PP/PA 6 blends was examined using a scanning electron microscopy (SEM). Before the SEM observation, samples were fresh fractured and then subjected to formic acid treatment at room temperature overnight under mild stirring to remove the dispersed phase domains (PA 6). The surfaces of the fractured samples were gold-sputtered. A semi-automatic digital image analysis technique was used for determining the number average diameter, d_n, of the PA 6 domains from SEM photographs using NIH Image software. At least 400 particles were counted in order for the values of d_n to be statistically meaningful.

4. Results

4.1. Melt free radical grafting of TMI onto PP

Free radical grafting of a vinyl monomer onto PP inherently faces two problems: low grafting content and severe PP chain degradation by β-scission. Free radical grafting is concerned with a reaction between a vinyl monomer and a tertiary PP macro-radical. As such, the steric hindrance effect is very large and the reactivity between a vinyl monomer and a tertiary PP macro-radical is low. This is particularly so when the vinyl monomer is bulky like TMI. In such a case, the comonomer concept can be of great help. As discussed in previous works [12,14], a comonomer can improve the free radical grafting reactivity of a vinyl monomer only if its free radical grafting reactivity toward the polymer backbone is much higher than that of the vinyl monomer and it can copolymerize readily with the vinyl monomer. St has been found to be a very good comonomer for many polymer/monomer pairs. This is because St has a free radical grafting reactivity, which is much higher than many other vinyl monomers, and it can copolymerize easily with many monomers like maleic anhydride, glycidyl methacrylate and acrylic acid.

In this study, St was found to be able to improve TMI's grafting yield (Fig. 4) and reduce PP chain degradation (Fig. 5). The presence of an equimolar amount of St with respect to TMI almost doubled TMI's grafting yield. Nevertheless, under the specified conditions, the conversion of TMI to grafted TMI was still less than 15%. The torque values of the grafting system characteristic of the PP's molecular weight were much higher with St than without. Moreover, it decreased with increasing DHBP's concentration without St and was little affected by DHBP's concentration with St.

4.2. Reactivity between PP-g-TMI and ε-CL

The isocyanate group of the grafted TMI onto PP had to be stable enough under process conditions (high temperature and exposure to air and moisture) in order to be able to initiate the polymerization of ε-CL. The PP-*g*-TMI was found to be stable enough in the batch mixer at 200°C for at least 1 h. The high stability of the isocyanate group of the PP-*g*-TMI with respect to classical isocyanates may be explained by the protective steric effect of the two adjacent methyl groups of TMI (Fig. 2).

According to reaction 1 of the chemical process of the

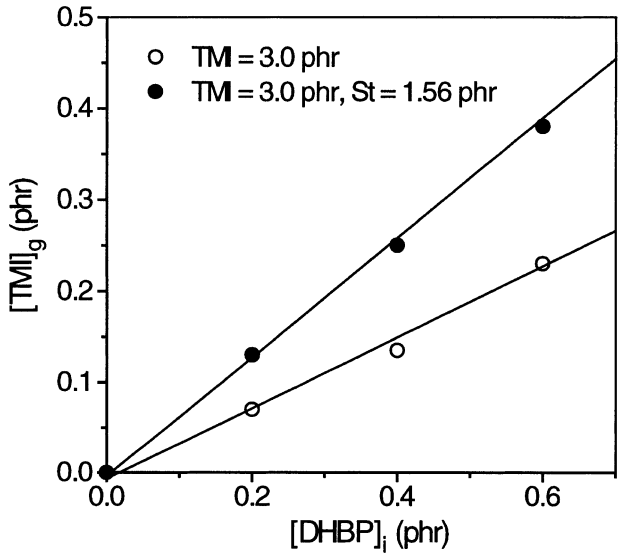


Fig. 4. Effect of adding St on TMI's grafting yield as a function of DHBP's concentration. Set temperature = 180°C, $[TMI]_i = 3.0$ phr, $[St]_i/[TMI]_i = 0$ (○) or 1.0 mol/mol or 0.52 g/g (●). The abbreviation 'phr' stands for parts per hundred parts of PP.

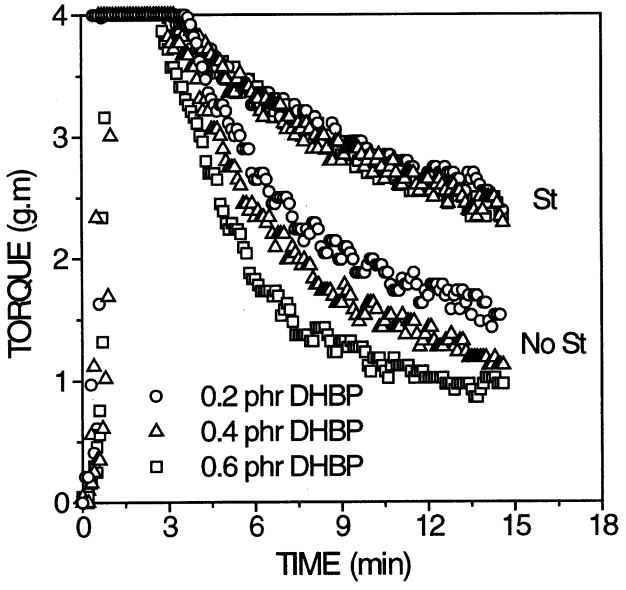


Fig. 5. Effect of adding St on the torque of the PP/TMI/DHBP grafting system as a function of time in the batch mixer for different DHBP's concentrations. $[TMI]_i = 3.0$ phr, $[St]_i/[TMI]_i = 0$ or 1.0 mol/mol, $[DHBP]_i = 0.2$ (○), 0.4 (△) and 0.6 phr (□).

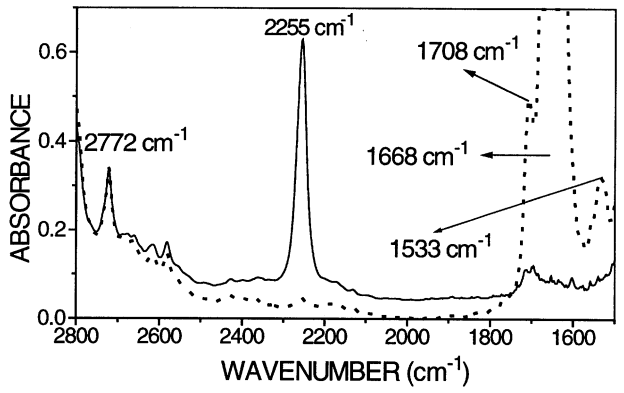


Fig. 6. FTIR spectra of PP-*g*-TMI (0.4 phr grafted TMI) before (solid line) and after reaction (dotted line) with an excess of ε-CL.

activated anionic polymerization of ε-CL, the formation of acyl caprolactam between PP-*g*-TMI and ε-CL is crucial for the subsequent propagation of PA 6 chains along the PP-*g*-TMI backbone. Fig. 6 shows the IR spectra of PP-*g*-TMI before and after reaction with ε-CL. After reaction, the peak at 2255 cm^{-1} characteristic of the isocyanate group of TMI disappeared and three new peaks appeared in the wavelength between 2800 and 1500 cm^{-1}. They were located at 1708, 1668 (saturated) and 1533 cm^{-1}, corresponding to the C=O of the tertiary amide, C=O of the urea and NH of the urea of the acyl caprolactam, respectively (see reaction 1 of Fig. 1).

The reactivity between PP-*g*-TMI and ε-CL was evaluated under real polymerization conditions in the batch mixer. For that purpose, a mixture of PP-*g*-TMI (75%) and ε-CL (25%) was mixed in the batch mixer at 180 or 200°C. The PP-*g*-TMI used contained 0.4 phr TMI and the corresponding [ε-CL]/[isocyanante] molar ratio was 1.49. The reaction kinetics in terms of the disappearance of the isocyanate group was followed up by taking samples from the mixing chamber at various time intervals and then quenching them quickly in liquid nitrogen. The amount of the remaining isocyanate group was easily measured by following the absorbance of the peak at 2255 cm^{-1}. As can be seen from Fig. 7, the reactivity between the isocyanate group of the PP-*g*-TMI and ε-CL was very high since it disappeared completely in less than 3 min. That time period included the time necessary for melting PP and homogenizing the system. Thus the real time required for a complete reaction was much shorter.

4.3. Bulk activated anionic polymerization of ε-CL

Activated anionic polymerization of ε-CL in a polymer processing machine like a screw extruder was studied in the literature [16–21]. Its behavior in an internal batch mixer and the characteristics of the PA 6 thus obtained were examined in order to be served as references for subsequent study. Fig. 8 shows the evolution of the torque and the temperature of the ε-CL/NaCL/activator polymerizing system as a function of time. The initial torque of the system was not measurable because its viscosity was very low. After an induction period of about 80 s, it increased abruptly, reaching a maximum in 50 s and then decreased drastically before it leveled off. The rapid increase in torque implies that the activated anionic polymerization of ε-CL proceeded very rapidly. The subsequent decrease in torque was due to the temperature rise resulting from the polymerization heat release and viscous dissipation. It could also be related to PA 6 chain degradation as a result of prolonged mixing.

The melting and recrystallization temperatures of the PA 6 synthesized in the batch mixer were measured by DSC and were 215 and 163°C, respectively (see Fig. 9). Those values were close to those of PA 6 obtained by a classical hydrolytic

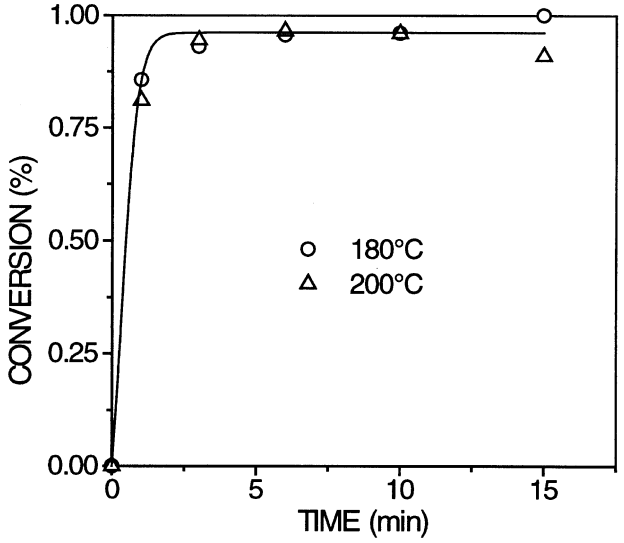


Fig. 7. Reaction between PP-*g*-TMI (75 wt%.) and ε-CL (25 wt%) at 180 or 200°C. TMI's grafting yield = 0.4 phr; [ε-CL]/[isocyanate] = 1.49.

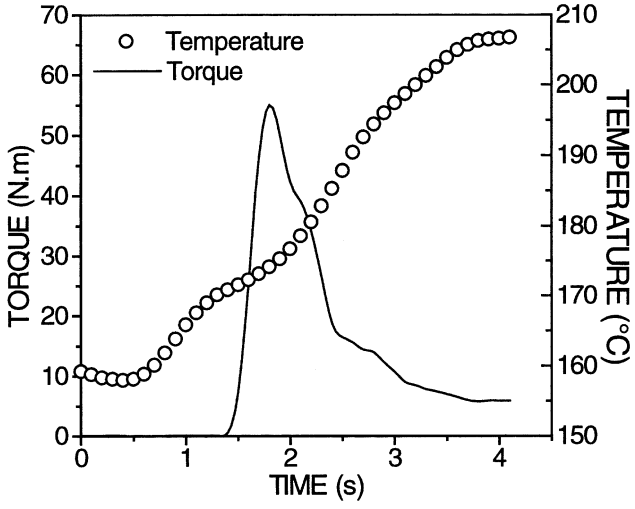


Fig. 8. Evolution of the torque and temperature during the reaction of the ε-CL/NaCL/activator (100/3/3 by weight) system in the batch mixer.

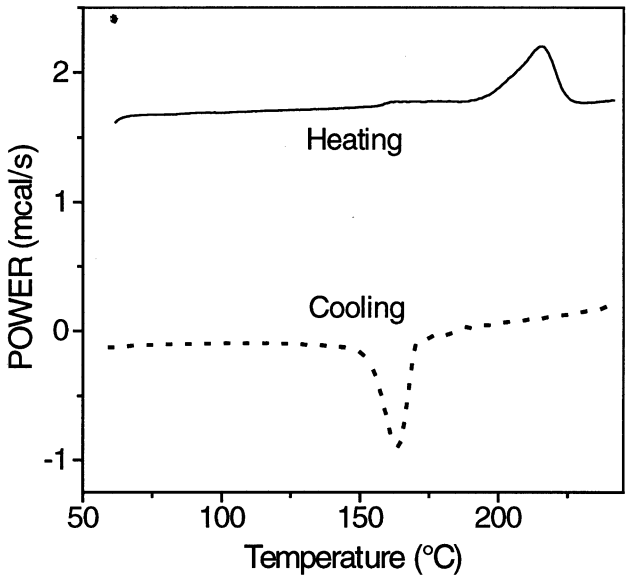


Fig. 9. Melting and recrystallization behavior of the PA 6 synthesized in the batch mixer characterized by DSC. Heating and cooling rate = 10°C/min.

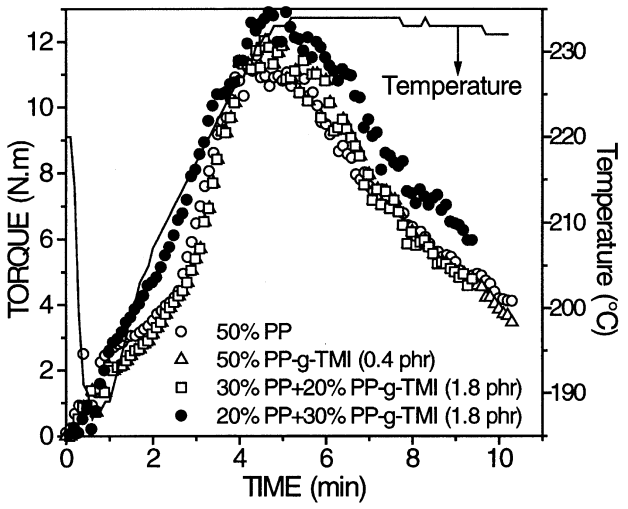


Fig. 10. Evolution of the torque and temperature during the in situ polymerization of ε-CL in the batch mixer in the presence of PP or PP-*g*-TMI. $[NaCL]_i = [activator]_i = 3.0$ g/100 g of ε-CL + PP or ε- CL + PP + PP-*g*-TMI. All the polymerizing systems had almost the same temperature profile, as shown by the single temperature-time curve.

process. The PA 6 was soluble in formic acid, indicating that crosslinking, if there was any, was insignificant.

4.4. Polymerization of ε-CL in the presence of PP or PP + PP-*g*-TMI

The evolution of torque and temperature as a function of time was examined for four in situ polymerizing systems in the batch mixer (Table 1). As shown in Fig. 10, the evolution of torque and temperature as a function of time was similar for all the four polymerizing systems mentioned above. It increased first in a very rapid manner, reaching a maximum at about 4–5 min and then decreased in a drastic way. This indicates that in all the polymerizing systems, ε-CL started to polymerize immediately after the reactants of the systems were charged to the mixing chamber. It is likely that it went to completion within 5 min of reaction. The ultimate decrease in torque may imply that after the polymerization was accomplished, the resulting biphasic PP/PA 6 systems underwent a sort of morphological rearrangements. A slightly higher torque was observed for the ε-CL/PP + PP-*g*-TMI/NaCL/activator (50/20 + 30/3/3) system. It is likely that more PP-*g*-PA 6 copolymer was formed in that particular system, causing a slight viscosity increase with respect to the other systems.

Table 1
Four different in situ polymerization experiments

Polymerizing system	Final material
ε–CL/PP/NaCl/activator (50/50/3/3)	Uncompatibilized PP/PA 6 blend
ε–CL/PP-*g*-TMI/NaCl/activator (50/50/3/3), TMI content in PP-*g*-TMI = 0.4 phr	Compatibilized PP/PA 6 blend
ε–CL/PP + PP-*g*-TMI/NaCl/activator (50/20 + 30/3/3), TMI content in PP-*g*-TMI = 1.8 phr	Better compatibilized PP/PA 6 blend
ε–CL/PP + PP-*g*-TMI/NaCl/activator (50/30 + 20/3/3), TMI content in PP-*g*-TMI = 1.8 phr	Best compatibilized PP/PA 6 blend

Fig. 11 compares the DSC thermograms of the pure PA 6, uncompatibilized PP/PA 6 blend and compatibilized PP/PA 6 blend obtained from the ε-CL/NaCL/activator (100/3/3), ε-CL/PP/NaCL/activator (50/50/3/3) and ε-CL/PP-*g*-TMI/NaCL/activator (50/50/3/3), respectively. Upon heating (Fig. 11a), both PP/PA 6 blends displayed two distinct peaks at 161 and 212°C, corresponding to the melting temperatures of PP and PA 6, respectively. Upon cooling (Fig. 11b), the uncompatibilized PP/PA 6 blend yielded two distinct peaks at 101 and 160°C, respectively. They corresponded to the recrystallization temperatures of PP and PA 6, respectively. However, the compatibilized PP/PA 6 blend exhibited only one peak at 101°C and the one at 160°C was not seen. The latter was not observed for the two other compatibilized PP/PA 6 blends obtained in the presence of PP-*g*-TMI. This phenomenon is typical of a compatibilized PP/PA 6 blend and its occurrence was viewed as an evidence that the PP-*g*-TMI acted as a macro-activator to form a graft copolymer of PP-*g*-PA 6. It should be noted that the cooling rate for the above crystallization experiments was 10°C/min. When it was reduced to as low as 0.5°C/min, the peak corresponding to the recrystallization of PA 6 was still not observed in the compatibilized PP/PA 6 blends. This does not mean that the PA 6 was not crystallized during cooling. In fact, when it was heated up again from the room temperature, the same melting peak as that observed during the first heating was observed. Thus the question remains of why it was impossible to observe by DSC the recrystallization of PA 6 in the compatibilized

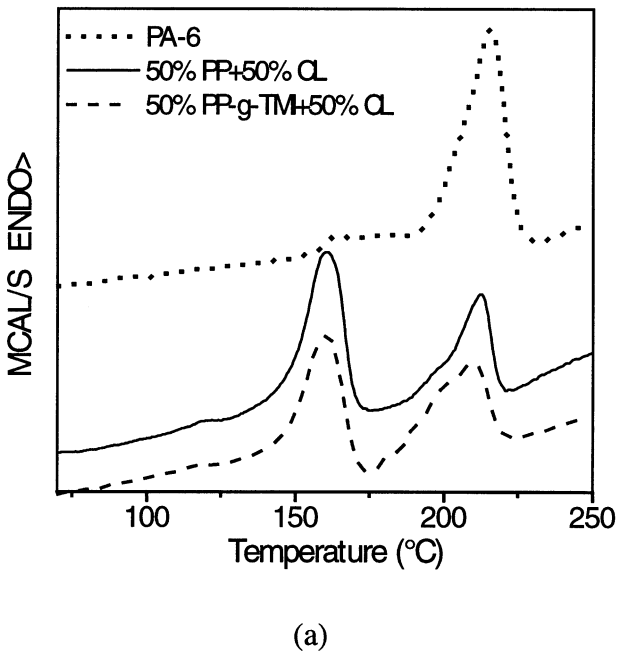


Fig. 11. Comparison of the DSC thermograms between the PP/PA 6 (50/50) blend resulting from obtained during heating (a) and cooling (b). Heating and cooling rates = 10°C/min.

PP/PA 6 blends even when cooling was very slow. The presence of a PP-*g*-PA 6 graft copolymer had two effects on the PP/PA 6 blends: reduction in the PA 6 domain size and possible modification of the PA 6 chain mobility, at least at the interfaces. The effect of the reduction in PA 6 domain size could be much more important. This is because a separate study [22] showed that the PA 6 in two PP/PA 6 blends having the same PA 6 domain size in the PP matrix

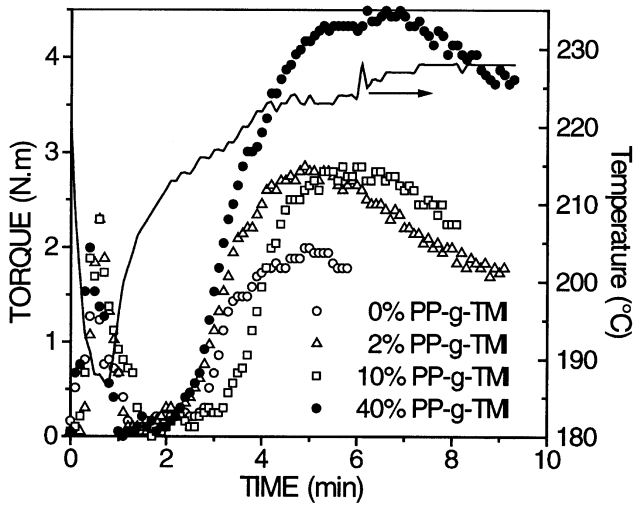


Fig. 12. Evolution of the torque and temperature during the in situ polymerization of the ε-CL/PP/PP-*g*-TMI/NaCL/activator (30/70-*x*/*x*/3/3) system in the batch mixer. Only one temperature profile is shown in the figure because it was virtually the same for all the polymerizing systems.

with one containing a small amount of a PP-*g*-PA 6 graft copolymer had virtually the same recrystallization behavior in DSC. A partial explanation would be that when the PA 6 domains were small, the density of nucleating sites per each PA 6 domain became small. Consequently, the crystallization rate was reduced. Work is underway to further investigate this phenomenon.

Table 2 gathers thermodynamic data of various materials obtained in terms of the enthalpies of fusion (ΔH_f) and recrystallization (ΔH_c), and the melting and recrystallization temperatures, T_m and T_c. Basically, there was practically not much change for PP. The same was true for PA 6 except for the PA 6 of the compatibilized PP/PA 6 blend in which no recrystallization peak was observed.

4.5. Influence of the amount of PP-g-TMI

The polymerization kinetics and the morphology of the ε-CL/PP/PP-*g*-TMI/NaCL/activator (30/70-*x*/*x*/3/3) polymerizing system were expected to be influenced by the composition of the PP-*g*-TMI, *x*. Fig. 12 shows the evolution of torque and temperature as a function of time in the batch mixer for four different PP-*g*-TMI compositions ($x = 0$, 2, 10 and 40). In all experiments, PP started to melt soon after the polymerizing system was charged to the mixing chamber. The melting process corresponded to the first peak of the torque histogram. The torque value then went down quickly to almost zero because the low viscosity ε-CL was the major phase. It started to increase very rapidly thereafter, indicating that the polymerization of ε-CL proceeded rapidly. A maximum value was reached after about 5 min of mixing. It finally decreased in a gradual manner. The higher the amount of PP-*g*-TMI, the more the

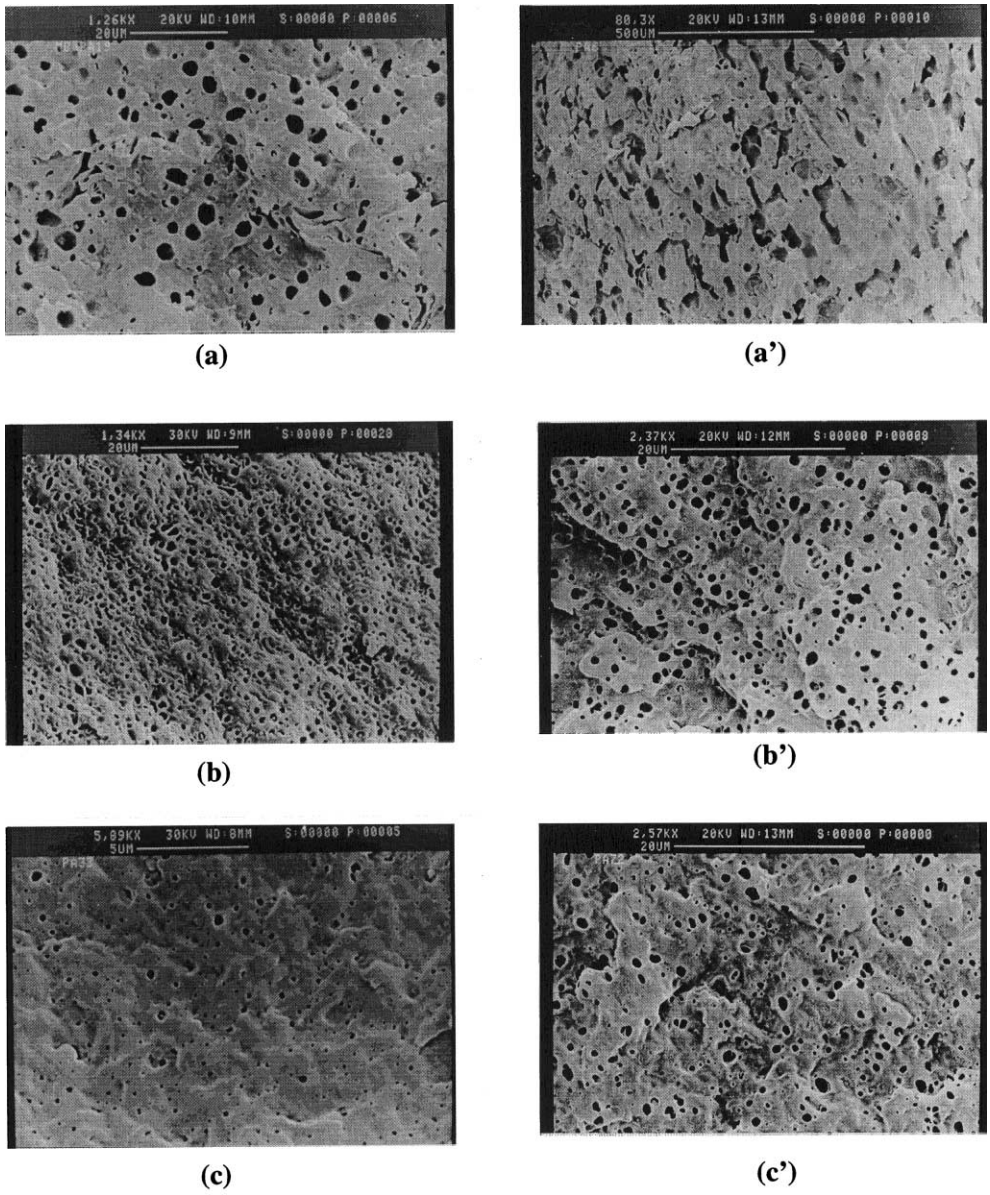


Fig. 13. Effect of the amount of PP-*g*-TMI (1.8 phr grafted TMI) on the morphology of ε-CL/PP + PP-*g*-TMI/NaCL/activator polymerizing systems: ε-CL/PP + PP-*g*-TMI/NaCL/ activator (30/70-*x* + *x*/3.0/3.0) systems with (a) $x = 0$, (b) $x = 2.0$, (c) $x = 40$; ε-CL/PP + PP-*g*-TMI/NaCL/ activator (50/50-*x* + *x*/3.0/3.0) systems with (a′) $x = 0$, (b′) $x = 20$, (c′) $x = 30$.

PP-*g*-PA 6 graft copolymer formed in the system and the greater the maximum and final values of the torque.

Fig. 13 shows the SEM photographs illustrating the effect of the amount of PP-*g*-TMI on the morphology of the ε-CL/PP/PP-*g*-TMI/NaCL/activator system after polymerization. When ε-CL/PP + PP-*g*-TMI was 30/70 by weight, the number average size of the dispersed phase (PA 6) was about 3.5 μm in the absence of PP-*g*-TMI. Addition of

Table 2
Thermodynamic data of the pure PP, PA 6 and PP/PA 6 blends

	ΔH_f (J/g)	ΔH_c (J/g)	T_m (°C)	T_c (°C)
Pure PP	69.0	68.9	160.9	100.5
PP in the uncompatibilized blend	68.5	69.1	161.0	100.4
PP in the compatibilized blend	61.5	63.1	160.8	101.2
Pure PA 6	44.5	50.1	215.3	163.6
PA 6 in the uncompatibilized blend	49.8	51.2	212.1	158.6
PA 6 in the compatibilized blend	43.2	No peak	211.1	No peak

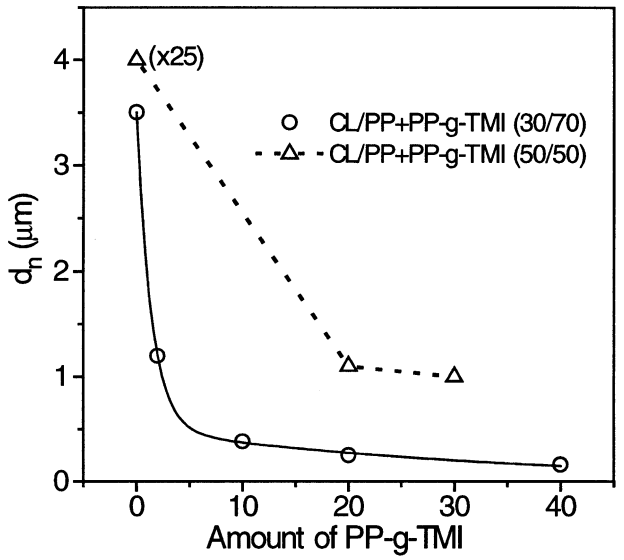


Fig. 14. Effect of the amount of PP-*g*-TMI (1.8 phr grafted TMI) on the morphology of ε-CL/PP + PP-*g*-TMI polymerizing system in terms of the number average size of the PA 6 phase. The size of the PA 6 domains corresponding to the blend from the ε-CL/PP + PP-*g*-TMI (50/50) system in the figure should read 4 μm × 25, i.e. 100 μm.

2.0% PP-*g*-TMI reduced it to 1.2 μm. A further increase in the amount of PP-*g*-TMI further decreased the PA 6 particle size. It was as small as 0.16 μm when 40 wt% PP-*g*-TMI was present in the polymerizing system. Similar results were obtained for the case where the ε-CL/PP + PP-*g*-TMI was 50/50 by weight. It is remarkable to note that without PP-*g*-TMI, the size of the PA 6 phase was as big as some 100 μm. It was reduced to the micrometer range in the presence of 20 or 30 wt% PP-*g*-TMI. Fig. 14 shows the evolution of the number average particle size as a function of the amount of the PP-*g*-TMI for the ε-CL/PP + PP-*g*-TMI (30/70) and (50/50) polymerizing systems.

5. Discussion

The results presented above show that the concept of in situ polymerization and in situ compatibilization was feasible for PP/PA 6 blends starting with ε-CL/PP/PP-*g*-TMI/NaCL/activator. The compatibilizing efficiency of this novel process was very high compared with that of the classical compatibilization method starting with premade PP, PA 6 and a maleic anhydride modified PP, denoted as PP-*g*-MA. This can be explained as follows. In the classical compatibilization method, a copolymer of PP and PA 6 is formed through an interfacial reaction between maleic anhydride functionalized PP and the terminal amine group of PA 6. As such, the amount of copolymer formation depends very much on the interfacial volume available in the system. Since it is usually very small for immiscible polymer pairs, the amount of copolymer formation is often small, say, less than 5%. Moreover, a reaction at a polymer–polymer interface can be limited by the crowding of the interface with the copolymer. Once the amount of the copolymer formed reaches a certain threshold corresponding to the saturation of the interface by the copolymer chains, it will literally stop. In the novel process, however, the copolymer is formed through the growth of polymerizing PA 6 chains from isocyanate bearing PP backbone. Therefore, the amount of the copolymer formation is no longer limited by the interfacial volume. The problems related to the interfacial saturation also disappear.

An attempt was made to quantify the amount of the copolymer formed in the process. The PP was soluble in hot xylene and the PA 6 in formic acid. For an uncompatibilized PP/PA 6 blend, the PP and PA 6 phases were solubilized completely in hot xylene and formic acid, respectively. As for a compatibilized PP/PA 6 blend, after successive extraction from hot xylene and formic acid, there was a certain amount of product insoluble in either of the two solvents. That insoluble part was not crosslinked because it behaved as a thermoplastic material. Thus it was considered as the graft copolymer of PP and PA 6. The amounts of the insoluble part of various PP/PA 6 blends are gathered in Table 3. Note that the only difference among those blends was the ratio between PP and PP-*g*-TMI. Clearly, the higher the amount of PP-*g*-TMI, the more important the insoluble part. When the whole PP phase was only composed of PP-*g*-TMI, the copolymer formed reached as high as 16.1%. The real percentage of the copolymer was much higher because certain amounts of the copolymer were soluble in hot xylene and/or formic acid. A separate study [11] showed that a pure PP-*g*-PA 6 graft copolymer can be produced if one starts with PP-*g*-TMI/ε-CL/NaCL without a low molecular weight activator like the one used in this study. PP-*g*-TMI is the only activator from which the polymerization of ε-CL is initiated and then propagated.

A question was asked about whether the high compatibilizing efficiency of PP-*g*-TMI was through a compatibilizing mechanism similar to that of PP-*g*-MA. From a chemical viewpoint, the isocyanate group of the PP-*g*-TMI could react with the terminal amine or carboxylic group of the PA 6. In an ε-CL/PP + PP-*g*-TMI/NaCL/activator polymerizing system, one might imagine that ε-CL

Table 3
Amounts of the insoluble part of various PP/PA 6 blends after successive extraction in hot xylene and then in formic acid. The PP-*g*-TMI used contained 1.8 phr TMI. The percentages in the third column was based on the total amount of the PP/PA 6 blends. For example, 16.1% means that there were 16.1 g insoluble product per 100 g PP/PA 6 blend

PP/PP-*g*-TMI/ε-CL/NaCL/activator (by weight)	PP-*g*-TMI/activator (by mole)	Insoluble part (wt%)
50/0/50/3/3	0	0
48/2/50/3/3	0.03	2.4
30/20/50/3/3	0.30	12.1
0/50/50/3/3	0.75	16.1

was first converted to PA 6. The latter then reacted with the isocyanate group of the PP-*g*-TMI leading to the formation of the copolymer necessary for compatibilization. That scenario was checked in the batch mixer. The PP-*g*-TMI containing 1.8 phr TMI was added to the PP/PA 6 blend obtained from the polymerization of an ε-CL/NaCL/activator/PP polymerizing system. No morphology change was observed. Thus, the compatibilizing efficiency of PP-*g*-TMI was directly related to its ability to initiate the anionic polymerization of ε-CL.

6. Conclusion

This study showed the feasibility of the concept of in situ polymerization and in situ compatibilization of immiscible polymer blends in a batch mixer. Unlike the classical compatibilization process in which a copolymer is added or created in situ during blending, the new process polymerizes a monomer of polymer A in the presence of polymer B. A fraction of polymer B chains bear initiating sites either at the chain end(s) or along the chain backbones, from which polymer A chains can grow. This way, both polymerization of monomer A and formation of a copolymer of A and B take place simultaneously, leading to in situ polymerized and in situ compatibilized A and B polymer blends. For example, polymerization of ε-CL in a mixture of PP and an isocyanate bearing PP led to compatibilized PP/PA 6 blends in the presence of sodium ε-CL as a catalyst and an aliphatic diisocyanate as an activator. This process has at least two advantages over the classical compatibilization process. First of all, to make a PP/PA 6 blend, one does not have to use PA 6 but ε-CL. Secondly, very large amounts of copolymer can be formed, allowing for very fine dispersion including nanometer-scale dispersion [3].

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