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Investigation of polymer blends of polyamide-6 and poly(methyl methacrylate) synthesized by RAFT polymerization

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Abstract Morphological and thermal properties of immiscible and incompatible polymer blends of commercial polyamide-6 (PA-6) and poly(methyl methacrylate) (PMMA) synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization have been studied in the presence of a compatibilizer consisting of either a random copolymer of styrene-maleic anhydride (SMA) or a diblock copolymer poly(methyl methacrylate) and polystyrene (PMMA-PS) also synthesized via RAFT polymerization. Blends of PA-6/PMMA were obtained by extrusion mixing. During melt compounding in the extruder, the functional groups of the polymer components were reacted in the presence of a compatibilizer, which changed considerably the morphology of the blend. After compatibilization, particles of PMMA in the PA-6 were smaller and better dispersed. The morphology and thermal properties of the blends were characterized using scanning electron microscopy (SEM) and differential scanning calorimetry (DCS).

Keywords Polyamide-6 · PMMA · Compatibilization · Morphology

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Introduction

Polymer blends are materials in which two or more polymers are blended together to create a new material with different physical properties. Polymer blends can be broadly divided into miscible, partially miscible, and immiscible blends, the latter being by far the most populous group. Blending different polymers while conserving their individual properties in the final mixture is a very attractive way of obtaining new structural materials. Blends have been intensively studied since the dawn of polymer science, and they usually consist of a particulate minority phase dispersed in a matrix. The properties of polymeric blends are not only determined by the properties of the component polymers, but also by their morphology [1–3]. The conditions of preparation are an important factor in the final morphology of the resulting blend. The most common industrial route to polymer blends is the mixing of molten polymers in a twin-screw extruder, which lead to blends which morphologies are very dependent on their processing and thermal history [4]. Beyond the preparation, the interaction between the polymer components of a blend also affects the final morphology. The entropy of mixing of polymers is usually very low, which explains why the majority of polymer mixtures give rise to a two-phase system. Such systems are characterized by coarse and unstable phase morphology, and a poor interfacial adhesion between phases, resulting in materials of poor physical properties (mechanical, thermal, etc.) [5]. The miscibility of polymer pairs depends on specific interactions such as hydrogen bounding, dipolar interactions, phenyl group coupling, or ionic interactions. Phenyl group coupling or ionic interactions may contribute to a negative heat of mixing making homogeneous polymer blends thermodynamically stable. However, most of the polymer blends are obtained and used at conditions that are far from their thermodynamic equilibrium. The morphology of polymer mixtures becomes even more complex if one of the components is able to crystallize.

One solution to this problem is the use of a compatibilizer, which increases the compatibility between two dissimilar polymers by modifying the interfacial properties of the blended phases. For two homopolymers, A and B, examples of effective compatibilizers include block (A-*b*-B) and graft (A-*g*-B) copolymers designed to act as a macromolecular surfactant forming a layer at the interface between the two homopolymers, thereby reducing the interfacial tension between the two domains and stabilizing the microscopic morphologies [5] [6]. The location of the compatibilizer at the interface between the individual phases of a blend is a necessary requirement for an efficient compatibilization and stable phase morphology, stabilization upon further re-processing or thermal annealing [7]. The composition, molecular weight, and miscibility of the compatibilizer with the individual blend phases, its functionality and molecular architecture are key parameters which affect its stable location at the interface [7] [8]. This approach is now well supported by theory [9], and blends can now be designed with a characteristic dispersed phase size [10, 11]. The compatibilizer usually stabilizes micrometer- to submicrometre-sized dispersions, and they have found applications in many of the compatiblized blends currently on the market. Unfortunately for many polymer pairs, it is very difficult to select the crucial polymeric compatibilizer.

In this study, the compatibilization of a crystalline polymer, polyamide-6 (PA-6) with an amorphous polymer, poly(methyl methacrylate) (PMMA), is investigated. This system was studied by Carone et al., and the authors found that the use of a diblock copolymer polyamide-*b*-poly(ethylene glycol) leads to a compatibilized blend. Wu et al. also studied a PMMA/PA-6 blend, formed by sequential polymerization of PMMA and ε-caprolactam, although the PMMA content was only varied from 0.5 to 10 wt%. The authors found that the PMMA component could act as heterogeneous nucleating agent for PA-6 [12]. In this study, we study the effect of two additives on a PMMA/PA-6 blend. Poly(styrene-*alt*-maleic anhydride) (SMA) seems a good candidate as compatibilizer, since it is compatible with PMMA, and the maleic anhydride function can react with the end groups of PA-6. On the other hand, PS is not miscible with PA-6, so the diblock copolymer poly(methyl methacrylate-*b*-styrene) (PMMA-*b*-PS) is not expected to act as a good compatibilizer for this blend.

Experimental section

Materials

Commercial PA-6 with molecular characteristics $M_n = 10{,}000$ g/mol was purchased from Aldrich. All monomers, solvents, and other reagents were purchased from Aldrich at the highest purity available and used for polymerization. Methyl methacrylate (MMA, 99%) and styrene (St, 99%) were filtered before using through an activated basic alumina (Brochmann I) column to remove radical inhibitors. PMMA was syntheses via reversible addition-fragmentation chain transfer (RAFT) polymerization, following a procedure from the literature ($\text{PMMA}_{\text{RAFT}}$), and via conventional free radical polymerization (PMMA_{FRP}). The thermally stable *S*-methoxycarbonyl phenymethyldithiobenzoate (MCPDB) was used as chain transfer agent to mediate the RAFT polymerization of MMA [13–15].

Blend preparation

Polyamide-6 and PMMA blends were mixed in a Thermo Electron Corporation co-rotating twin-screw extruder with length-to-diameter ratio of 40 in varying mass ratios. PA-6 was dried under high vacuum at 80 °C before extrusion. The temperature range along the screw was set to 210–240 °C, and the screw speed was 20 rpm. After extrusion, the blends were cooled to room temperature, before transformed into pellets.

Size exclusion chromatography

The number-average weight (M_n) and polydispersity index (PDI) were determined using size exclusion chromatography (SEC) equipped with a LC 1120 HPLC pump ((Polymer laboratories, UK), a MIDAS (type 830) auto sampler (Spark Holland, Netherlands), a differential refractive index (DRI) detector (Shodex, RI-101), a

Table 1 Molecular weight and PDI of the polymer considered in this study

	Samples	M_n	PDI
1	PA-6	10,000	–
2	PMMA-PS	46,600	1.77
3	PMMA(RAFT)	60,800	1.22
4	PMMA(FRP)	355,200	1.69
5	SMA(FRP)	59,970	1.15

5.0 μm bead-sized guard column (50 × 7.5 mm), and two PLgel 5.0 μm MIXED-C columns (300 × 7.5 mm) in series (Polymer laboratories, UK). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL min^{-1} at ambient temperature, and toluene was used as a flow marker. The SEC system was calibrated with polystyrene standards (Polymer laboratories, UK) with molecular weights ranging from 580 to 7,500,000 g/mol. The molecular weight and PDI of the samples considered in this study are given in Table 1.

Differential scanning calorimetry

The thermal properties of the initial materials and polymer blends were studied by differential scanning calorimetry (DSC) using a TA Instrument DSC 2010 thermal analyzer under a nitrogen atmosphere (200 $\text{cm}^3\ \text{min}^{-1}$). For measurement of the glass transition temperature (T_g), 10 mg samples were placed in aluminum pans and heated from 20 to 300 °C. The heating and cooling rate were set to 10 °C min^{-1}. An empty aluminum pan was used as a reference. The T_g value was determined from the onset, end and inflection of a step transition using the TA Instruments Thermal Advantage Universal Analysis software.

Scanning electron microscopy

The morphology of the blends was investigated using scanning electron microscopy (SEM) via a Jeol JSM-820 instrument. Extruded blends were made granular and gold-coated using a Bio-Rad SC500 diode sputter coating unit. SEM electron micrographs were recorded of the core region of the extrudate.

Results and discussion

Figure 1 shows SEM electron micrographs obtained from the various blends of interest to this study. When two immiscible polymers are extruded, the interfacial tension is of the same order of magnitude as the shear tension during processing. The mixing process starts by melting the two blend components, and the shear and elongational flow during processing give rise to threads and droplets. Although immiscible polymers, PMMA and PA-6 can interact via hydrogen bonding between the carbonyl group of PMMA and the amide group. In all blends, the PMMA component appears as particles in a PA-6 matrix. Figure 1b and c shows that an increase in $PMMA_{RAFT}$ content from 10 to 15% does not affect the size of the PMMA particles in the PA-6 matrix (ca. 2–5 μm). The addition of PMMA-*b*-PS and SMA as compatibilizers has a direct effect on the blend, by dramatically decreasing the size of the PMMA particles to less than 1.1 and 1.29 μm, respectively. Such a decrease in size is a clear indication of the better compatibilization of the PMMA component in the PA-6 matrix [4, 12]. The morphological differences are clear evidence of the better adhesion between PA-6 and the particles of PMMA. This better adhesion can be explained in the case of PMMA-*b*-PS by the location of the block copolymer at the interface between the two components of the blend, thus decreasing the particle size. Indeed, since PMMA and PS are not compatible, the block copolymer will form a PS layer at the interface between the PMMA and PA-6 phases. The dithiobenzoate moiety at the chain end of the PS block may then react with the terminal amine group on the PA-6 chains to form a thiol. The thiol end group could then react further with the amide bond of the PA-6 component via transesterification, to yield a covalent bond between the PS and PA-6, which would favor compatibilization. Although possible, this reaction would, however, be of very low yield. During the cooling process, the PA-6 phase crystallizes, leading to a further significant decrease in particle size. In the case of SMA, the anhydride side groups react with the amino end groups of PA-6, thus leading to the formation of a graft copolymer at the interface PMMA/PA-6, which also improves adhesion [16]. Figure 1f shows the size of PMMA particle (ca. 2–10 μm) for a PMMA component synthesized by conventional free radical polymerization. By comparing this image to Fig. 1b, one can clearly observe the effect of the molecular weight on the morphology of the PMMA domains. High molecular weight ($M_n = 355{,}200$ g/mol) with broad molecular weight distribution (PDI = 1.69) leads to larger particles than lower molecular weight PMMA ($M_n = 60{,}800$ g/mol) of narrower molecular weight distribution (PDI = 1.22) (particle size ca. 2–5 μm). An alternative explanation could be the reaction of the dithiobenzoate end group of the $PMMA_{RAFT}$ polymer with the amine end group of the PA-6 component during the extrusion process to form a thiol-terminated PMMA (PMMA-SH). This PMMA-SH could then react with the PA-6 backbone to form, in situ, PA-6-*b*-PMMA block copolymers, which would act as good compatibilizers for the blend. Although such side products are unlikely to be formed in large concentration, they may influence the structure of the blend. The introduction of a compatibilizer (SMA) in the blend PA-6/$PMMA_{FRP}$ clearly leads to smaller particles (ca. 1–5 μm), although they are larger than the PMMA particle from PMMA synthesized via RAFT, and of broader size distribution Scheme 1.

The thermal stability of the blends morphology was assessed. Figure 2 shows SEM electron micrographs of samples annealed under high vacuum at 160 °C for 2 h. In all samples, the annealing of the polymer blends resulted in the coalescence of the dispersed particles of PMMA. The sample without compatibilizer shows a narrower distribution of particle sizes by comparison to the same sample before annealing. The samples including compatibilizers show similar feature to the samples before annealing, although the PMMA particles in the blends made in the presence of PMMA-*b*-PS seem to have a broader size distribution after annealing. This demonstrates that the addition of compatibilizers prevents the coalescence of

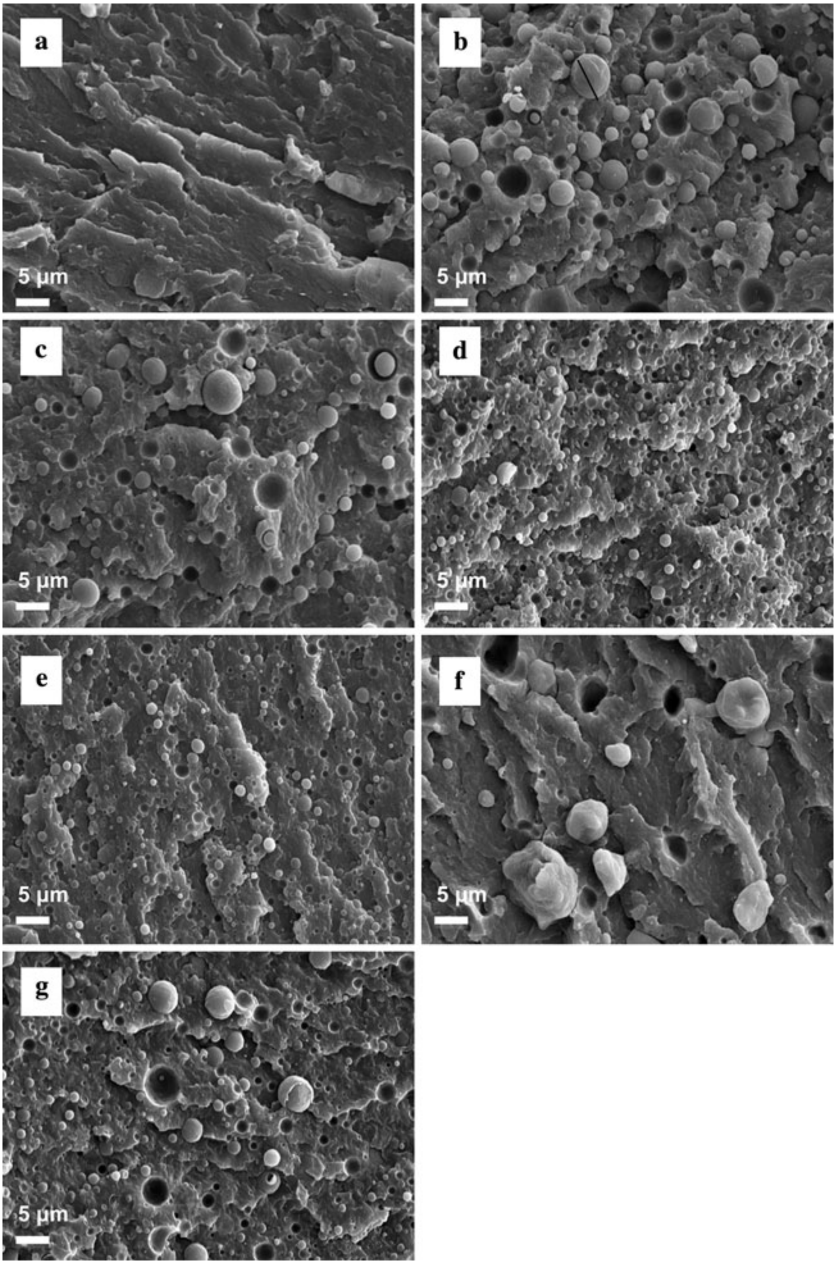
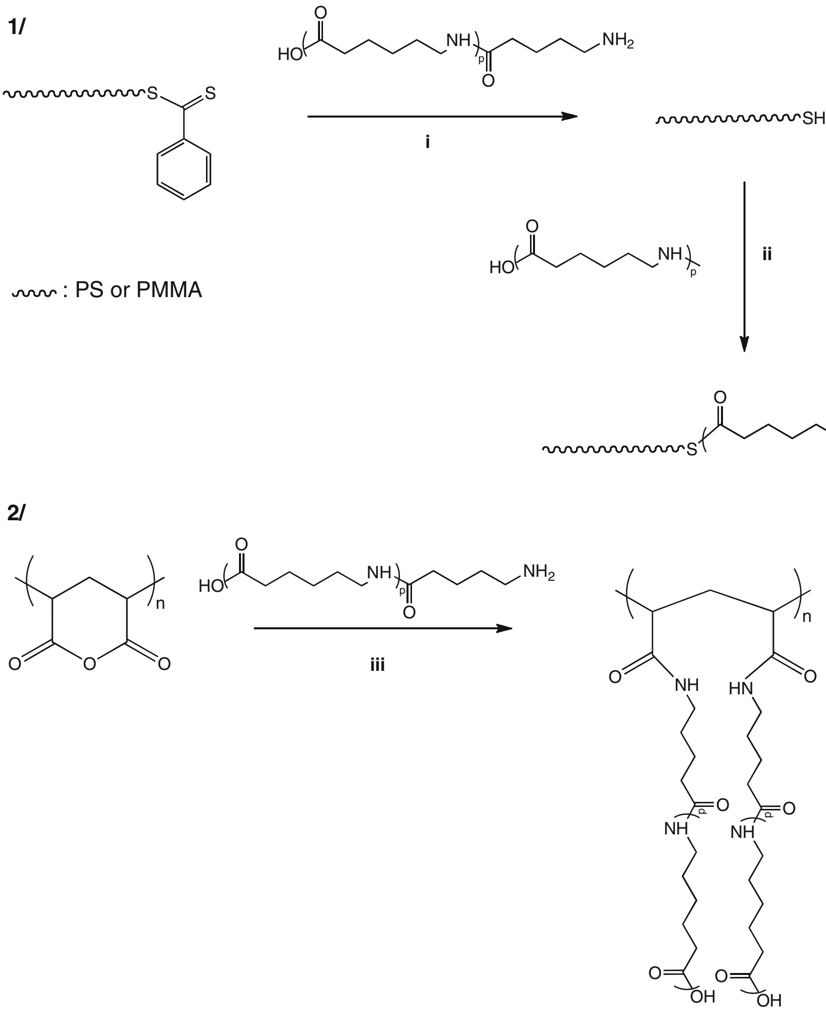


Fig. 1 SEM micrographs of PA-6 (**a**), blend PA-6/PMMA$_{\mathrm{RAFT}}$ in ratio 90/10 by weight (**b**), blend PA-6/PMMA$_{\mathrm{RAFT}}$ in ratio 85/15 by weight (**c**), blend PA-6/PMMA$_{\mathrm{RAFT}}$/PMMA-*b*-PS in ratio 85/15/5 by weight (**d**), blend PA-6/PMMA$_{\mathrm{RAFT}}$/SMA in ratio 85/15/5 by weight (**e**), blend PA-6/PMMA$_{\mathrm{FRP}}$ in ratio 90/10 by weight (**f**), and blend PA-6/PMMA$_{\mathrm{FRP}}$/SMA in ratio 85/15/5 by weight (**g**)



Scheme 1 Schematic of the potential chemical reactions during extrusion. *i* aminolysis of the dithioester end group of PS or PMMA in the presence of the amine end group of PA-6; *ii* reaction between a thiol-terminated PS or PMMA and PA-6; and *iii* reaction between the amine end group of PA-6 and the maleic anhydride repeating units

the PMMA particles and reduces the interfacial tension between the PA-6 and PMMA components of the blends.

The thermal profiles of the blends were also investigated. Figure 3 shows the thermograms of all the PA-6/PMMA blends used in this study, and all the blends clearly exhibit the melting temperature of the PA-6 component around 220 °C, and its glass transition temperature around 56 °C (See Table 2). The blend PA-6/PMMA$_{\mathrm{RAFT}}$ exhibits a wide endothermic peak around 125 °C which becomes more pronounced as the content in PMMA is increased (curves 2 and 3), thus suggesting it relates to the melting of the PMMA component. A similar peak is observed for

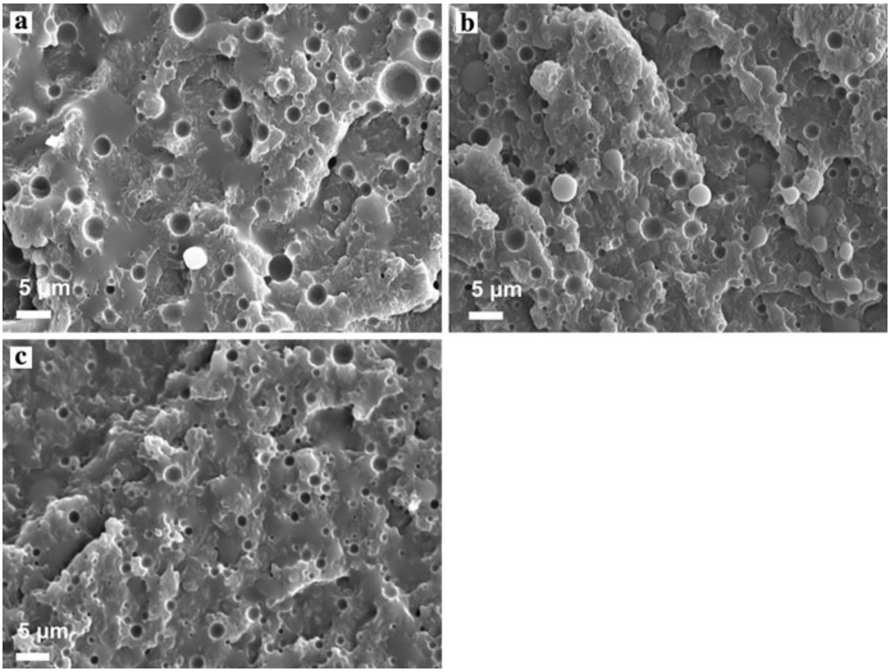


Fig. 2 SEM micrographs after thermal treatment at 160 °C for 2 h of blend PA-6/PMMA$_{RAFT}$ in ratio 90/10 by weight (**a**), blend PA-6/PMMA$_{RAFT}$/PMMA-*b*-PS in ratio 85/15/5 by weight (**b**), and blend PA-6/PMMA$_{RAFT}$/SMA in ratio 85/15/5 by weight (**c**)

PA-6/PMMA$_{FRP}$ at higher temperatures. Upon introduction of PMMA-*b*-PS and SMA, the endothermic peak from the melting of PMMA is not observed, thus demonstrating the good compatibilization of the blend. The endothermic peak corresponding to the melting of the PA-6 becomes narrower and more intense in the case of blends PA-6/PMMA$_{RAFT}$ with ratios 90/10 and 85/15 (Fig. 3, curves 2 and 3, respectively), which suggests the formation of more crystalline domains. This observation is in agreement with findings by other groups [12] who showed that the PMMA component favors the crystallization of PA-6. It is noteworthy that the crystalline domains of PA-6 seem better defined in the presence of PMMA$_{RAFT}$ than in the presence of PMMA$_{FRP}$ (Curves 2 and 6, respectively). The addition of a compatibilizer (curves 4 and 5) clearly affects the nucleating effect of PMMA on the crystallization of PA-6, since the endothermic peaks become broader and less intense.

Conclusion

The morphology of incompatible polymer blends of commercial PA-6 and PMMA synthesized via a RAFT polymerization and via conventional free radical polymerization was investigated in the presence of a compatibilizer, consisting of

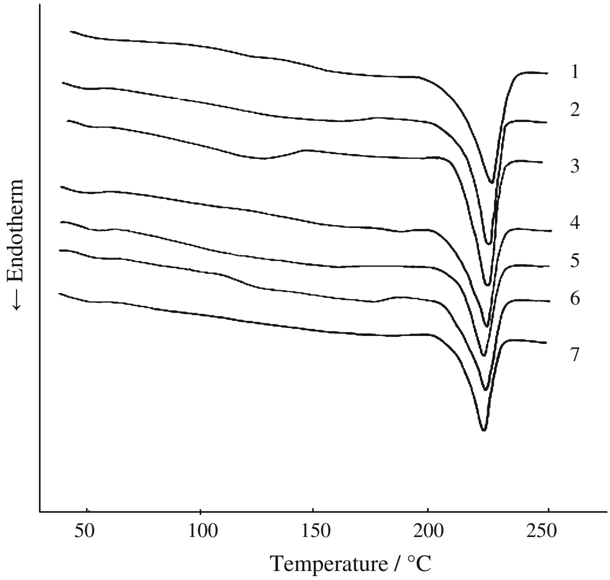


Fig. 3 DSC thermograms of PA-6 (*1*), blend PA-6/PMMA$_{\mathrm{RAFT}}$ in ratio 90/10 by weight (*2*) and 85/15 by weight (*3*), blend PA-6/PMMA$_{\mathrm{RAFT}}$/PMMA-*b*-PS in ratio 85/15/5 by weight (*4*), blend PA-6/PMMA$_{\mathrm{RAFT}}$/SMA in ratio 85/15/5 by weight (*5*), blend PA-6/PMMA$_{\mathrm{FRP}}$ in ratio 90/10 by weight (*6*), and blend PA-6/PMMA$_{\mathrm{FRP}}$/SMA in ratio 85/15/5 by weight (*7*)

Table 2 Glass transition temperature (T_g) and melting temperatures (T_m) of the blends investigated in this study

	Sample	T_g °C	T_m °C
1	PA-6	54.1	226.0
2	PA-6/PMMA$_{\mathrm{RAFT}}$ (90/10)	53.0	223.9
3	PA-6/PMMA$_{\mathrm{RAFT}}$ (85/15)	53.1	224.2
4	PA-6/PMMA$_{\mathrm{RAFT}}$/PMMA-*b*-PS (85/10/5)	53.3	224.4
5	PA-6/PMMA$_{\mathrm{RAFT}}$/SMA (85/10/5)	53.1	223.6
6	PA-6/PMMA$_{\mathrm{FRP}}$ (90/10)	53.2	223.0
7	PA-6/PMMA$_{\mathrm{FRP}}$/SMA (85/10/5)	53.0	223.9

either a random copolymer of styrene-maleic anhydride (SMA) or a diblock copolymer PMMA and polystyrene (PMMA-*b*-PS), also synthesized via a RAFT polymerization. SEM electron micrographs showed that the morphology of the polymer blends was changed considerably after the addition of the compatibilizer, and smaller and better dispersed particles of PMMA were observed in the PA-6 matrix. Thermal analyses also showed that the crystallization of the PA-6 component was influenced by both compatibilizers and the PMMA component.

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