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Thermal properties of nylon6/ABS polymer blends: Compatibilizer effect

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Nylon6/ABS binary blends are incompatible and need to be compatibilized to achieve better performance under impact tests. Poly(methyl methacrylate/maleic anhydride) (MMA-MA) is used in this work to compatibilize *in situ* nylon6/ABS immiscible blends. The MA functional groups, from MMA-MA copolymers, react with NH_2 groups giving as products nylon molecules grafted to MMA-MA molecules. Those molecular species locate in the nylon6/ABS blend interfacial region increasing the local adhesion. MMA-MA segments are completely miscible with the SAN rich phase from the ABS. The aim of this work is to study the effects of ABS and compatibilizing agent on the melting and crystallization of nylon6/ABS blends. This effect has been investigated by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). Incorporation of this compatibilizer and ABS showed little effect on the melting behavior of the PA6 crystalline phase, in general. DMTA analysis confirmed the system immiscibility and showed evidence of compatibility between the two phases, nylon6 and ABS, produced by MMA-MA copolymer presence. The nylon6/ABS blend morphology, observed by transmission electron microscopy (TEM), changes significantly by the addition of the MMA-MA compatibilizer. A better dispersion of ABS in the nylon6 phase is observed.

1. Introduction

Multiphase polymeric systems offer several advantages through the combination of attractive properties of each material or by reducing deficiencies in the single component materials. New polymers can be obtained by copolymerization or blending. The polymeric mixtures or polymer blends are more viable economically compared to copolymers and offer a diversity of possible routes to obtain materials with desirable properties [1]. The use of polymer blends to improve the impact strength of semicrystalline thermoplastics has attracted special attention and is an established toughening process. The toughening process increases the capacity to absorb energy before rupture [1]. Nylon6 (Ny6) is a semi-crystalline thermoplastic, which has strong chemical resistance to organic solvents, an adequate melt viscosity under processing conditions and an excellent mechanical performance for engineering end uses. On the other hand, Ny6 has as disadvantages very high sensitivity to notch propagation under impact test, high moisture sorption, poor dimensional stability, low heat distortion temperature and very low notched impact strength at sub-zero temperatures [2]. Blending it with another thermoplastic can prevent some of those Ny6 disadvantages. Acrylonitrile-butadiene-styrene (ABS) copolymers have been used to modify some of the Ny6 properties [3–16]. ABS is a thermoplastic, which has excellent impact strength at low temperatures. In addition it is less sensitive to notch propagation and it has lower cost than Ny6. The Ny6/ABS blends usually are incompatible; therefore it is necessary to add a compatibilizer to the blend to reach the desired properties. Nylons have functional end groups in their molecules, such as amines and carboxylic groups, which allow them to be compatibilized *in situ* under melt blending [17]. The reactive compatibilization for nylons blends frequently shows high efficiency [4, 18–20]. Compatibilized Ny6/ABS blends have shown excellent mechanical behavior, mouldability and dimensional stability [16]. Reactive *in situ* compatibilization for polymer blends is based on grafting of the compatibilizer molecules in the functionalized polymeric blend component molecules, which species stay in the interfacial region leading to better interfacial adhesion. The degree of grafting may be significantly high to modify some characteristics of the functionalized component in the polymer blend. Ny6 may have crystallization behavior modified by the compatibilizer grafting. The kinetics of crystallization of Ny6 has been modified as a result of grafting [6, 19–24]. This work examines the effects of ABS and MMA-MA copolymers on the melting and crystallization of Ny6.

2. Experimental

Table I summarizes the characteristics of the materials used in this study. The nylon 6 is a commercially available material. Prior to each processing step, all nylon-containing materials were vacuum dried in an oven for at least 24 h at 80°C to remove absorbed water. An emulsion-prepared ABS material was used as impact modifier, which contains 50 wt% rubber in the form of polydisperse particles typically in the range 0.18–0.20 μm diameter and a SAN matrix containing 25 wt% AN. Methyl methacrylate (MMA) and maleic anhydride (MA) co-monomers were supplied by Merck, Metacril, and Reidel-deHaen, respectively. The MMA-MA copolymer was synthesized with 3, 5, 10 and 20 wt% of MA by solution polymerization using dimethyl sulfoxide (DMSO) as solvent. The procedures for synthesizing these copolymers are described in detail elsewhere [1].

The Ny6/ABS (50/50 wt%) binary blends and Ny6/ABS/MMA-MA (47,5/47,5/5 wt%) ternary blends were prepared in a corotating twin-screw extruder. The procedures for melt processing, rheological, mechanical and morphology determination of the blends are given elsewhere [25].

Differential scanning calorimetry (DSC) was used to characterize the melting and the crystallization behavior of Ny6/ABS blends. Samples taken from moulded specimens were tested through a Modulated DSC from TA Instruments, model 2920. The samples were first heated room temperature up to 260°C and kept for 3 min before cooling down to room temperature. A second heating was used to observe the melting behavior of the Ny6/ABS blends. All heating and cooling steps were done at 10°C/min. At least two DSC tests were done for each sample.

Samples for the dynamic mechanical thermal analysis (DMTA) were prepared by Arburg Allrounder injection moulding process at 230°C, with a mould temperature of 50°C. The dynamic mechanical thermal analysis was conducted using a Polymer Laboratories, model Mk II, at 3°C/min and a frequency of 1 Hz.

3. Results and discussion

Semi-crystalline nylon 6 may have its melting and crystallization behavior changed by the presence of a second component in Ny6 polymer blends [26]. Any significant modification of Ny6 melting and/or crystallization behavior in the blend can lead to changes in properties of moulded parts. Those changes can become more significant when *in situ* reactive compatibilization is used for the blending. Ny6 molecular grafting, due to reactive compatibilization, may modify its kinetics of crystallization, which certainly would lead to different crystal dimensions and different degree of crystallinity compared to plain Ny6. Parameters such as heat of fusion (ΔH_m) and heat of crystallization (ΔH_c) were used to observe Ny6 melting and crystallization behavior in the blends with ABS compatibilized by MMA-MA. The degree of crystallinity (X_c), calculated from ΔH_m was also used observe melt blending and reactive compatibilization of Ny6.

Table II shows melting and crystallization characteristics for Ny6/MMA-MA blends obtained from injection-moulded parts, after melt blending. The first heating run shows that the melting temperature (T_{m1}) for the Ny6/MMA-MA blends is lower than for plain Ny6. However, the decrease in T_{m1} values for the blends are not so significant. That trend is similar for both change in the blend composition and the amount of MA in the MMA-MA copolymer. Depression in T_{m1} could be a result of miscibility between PA6 and grafted Ny6-g-MA-MMA molecules. The presence of MMA-MA in Ny6 blends also reduces the heat of fusion (ΔH_{m1}) for the first heating run. Blends containing 10% of

TABLE I Materials used in this study

Material	Description	Composition	Molecular weight (g/mole)	Haake[d] torque (N · m)	Source
Nylon 6	Ultramid B3	End-group content: NH_2, 43.2 μeq g^{-1}; COOH, 51.5 μeq g^{-1}	$M_n = 21000$[a]	1.07	Basf
ABS	SAN-grafted emulsion rubber	50% rubber 25% AN in SAN	$M_n = 40000$[b] $M_w = 110000$[b]	10.4	Nitriflex SA (Bayer)
MMA-MA	Poly(methyl methacrylate-co-maleic anhydride)	3 wt% MA 5 wt% MA	$M_n = 20900$[c] $M_w = 40400$[c]	0.1	Synthesized in laboratory
		10 wt% MA	$M_n = 15800$[c] $M_w = 37900$[c]	0.1	”
			$M_n = 13100$[c] $M_w = 26200$[c]	0.1	”

[a] Measurements were taken by end groups chemical analysis.

[b] Molecular weight of the SAN matrix grafted free, determined by SEC.

[c] Determined by SEC.

[d] Torque was taken at 240°C and 60 rev min^{-1} after 10 min.

TABLE II Melting and crystallization parameters for Ny6/MMA-MA blends

	First heating		Cooling		Second heating		D.C.
Samples (wt%)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_c (°C)	ΔH_c (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	X_c(%)
Ny6							
100	223.5	56.6	191.1	69.1	222.0	48.4	25.3
Ny6/MMA-MA (3%MA)							
95/5	222.9	55.7	190.1	63.1	221.2	61.9	32.4
90/10	221.9	53.6	189.4	61.1	220.8	59.7	31.3
80/20	221.1	55.7	189.9	59.8	219.5	59.8	31.3
Ny6/MMA-MA (5%MA)							
95/5	222.4	54.0	190.7	60.8	220.7	59.3	31.0
90/10	221.5	47.0	189.0	58.5	220.2	57.9	30.3
80/20	222.3	50.1	187.8	57.6	220.5	52.6	27.5

T_m: Melting temperature taken at the melt peak; T_c: Crystallization temperature taken at the crystallization peak; ΔH_m: Heat of fusion due to PA6 melting, measured through the melting peak; ΔH_c: Heat of crystallization due to PA6 crystallization, measured through the crystallization peak; X_c: Degree of crystallinity, taken from $\Delta H_{m2}/\Delta H_{mo}$; ΔH_{m2}: Heat of fusion for PA6 measured in the second heating; D.C.: Degree of crystallinity; ΔH_{mo}: Heat of fusion for PA6, 100% crystalline, 191 J/g $^{(27)}$.

MMA-MA have their heat of fusion reduced by large amounts, compared to Ny6. That reduction in ΔH_{m1} becomes more significant when MMA-MA has a larger concentration of MA. The grafting reaction efficiency between the Ny6 and MMA-MA molecules, which occurs during the blending and the moulding steps, depends on the relative amounts of amine end groups in nylon and maleic anhydride groups in the MMA-MA copolymer. The balance between the concentrations of both chemical groups may lead to a higher degree of grafting. Therefore, the maximum of grafting may be reached for a particular combination of MMA-MA concentration in the blend and MA weight percentage in the copolymer. The Ny6 crystallization temperature, T_c, was not significantly affected by the presence of MMA-MA in the blends. For most blend compositions the T_c was few degrees lower than for Ny6. The reduction in T_c was significant for higher amounts of MMA-MA and MA, simultaneously, in the Ny6/MMA-MA blends. On the other hand, the heat of crystallization, ΔH_c, showed a large decrease for most of blend compositions. It seems that Ny6/MMA-MA blends produce less exothermic heat on crystallization than does Ny6. It may be concluded that the grafted molecular species work as nuclei for Ny6 crystallization. That hypothesis is confirmed by the behaviour of the heat of fusion for the blends in the second heating run. As observed in Table II, the heat of fusion for Ny6 crystallized in the DSC at 10°C/min (ΔH_{m2}) is lower than that for Ny6 crystallized at the moulding conditions. On the other hand, the ΔH_{m2} values for the blends were found well above the ones observed in the first heating run. As a consequence, the degree of crystallinity (X_c) has significantly increased compared to plain Ny6. The Ny6-g-MMA-MA grafted molecules may have allowed the Ny6 molecules to crystallize more easily thereby leading to larger amount of crystals or may have led to more perfect crystals. The melting temperature (T_{m2}) has not shown any evidence for that hypothesis. Its values were found lower than for Ny6. The explanations for the observed phenomenon are not clear at the moment and they need to be further investigated.

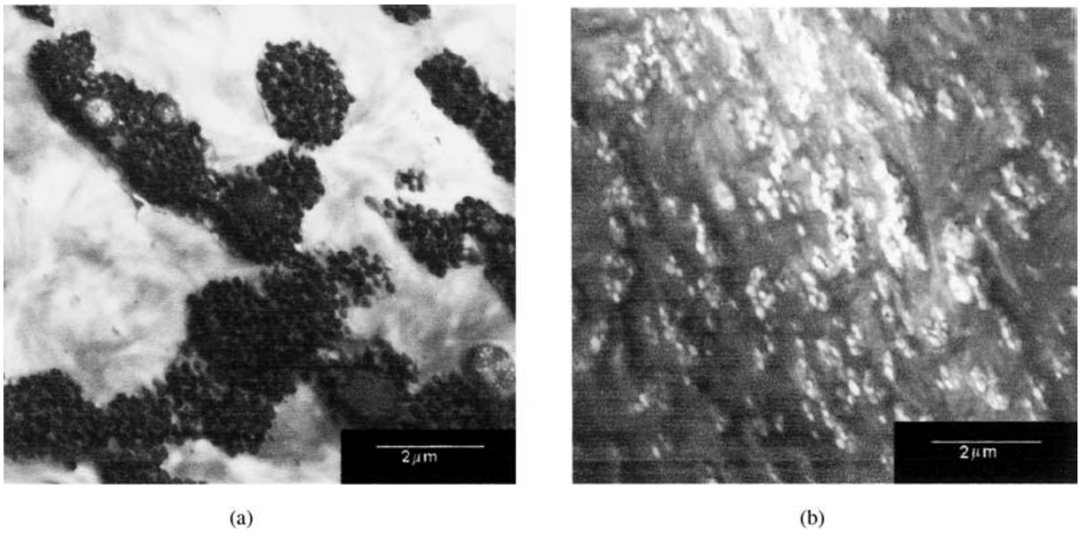
Table III shows melting and crystallization parameters for Ny6/ABS binary blends and Ny6/ABS/

TABLE III Melting and crystallization parameters for Ny6/ABS/MMA-MA blends

	First heating		Cooling		Second heating		D.C.
Samples (wt%)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_c (°C)	ΔH_c (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	X_c(%)
Ny6							
100	223.5	56.6	191.1	69.1	222.0	48.4	25.3
Ny6/ABS							
70/30	222.5	57.1	189.3	59.7	221.1	61.0	31.9
50/50	222.0	51.0	187.2	55.3	220.7	56.1	29.4
Ny6/ABS/MMA-MA (3%MA)							
66,5/28,5/5	221.8	51.0	187.1	54.5	221.2	49.8	26.0
68,25/29,25/2,5	222.0	60.5	187.9	64.1	221.1	62.0	32.4
47,5/47,5/5	221.1	63.9	185.4	63.2	220.0	64.2	33.6
Ny6/ABS/MMA-MA (5%MA)							
66,5/28,5/5	221.7	55.0	187.6	61.2	221.0	57.1	30.0
68,25/29,25/2,5	221.8	55.9	187.5	59.5	220.8	57.5	30.1
47,5/47,5/5	221.0	54.6	186.6	52.3	219.8	50.4	26.4

T_m: Melting temperature taken at the melt peak; T_c: Crystallization temperature taken at the crystallization peak; ΔH_m: Heat of fusion due to PA6 melting, measured through the melting peak; ΔH_c: Heat of crystallization due to PA6 crystallization, measured through the crystallization peak; X_c: Degree of crystallinity, taken from $\Delta H_{m2}/\Delta H_{mo}$; ΔH_{m2}: Heat of fusion for PA6 measured in the second heating; D.C.: Degree of crystallinity; ΔH_{mo}: Heat of fusion for PA6, 100% crystalline, 191 J/g $^{(27)}$.

MMA-MA ternary blends. The addition of the ABS component to the PA6 blends has not changed the melting temperature (T_{m1}) in the first heating run. The heat of fusion (ΔH_{m1}) for the first heating has been affected only for larger amounts of ABS in the binary blends. During cooling, the crystallization temperature (T_c) has shown a decrease as ABS is blended with Ny6. Therefore, there is evidence that ABS interferes in the crystallization of Ny6. The heat of crystallization (ΔH_c) for the binary blends has also shown a reduction compared to Ny6, which, may be a result of a crystallization depression. Hage *et al.* [28] has shown similar behavior for PBT/ABS binary blends, where ABS has significantly reduced the crystallization temperature and the heat of crystallization. One of the reasons for the similar phenomenon is a thermal degradation of PBT due to residual chemical species from ABS copolymerization such as acid base emulsion agent and specific catalyst. Melting for the Ny6/ABS binary blends crystallized from the cooling conditions in the DSC has shown no significant changes in the melting temperature (T_{m2}). However, an increase in the heat of fusion (ΔH_{m2}) of Ny6 could be observed due to the presence of ABS in the blends. Differences between the heat of crystallization (ΔH_c), under cooling, and the heat of fusion (ΔH_{m2}), in subsequent melting, may be due to the recrystallization of Ny6 in the second heating run. Nylons usually have high crystallization rate above the glass transition temperature (T_g). Therefore, any heating above T_g would allow further crystallization. Thus, ABS has shown strong effects on the crystallization of Ny6 in Ny6/ABS binary blends. Bhardwaj *et al.* [26] have observed a decrease in the melting temperature of Ny6 in Ny6/ABS binary blends as the ABS concentration was increased. There was also a depression in the crystallization temperature and the heat of crystallization as function of the ABS concentration. Therefore, MMA-MA copolymers can strongly affect Ny6 melting and crystallization in Ny6/MMA-MA binary blends. Its presence in Ny6/ABS/MMA-MA ternary blends also modifies those state transitions. Table III shows some melting and crystallization parameters for Ny6/ABS/MMA-MA ternary blends. For lower amounts of MA in the copolymer, i.e., 3%, an increase in ΔH_{m1} compared to plain Ny6 and binary blends can be observed. The difference is more significant for higher amounts of ABS in the ternary blends. As MMA-MA is added to the blend, the crystallization temperature (T_c) decreases, thereby showing a delay in the PA6 crystallization process. Addition of MMA-MA to the Ny6/ABS binary blends improved the heat of crystallization (ΔH_c), however, it still kept the value for Ny6 crystallized as pure. MMA-MA also improves the heat of fusion (ΔH_{m2}), which leads to higher degree of crystallinity (X_c). Jannasch *et al.* [29] have observed that addition of reactive compatibilizer may affect nylons crystallization. Compatibilization of Ny6/PS blends made by styrene-maleic anhydride (SMA) copolymers strongly changed the crystallization parameters. It was shown for Ny6/PS binary blends that the interface region works as a nucleation site for Ny6. This nucleating effect was observed by polarized light optical microscopy. As SMA was added to the Ny6/PS blend the nucleating improvement gradually disappeared and the number of nucleating sites in the interface was reduced. The reactive compatibilizer, i.e., SMA, for Ny6/PS blends has decreased its crystallization rate. Fig. 1 shows transmission electron microscope (TEM) photographs of binary Ny6/ABS and ternary Ny6/ABS blends with MMA-MA copolymer. Dark regions in Fig. 1a represent the unsaturated rubber phase in ABS that has been stained with OsO_4. Dark regions in Fig. 1b represent the Ny6 phase that has been stained with phosphotungstic acid (PTA). In Fig. 1a, nylon6 clearly forms a continous phase while the ABS forms large domains with some tendency for interconnectivity. The poor rubber particle distribution in these blends is without doubt a major factor responsible for the poor mechanical properties observed [25]. In Fig. 1b, the ABS dispersed phase forms uniformly



(a) (b)

Figure 1 TEM photomicrographs of blends: (a) 70/30 Ny6/ABS blend; (b) 66,5/28,5/% Ny6/ABS/MMA-MA blends containing 3%MA. The unsaturated rubber phase in ABS has been stained with OsO_4 (a). The nylon phase has been stained with PTA (b).

TABLE IV Glass transition temperature and secondary transitions of Ny6/ABS/MMA-MA blends, measured by DMTA

	ABS			PA6	
Samples (wt%) Ny6/ABS/MMA-MA	T_g (°C) rich phase in PB	T_1 (°C) rich phase in PB	T_g (°C) rich phase in SAN	T_2 (°C)	T_g (°C)
100/0/0	–	–	–	−54.7	57.9
0/100/0	−65.9	−40.6	112.0	–	–
70/30/0	−69.5	−46.6	110.5	102.1	55.9
66,5/28,5/5 5%MA	−69.6	−45.9	108.7	102.8	55.4
66,5/28,5/5 3%MA	−69.9	−47.3	110.1	104.3	56.7
68,25/29,25/2,5 5%MA	−68.5	−45.8	112.2	103.5	54.3
68,25/29,25/2,5 3%MA	−69.2	−47.3	111.5	105.0	52.3
50/50/0	−69.2	−45.1	110.8	103.6	56.0
47,5/47,5/5 5%MA	−68.5	−45.1	105.7	–	47.2
47,5/47,5/5 3%MA	−69.2	−45.2	107.3	–	52.3

T_1: Secondary transition temperature of the rich phase in PB of the ABS; T_2: Secondary transition temperature of the neat PA6 and of the rich phase in SAN, to some blends.

diminished particles in the Ny6 matrix. The ABS domains become clearly more efficiently dispersed. The presence of the MMA-MA compatibilizer appears to restructure the ABS domains. The presence of another component in a semicrystalline polymer may increase or decrease the nuclei formation rate depending on the melt viscosity at the crystallization temperature and on the energy barrier to form stable nuclei for further crystal growth [28]. It seems in this case that the melt viscosity is sufficient to overcome the interfacial energy due to the presence of the ABS component in the polymer blend.

Table IV gives the results obtained for the blends and the neat components, Ny6 and ABS, by DMTA. The data from Table IV show two transitions for Ny6, at −54.7 and 57.9°C. The first can be the β relaxation attributed to the mobility of the attraction between H of one molecular chain and C=O groups on the adjacent chain. The other transition can be the T_g (α relaxation), according to the literature [30]. For the ABS were observed three transitions. The first at −65.9°C is attributed the T_g of the polybutadiene (PB) rich phase; the second at −40.6°C can be attributed to a secondary transition and the third at 112.0°C can be the T_g of the SAN rich phase. The T_gs in the blends, in general, are not affected when compared with the neat components, i.e., two peaks in tan δ mean that the system is immiscible at all the studied compositions. Fig. 2 shows tan δ curves for Ny6/ABS/MMA-MA blends. T_g and T_1 temperatures, of the PB rich phase in the ABS, are not affected significantly. The presence of the MMA-MA copolymer in the blend did not affect significantly the T_gs of the SAN phase. DSC results showed that MMA-MA copolymer can contribute to the crystallization process of the Ny6, i.e., these data indicate that the compatibility among the two phases is improved by the presence of the MMA-MA.

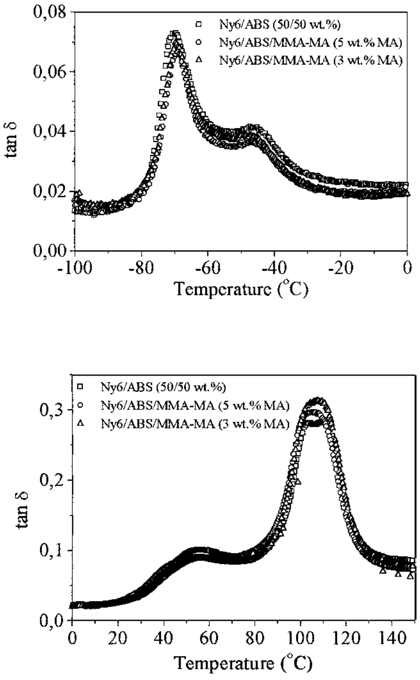


Figure 2 Tan δ curves for Ny6/ABS/MMA-MA blends. In (a) interval of temperature of −100 to 0°C; in (b) interval of temperature of 0 to 150°C.

4. Conclusions

The effect of ABS and MMA-MA compatibilizer on the melting and crystallization behavior of Ny6 was studied. Presence of ABS copolymers in Ny6 blends strongly affects the Ny6 crystallization by modifying the heat of crystallization and decreasing the crystallization temperature. Addition of MMA-MA copolymers, as compatibilizer, in the Ny6/ABS blends also affects Ny6 crystallization parameters. Both components increase the degree of crystallinity of Ny6 for samples crystallized in the DSC. DMTA confirmed the system imiscibility and determined the T_gs of the two phases in the polymer blend. No significant change in the T_gs was observed. On the other hand, evidence of the compatibility among the two phases, Ny6 and ABS, was observed in the presence of MMA-MA. This is in agreement with the morphology observed for Ny6/ABS/MMA-MA blends through reducing the dispersed phase size.

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