Compatibilization of PA6/PPO Blend with Carboxylated Poly(styrene) Compounds

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ABSTRACT: PA6/PPO 70/30 blends were reactively compatibilized using carboxylated polystyrene (PS) and poly(styrene-*block*-4-methylstyrene) with various degrees of carboxylation. The high carboxylation of PS (up to about 50%) caused a decrease of dispersed PPO dimensions with a simultaneous deterioration of properties, especially of toughness and elongation. The best mechanical behavior was found for PS with 1% degree of carboxylation and for neat PS. On the other hand, degrees of carboxylation higher than 50% caused an increase in particle size. This was most significant for block copolymers, where a marked change in size and shape occurred, from spherical particles of about 1 μm in size to large, elongated particles about 50 μm long or a similar rough cocontinuous structure. The deteriorated mechanical behavior is tentatively explained by unsuitable properties of the reactively formed compatibilizer and thus of the interface. The enhanced rigidity of highly carboxylated poly(4-methylstyrene) chains (and its product of grafting with PA6), causing its decreased emulsification ability together with the expected rigid interface, which probably suppresses breakup of the PPO phase, may be responsible for the increase of the dispersed PPO dimensions found. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2273–2280, 2001

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INTRODUCTION

Blends of polyamide 6 (PA6) with poly(phenylene oxide) (PPO) are systems that successfully combine the advantages of both components. Because of their immiscibility, proper compatibilization is necessary to achieve their high performance.

Except for the addition of suitable copolymers (e.g., PA-*g*-PPO,[1–3]) reactive compatibilization using the amino groups of PA6 is applied more frequently. Campbell et al.[4] used maleic anhydride(MA)-functionalized PPO for *in situ* generation of PA-PPO copolymer (also by MA addition directly during blend preparation), whereas tetrafunctional epoxy monomer[5] and poly[methylene(phenylene isocyanate)][6] are reported to react with both PA6 and PPO. Mostly, polymers or copolymers miscible or compatible with PPO bearing functional groups capable of reacting with PA are used. Examples are poly(styrene-*co*-maleic anhydride),[7–9] poly(styrene-*co*-glycidyl methacrylate),[10] partly hydrolyzed styrene-*tert*-butyl acrylate diblock copolymer[11] and styrene-acrylic acid random copolymer.[12] In the last case, best results have been obtained with high acrylic contents (35 mol %); miscibility of the copolymers with PPO was not evaluated. This result is in contradiction

Table I   Structures of Compatibilizers Block Copolymers of Poly(4-methylstyrene) (PMS) with Poly(styrene) (PS)

A	PMS(54%)-*b*-PS(46%), 71% of PMS carboxylated
B	PMS(54%)-*b*-PS(46%), 14% of PMS carboxylated
C	PMS(14%)-*b*-PS(86%), 53% of PMS carboxylated
D	PMS(90%)-*b*-PS(10%), PMS with high degree of carboxylation
E	Shellvis SV 50, hydrogenated poly[isoprene(47%)-*block*-styrene(53%)], $\sim$ 80% of PS carboxylated
PS(1–60%)	Polystyrene ($M_n \sim$ 150,000), with degree of carboxylation 1, 2.5, 7, 50, and 60%

with SMA compatibilization, where the best efficiency was found for SMA miscible with PPO, i.e., those having MA contents below 8%. This discrepancy may be tentatively explained by different reactivity of MA in comparison with acrylic acid. Especially in the case of compatibilizers containing less reactive groups,[12] the situation is not quite clear.

Except for miscibility evaluation also the relation between phase structure and toughness was not shown. Therefore, we focused on the influence of (1) compatibilizer reactivity, using PS with broad range of carboxylation and (2) compatibilizer composition using poly(styrene-*block*-4-methylstyrene) copolymers with different block lengths and different degrees of carboxylation of the poly(4-methylstyrene) (PMS) block.

EXPERIMENTAL

Materials

Noryl EN 110, a commercial PPO resin (PPOC) containing about 40% of impact-modified PS (see below for DSC results and morphology), and PPO resin 646-111, a neat PPO (PPON), were obtained from GE Plastics (USA). Polyamide 6 (PA6; Ultramid B4, M_n = 33,000) was obtained from BASF (Germany). Polystyrene (PS; homopolymer, M_w = 200,000) was obtained from Kaučuk (Czech Republic). The compositions of compatibilizers are shown in Table I.

Poly(styrene-*block*-4-methylstyrene) was prepared by anionic copolymerization in tetrahydrofuran (THF) at −78°C, using benzylpotassium as initiator. The weight content of individual monomers in the block copolymer was ascertained by ^{1}H–NMR.

The above-mentioned copolymers and PS were carboxylated as follows.[13] The block copolymer was selectively methylated only at 4-methyl groups using phenylpotassium (prepared *in situ*

from 2-ethylhexyllithium and potassium *tert*-pentoxide in benzene) as methylating agent. The methylation of polystyrene in the ring was accomplished by 2-ethylhexylpotassium, made of 2-ethylhexyllithium and potassium *tert*-pentoxide in cyclohexane.

The resulting polymethylated intermediates were then quenched with solid CO_2 in THF, thus generating polycarboxylated products. The various degrees of carboxylation were achieved using different methylation ratios. The content of carboxylic groups in the (co)polymer was checked by ^{1}H–NMR from the content of the corresponding methoxycarbonyl groups after transformation of the COOH groups by diazomethane.

Blend Preparation and Testing

Prior to mixing, PA6 was dried for at least 12 h at 85°C in a vacuum oven. The blends were prepared by mixing the components in the W50EH chamber of a Brabender Plasti-Corder at 260°C and 50 rpm for 10 min. The material removed from the mixing chamber was immediately molded at 260°C in a laboratory press to form 1-mm-thick plates.

Tensile tests were carried out at 22°C. Dog bone–shaped specimens with a gauge length of 30 mm were tested at a crosshead speed of 15 mm/min. The stress at break σ_b (experimental error ± 2–4%) and corresponding strain ϵ_b (experimental error ± 5–10%) were evaluated. The storage shear modulus G' was measured using a free oscillating torsional pendulum at a frequency of 1 Hz (experimental error < ±2%).

Tensile impact strength a_t was measured using unnotched samples and a hammer with energy of 4 J (experimental error ± 10–15%).

For all mechanical tests, dry samples (i.e., stored in a desiccator) were used.

Morphological observations were performed using a scanning electron microscope (SEM) and cryofractured samples. For better visualization of
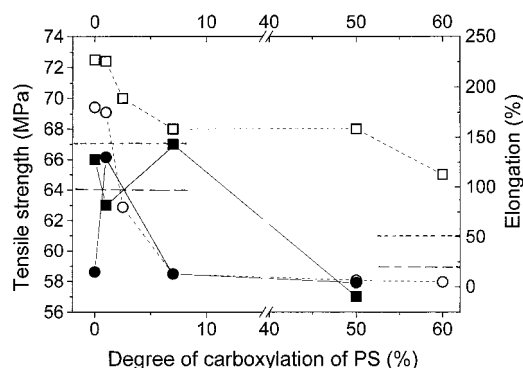
Figure 1 Dependence of tensile strength (■, □) and elongation-at-break (●, ○) on the degree of PS carboxylation for PA6/PPO 70/30 blend with 2.5% PS (●, ■) PPOC, (○, □) PPON [dashed lines show values of blend without compatibilizer: PPON (- - -), PPOC (——)].

the PPO phase, the samples were etched in toluene for 5 min. For transmission electron microscopy (TEM), microtomed and OsO_4-stained samples were used.

RESULTS AND DISCUSSION

Influence of PS Carboxylation on the Blend Properties

From Figures 1 and 2, it is clear that all mechanical parameters under study reached their highest values by the addition of 2.5% of unmodified PS or PS with 1% degree of carboxylation only. On addition of PS with higher degrees of carboxylation, the parameters deteriorate, particularly toughness and elongation. A simultaneous decrease in the particle size [lowest dimensions for PS (7%)] indicates the increased compatibilizing ability of PS with higher degrees of functionalization.

Considering the influence of carboxylation of PS on its miscibility with PPO, PS (7%) was already only partly miscible with PPO (according to DSC measurements). Therefore, a very low particle size with immiscible PS (50%) [smaller than that of miscible PS (2.5%)] is of interest. On the other hand, the toughness parameter value was lower than that for an uncompatibilized blend already for the PS (7%) blend; for the PS (50%) blend, only the strength slightly exceeded the value for the uncompatibilized blend. With PS (60%), the structure is comparable (although slightly rougher) to that of neat PS, for example, but with greatly inferior properties. The last find-

ing, i.e., a comparable phase structure for the blends with the best and worst mechanical behavior, virtually excludes explanation of this particle size/properties relationship by a possible subcritical particle size of the dispersed phase known for systems containing dispersed elastomers. Other aspects seem more important than the (average) particle size, probably properties of the interface and a possible influence of particle size distribution (or a harmful effect of dispersed micelles of the *in situ*–generated compatibilizer).

The lower effectivity of compatibilization by polymers with high degrees of carboxylation is in agreement with the finding that a higher functionality can cause formation of so-called overgrafted (PSgPA) copolymers,[14] which can easily leave the interfacial area. By also taking into account a finer phase structure with higher-functionality polymers in our case, rather unfavorable properties of the interface created by a highly grafted product could be considered (additionally, the results in Ref. 14 were found for the SMA/PA12 system; the reactivity of MA is higher than that of the carboxylic group). On the other hand, Koriyama et al.[15] show that an increase in interfacial thickness (by interfacial reaction) enhances the toughness of the interface for a PA/PSU combination. A comparison with our results is limited, especially taking into account (except for other systems) that the testing of bilayer specimens is very dissimilar to the impact testing (with a considerably higher velocity) of a system with inclusions. Jo and Kim[12] (see above) found the highest strength for the PA6/PPO 70/30 blend
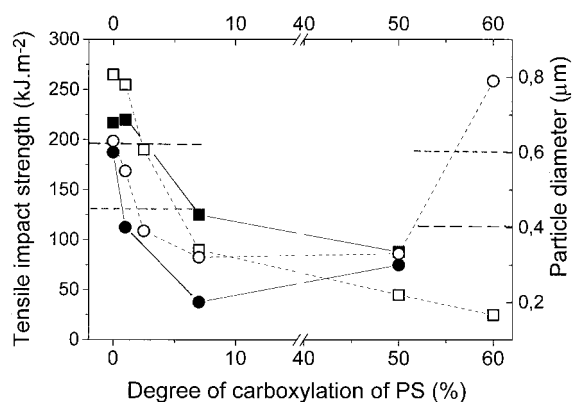

Figure 2 Dependence of tensile impact strength (■, □) and diameter of dispersed PPO particles (●, ○) on the degree of PS carboxylation for PA6/PPO 70/30 blend with 2.5% PS (●, ■) PPOC, (○, □) PPON [dashed lines show values for blend without compatibilizer: PPON (- - -), PPOC (——)].

Table II   Dependence of PA6/PPO 70/30 Blend Properties on the Amount of Added PS

	PS Content (%)	σ_b (MPa)	ε_b (%)	a_t (kJ m^{-2})	Particle Diameter (μm)
PPON	0	67	50	130	0.60
	1.5	70	70	220	0.55
	2.5	72.5	180	270	0.6
	5	68.5	40	190	0.6
	10	67.5	75	185	0.45
PPOC	0	64	15	195	0.4
	2.5	66	15	215	0.6
	5	62	10	125	0.7
	10	59	5.5	80	0.8

with the compatibilizer (styrene–AA copolymer) containing 35% of acrylic acid. Although this result seems to be in contradiction with our finding, taking into account an almost insignificant decrease in strength with enhanced degree of carboxylation (Fig. 2) in our case and the absence of toughness testing in Ref. 12, the discrepancy need not be very striking. The difference found can be the result not only of a different (higher) reactivity of carboxylated PS compared with that of styrene–acrylic acid random copolymer[12] but also the rather different PA6 and PPO types used.

Findings similar to our results, that is, enhanced interfacial adhesion and smaller size of dispersed particles resulting from reactive compatibilization that also does not cause enhancement of toughness and ductility, are reported in the literature.[16–18] These are only tentatively explained, for example, by the effect of a compatibilizer on matrix properties (less probable in our case because of its low content) or by low toughness of the compatibilizer (and thus of the interface) formed.[17] Generally, data from both our studies and the literature indicate that a more complete explanation of all aspects of reactive compatibilization (of two rigid polymers) still requires more investigation, particularly an understanding of the properties of the interface (the influence of interfacial parameters on the blend behavior) in a real system.

In Figures 1 and 2, a similar influence of the degree of PS carboxylation on the PA/PPOC behavior (especially on toughness and particle size) to that on PPON blend can be seen.

In view of the above-noted finding concerning the best mechanical behavior of both PPON and PPOC blends on addition of neat PS, its concentration dependence was studied. The PS used had

a relatively high molecular weight, showing higher efficiency compared to that of lower molecular weight types.[19] Table II shows that the optimum concentration is 2.5%, followed by a slight decrease of strength and, more significantly, of toughness, even though the particle size also slightly decreased (with 10% PS), apparently as a consequence of a lower viscosity of dispersed PPO. It is noteworthy that properties of the blend with the highest polydispersity (with the highest standard deviation of average diameter, data not shown), that is, a blend with 1.5% PS, are better than the properties of blends with both 5 and 10% PS.

On the other hand, the differences in the PPO particle size are not very significant, especially compared to that of the above-mentioned blends with different carboxylation degrees of PS. Moreover, the addition of miscible PS should practically not change properties of the interface of PA6/(PPO/PS) blend,[20] compared to those of PA6/PPON. Thus, for the observed change in mechanical properties, other factors, such as the change of PPO properties resulting from PS (having an optimum at 2.5% PS), should be responsible. Unfortunately, observation of the influence of small amounts of PS on PPO properties is practically impossible because of a too-high processing temperature (the decrease in T_g is still insufficient).

A similar improvement of mechanical properties by added PS was also found for the PA6/PPOC blend, that is, for a blend already containing a certain amount (about 40%) of impact-modified PS in the PPO phase. The TEM in Figure 3(e) shows typical morphology of PS toughened with styrene–butadiene copolymers[21]; because the presence of elastomer was not indicated by DSC or by thermomechanical analysis, its content
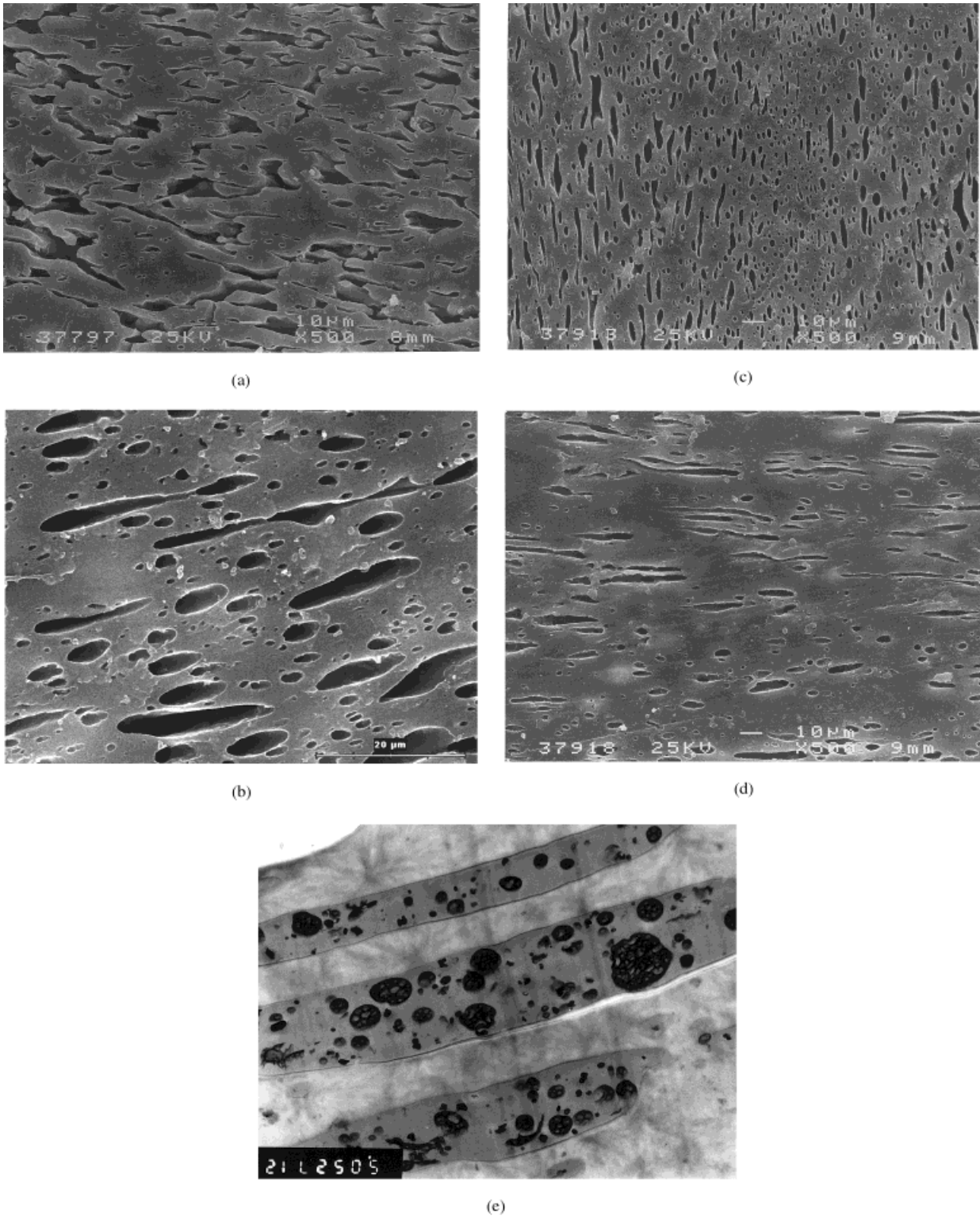
Figure 3 Phase structure of PA6/PPOC 70/30 blends with different compatibilizers: (a) 5% A; (b) 3% D; (c) 4.5% E; (d) 5% A, 80/20 blend; (e) 5% A, TEM observation.

Table III Dependence of PA6/PPOC 70/30 Blend Properties on the Structure of Compatibilizer

Compatibilizer		σ_m (MPa)	ε_b (MPa)	a_t (kJ m^{-2})	G (MPa)	Diameter (μm)
Type	Content (%)					
—	—	64	5.6	196	875	0.33
A	5	26	1.6	18	920	Length 50, width 10
A[a]	5	50	3.5	21	988	Length 50, width 10
B	2.5	62.5	29	138	950	0.42
B	5	67.7	33	153	865	0.3
C	5	65	7	138	988	0.33
D	2	56	4.1	44	990	1.1
D	3	60	4.3	60	955	1.20
E	4.5	42	3	47	950	Length 20, width 5
B[b]	2.8	68.5	71	135	920	0.35
C[b]	5	67.5	33	80	977	0.17

[a] 80/20 composition.
[b] PPON blend.

should be below about 5%, which is the resolution of these methods. In this case, the best mechanical properties were also found with a 2.5% PS addition, whereas 10% of added PS causes a significant deterioration in mechanical properties, especially in toughness. Of interest is that a similar trend in the dependence on the PS content was also found for PPON (see above), that is, for a system with a significantly lower (total) PS content. Therefore, the role of the added PS, simultaneously with PA6, seems to be more complex. The better properties of PPOC blend without added PS compared to those of PPON seem to be the result of PS already present in PPOC.

Compatibilization by Carboxylated Diblock Copolymers

Table I shows the structures of the poly(styrene-*block*-4-methylstyrene)-based compatibilizers of varied composition (block length) and/or the degree of poly(4-methylstyrene) block carboxylation used in this study.

From the results in Table III it is clear that the addition of these compounds to PPOC blends predominantly causes deterioration only of mechanical properties. The best results (at least slightly enhanced strength and reduced particle size) were found for copolymer B with a relatively low degree of carboxylation (14%). This is in agreement with the trend found for carboxylated PS (Figs. 1 and 2), although the efficiency of these copolymers is significantly lower; the lowered size of dispersed PPO particles and enhanced strength

were accompanied by decreased toughness (similarly to blends compatibilized with higher-carboxylated PS). Unfortunately, an analogous copolymer with a lower degree of functionalization was not available. Only a relatively lesser deterioration of properties and increase in the particle size was found for C (compared with those of B) with a relatively long PS block, but with an apparently predominating negative influence of high-carboxylated PMS. With PPON, even addition of 2.8% of B caused a certain compatibilizing effect (especially compared to that in PPOC blends) with a more significant particle size reduction and also with toughness greater than that for the uncompatibilized blend, but still lower than that for systems with addition of either neat PS or carboxylated PS (Tables II and III and Figs. 1 and 2). On the other hand, the properties of PPON blend with C are inferior to those of PPOC blend, in spite of the smallest particle size found (Table III).

Of interest is the quite unusual influence of A, D, and E types on the PPOC blend behavior; in addition to significant deterioration of strength and toughness, larger dimensions of dispersed particle and change of shape were also found (Fig. 3). This effect was most significant for 5% of A, where the partly interconnected (cocontinuous) structure with PPO domains of about 50 μm length and about 10 μm width was found. Larger elongated particles (not interconnected) were also found for the 80/20 blend [Fig. 3(d)], which supports the ability of the copolymer used to enlarge the dispersed phase size. At the same time, the
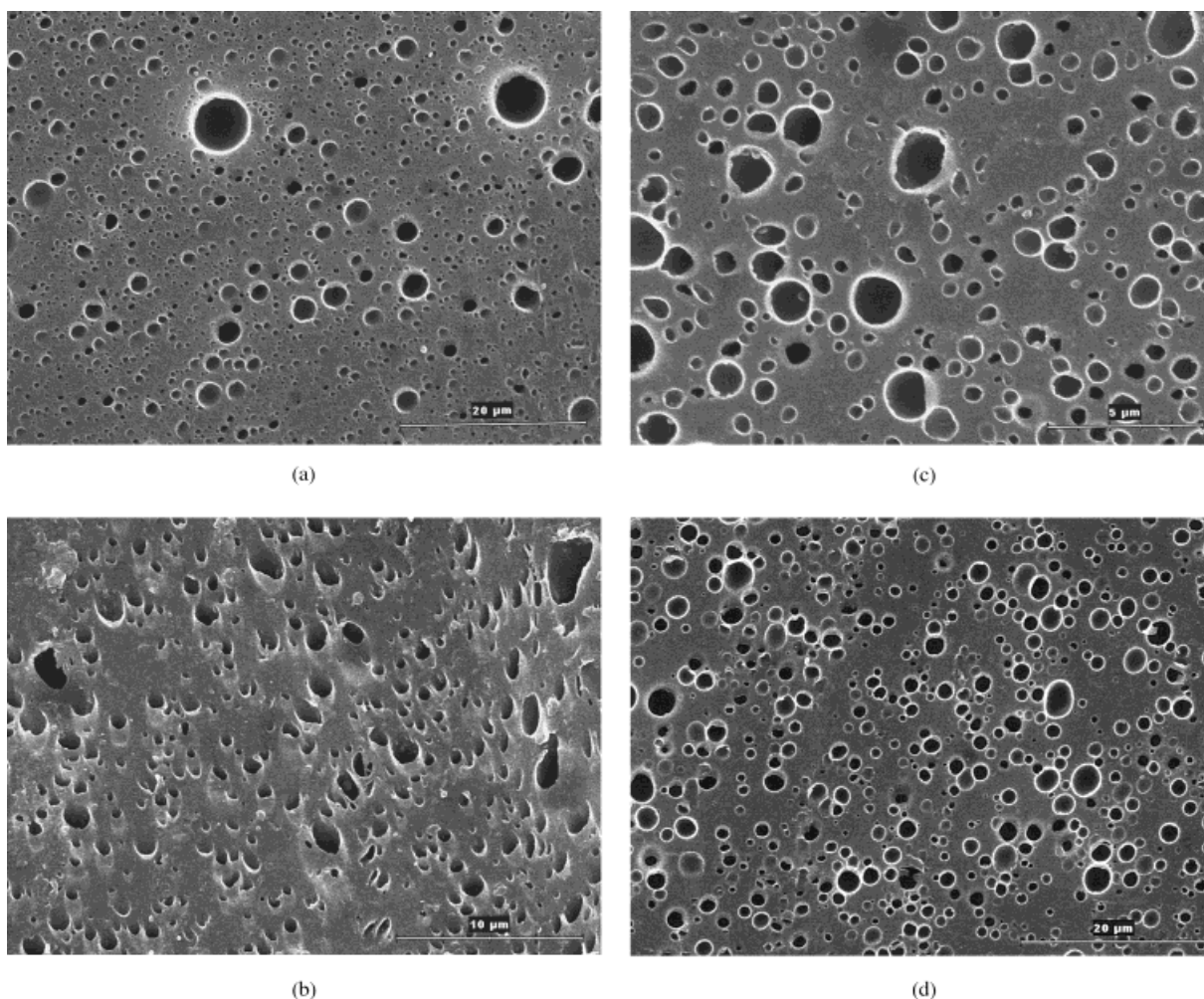
Figure 4 Phase structure of PA6/PPON 70/30 blends: (a) without compatibilizer; (b) 2.5% PS; (c) 2.5% PS(1); (d) 2.5% PS(60).

structure of large dispersed particles observed by TEM (showing the presence of impact-modified PS in PPOC; see above) was identical with the morphology of unblended PPOC. Therefore, these large inclusions most probably contain PPOC only (i.e., without dispersed PA6 matrix particles). The corresponding mechanical properties (Table III) are the lowest found; the rough structure is undoubtedly disadvantageous with respect to the mechanical behavior. This effect is most probably combined with the tendency found earlier for blends containing carboxylated PS, that is, the negative influence of enhanced carboxylation on mechanical properties (Fig. 2), even without significant enlargement of the dispersed phase size [Fig. 4(d)].

Very similar results were found by Takeda et al.[22] for PA6/various SAN blends compatibilized

with SMA with a different MA content. Whereas SMA2 and 6% MA gave dispersed SAN (in 75/25 blend) particles up to the about 3 μm size, with SMA13 the particles were found to be enlarged and more complex in shape (close to cocontinuous structure with a size up to 10 μm). Dedecker and Groeninckx[23] reported a shift of the cocontinuity range to a lower minority phase content together with its narrowing. On the contrary, Cho et al.[24] found, for a PA/SAN29, fair compatibilization using SMA28. A certain similarity is also shown by comparison of monofunctional (PA6) and difunctional (PA66) polyamides with dispersed SEBS-MA. The larger and more complexly shaped particles with the PA66 matrix are explained by the greater functionality of PA66, leading to crosslinking-type effects (probably supported by a relatively low intensity of mixing in the single-screw extruder applied). More important

is a finding that the compatibilizer with a more rigid chain has a lower emulsification capacity.[25] Moreover, the negative influence of possibly enhanced viscosity of the dispersed phase[26] by these copolymers can be of importance; just the localization of the compatibilizer in the PPO phase may be supported by the PS block. The explanation of this effect (why reactive compatibilizer may even lead to enlargement of the phase structure) and the difference between random and diblock copolymers needs further investigation. Probably, the unfavorable properties of high-carboxylated compatibilizer (lower emulsification capacity of more rigid chains of the compatibilizer) together with the more rigid (and immobile) interface created can suppress breakup of the PPO phase, an outcome that can be supported by a possible improved fixing of the compatibilizer at the interface resulting from the PS block (compared to that of the above-noted carboxylated PS); thus, an investigation of its localization also seems to be of importance.

CONCLUSIONS

Compatibilization of PA6/PPO with functionalized PS shows that increasing the degree of carboxylation of PS leads to a decrease in particle size and also to inferior mechanical properties. Except for PS with the lowest carboxylation, the best results were also obtained by addition of neat PS. Addition of PS together with PA6 also caused a slight enhancement of properties for commercial PPOC that already contained PS.

Evaluation of the phase structure showed significantly different properties for blends with comparable particle dimensions. Therefore, it can be concluded that their properties are predominantly determined by the properties of interface and/or by possible influencing of behavior of both phases by added compatibilizer (if dispersed within them, especially for neat PS).

Application of PS–carboxylated PMS block copolymers primarily caused a deterioration of blend properties. A pronounced enlargement of dispersed PPO particles was found, resulting from a high degree of carboxylation, from rather submicron spheres to either elongated particles about 50 μm long or a similar rough cocontinuous structure. Explanation of this interesting effect needs further investigation.

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