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Properties of compatibilized nylon 6/ABS blends
Part II. Effects of compatibilizer type and processing history

R.A. Kudva, H. Keskkula, D.R. Paul*

Department of Chemical Engineering and Texas Materials Institute, University of Texas at Austin, Austin, TX 78712, USA

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Abstract

The effects of processing history on the morphological, rheological, and mechanical behavior of blends of nylon 6 and acrylonitrile–butadiene–styrene (ABS) using an imidized acrylic (IA) polymer and a styrene/acrylonitrile/maleic anhydride (SANMA) terpolymer as compatibilizing agents have been investigated. Both compatibilizers yield blends that are super tough at room temperature; however, there are distinct differences in their effects on low temperature impact properties. For blends containing the IA polymer and a 1:1 ratio of nylon 6 to ABS, the low-temperature ductility compromises multiple extrusion steps. In general, the ductile-to-brittle transition temperature of blends containing high IA contents increase more rapidly with the number of extrusions than at lower IA contents. High IA content blends exhibited significant changes in morphology with increased number of extrusion steps; some of the ABS domains became larger, leading to a poorer dispersion of rubber particles. The ductile-to-brittle transition temperature is relatively insensitive to the number of extrusions for blends with less than 1 wt.% IA content or a higher ratio of nylon 6 to ABS. The morphology and low-temperature toughness of blends containing the SANMA terpolymer were generally unaffected by the number of extrusion passes during melt processing. The differences in low temperature toughness with respect to the processing history appear to stem from differences in the reactive nature of these two types of compatibilizers. Blends containing the IA polymer developed higher melt viscosities than blends containing the SANMA polymer (particularly at higher IA contents), since the nylon 6/IA reaction appears to continue with increasing processing time, whereas the nylon 6/SANMA reaction does not. Potential causes for these fundamental differences in blend rheology are considered in terms of the reactive functionality of the IA versus SANMA compatibilizer. When issues of processability, regrind, and recycling are considered, the SANMA material is a more attractive compatibilizer than the IA polymer, particularly at higher compatibilizer contents. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Nylon; ABS; Imidized acrylic polymer

1. Introduction

Interest in blends of polyamides with ABS stems from the possibility of combining the desirable characteristics of both of these materials. However, simple blends of polyamides and ABS generally exhibit poor mechanical properties and often require the use of a compatibilizing agent. Several approaches to the reactive compatibilization of nylon/ABS blends have been reported in the recent literature [1–14]. The most common compatibilization strategy has been to incorporate a functional polymer that is capable of reacting with the amine end groups of the polyamide and is miscible with the SAN phase of ABS. The previous article [15] has demonstrated that the mechanical properties of nylon 6/ABS blends is influenced by the ABS type and ratio of nylon 6 to ABS when an imidized acrylic (IA) polymer is used as a compatibilizing agent. It was also briefly shown that the amount of compatibilizer did not affect the room temperature toughness of these blends to a significant degree, but did influence the low temperature toughness and processability characteristics.

The previous article focused on blends compatibilized by an IA polymer and a fixed processing protocol (a single extrusion step prior to injection molding). The current study compares the effectiveness of this IA polymer to a styrene/acrylonitrile/maleic anhydride (SANMA) terpolymer for compatibilizing nylon 6/ABS blends over a range of compatibilizer contents. Patents and articles have described the use of such SANMA terpolymers as compatibilizers for polyamide/ABS systems [3–5]. This study will investigate in detail the effects of processing history (through the use of multiple extrusions) on the impact properties of these blends. Understanding the influence of multiple extrusion passes on blend performance is of

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* Corresponding author. Tel.: + 1-512-471-5238; fax: + 1-512-471-0542.

E-mail address: paul@che.utexas.edu (D.R. Paul)

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Table 1
Materials used in this study

Designation used here	Supplier designation	Composition	Molecular weight (g mol^{-1})	Brabender torque[a] (N m^{-1})	Izod impact strength[b] (J m^{-1})	Source
ABS	Starex	45% rubber, 25% AN in SAN	$\bar{M}_n = 35\ 000^c$, $\bar{M}_w = 90\ 000$	20.1	432	Cheil Industries
Nylon 6	Capron 8207F[d]	End-group content: NH_2 = 47.9 μeq g^{-1}, COOH = 43.0 μeq g^{-1}	$\bar{M}_n = 22\ 000$	7.3	50	Allied Signal
SAN	Tyril 1000	25% AN	$\bar{M}_n = 7\ ,000$, $\bar{M}_w = 152\ 000$	6.5	30	Dow Chemical
IA	EXL 4140	55.7% methyl glutarimide, 41.0% methyl methacrylate, 2.18% methacrylic acid, 1.08% glutaric anhyrdide	$\bar{M}_w = 95\ 000$	9.8	30	Rohm and Haas
SANMA	—	65.7% styrene, 33.0% acrylonitrile, 1.3 % maleic anhydride	$\bar{M}_n = 56\ 600$, $\bar{M}_w = 119\ 400$	7.8	15	Bayer

[a] Values taken at 240°C and 60 rev min^{-1} after 10 min.
[b] Room temperature notched Izod impact.
[c] Molecular weight is for free SAN.
[d] The designation of this material has recently been changed to B73WP.

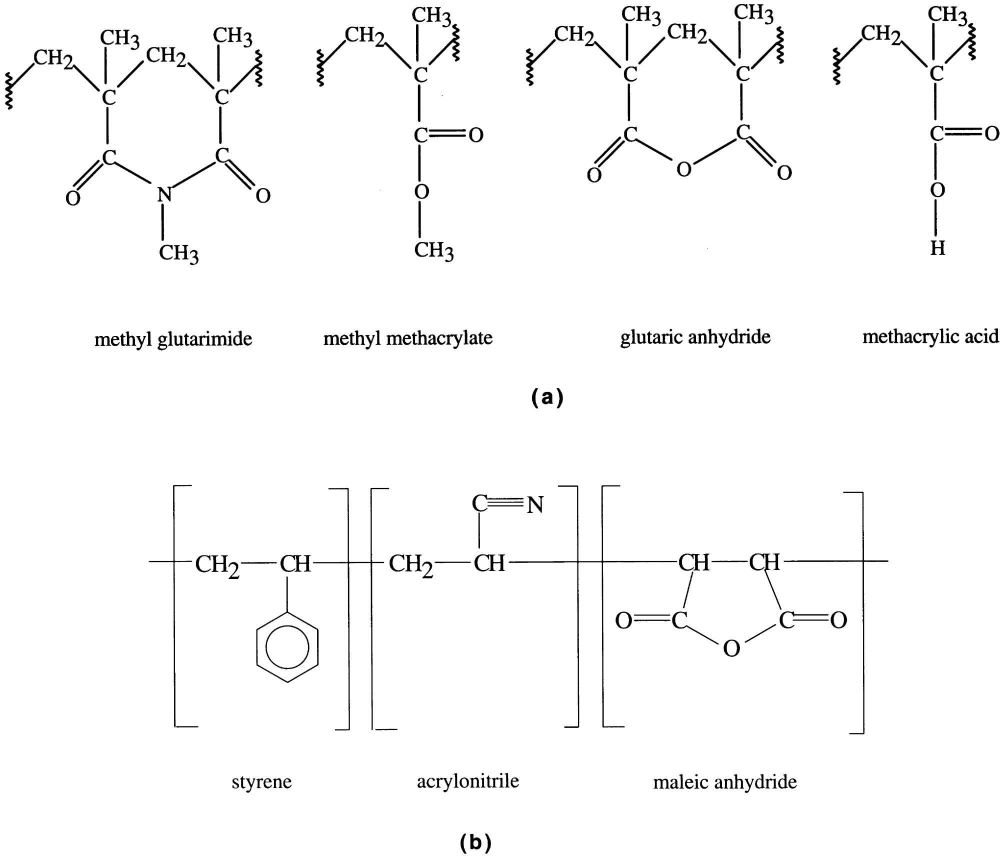


Fig. 1. Repeat units of (a) IA polymer and (b) SANMA terpolymer.

significant practical importance. The scrap or waste from a molding or extrusion process (referred to as regrind) is often returned to the process for reuse [16]. In addition, recycling involves subjecting the material to more than one processing cycle. Thus, it is of key importance to develop materials, which can retain their performance when subjected to multiple processing steps or long processing histories.

This article will show that the low temperature toughness of nylon 6/ABS blends compatibilized with an IA polymer can be severely compromised by multiple extrusions; whereas, analogous blends based on the SANMA terpolymer are generally unaffected by the same processing protocols. Potential causes for the differences in mechanical behavior among these compatibilized blends are examined in terms of the functionality of the two compatibilizers.

2. Experimental

Table 1 summarizes the characteristics of the materials used in this study. The ABS material used here is an emulsion-made SAN graft concentrate containing 45 wt.% butadiene rubber in the form of nearly monodisperse particles in the range of 0.3 μm in diameter. This material was designated as ABS-45-a in the previous article and will be referred to as “ABS” here. The nylon 6 is a commercially available material designated as Capron 8207F ($\bar{M}_n = 22\,000$) used in the previous study. A SAN material with an AN content typical of commercial ABS materials was used in limited miscibility studies. An IA polymer and a SANMA terpolymer were used as compatibilizers (see Table 1). The chemical structure of these materials and their potential reactions with nylon 6 are described in the following section.

Blends were prepared by simultaneous extrusion of all components in a Killion single screw extruder ($L/D = 30$, 2.54 cm diameter) at 240°C using a screw speed of 40 rev min^{-1}. Several blends were subjected to multiple extrusions. The extruded pellets were injection molded into standard 0.318 cm thick Izod bars (ASTM D256) using an Arburg Allrounder injection molding machine. Prior to every processing step, all polyamide-containing materials were dried in a vacuum oven for at least 16 h at 80°C. Notched Izod impact measurements were made using a TMI pendulum-type impact tester equipped with an insulated chamber for heating and cooling the specimens. For rheological characterization, the various polymers were tested in a Brabender torque rheometer outfitted with a

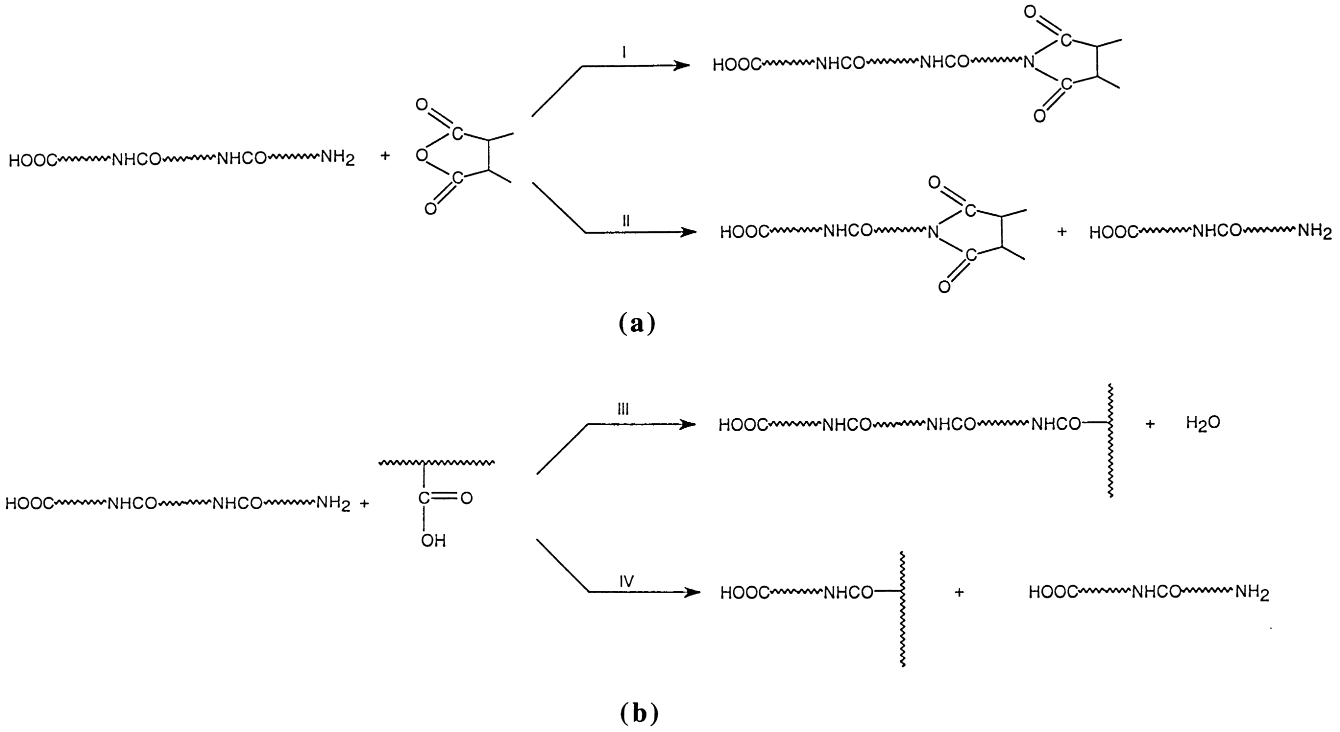


Fig. 2. Potential chemical reactions between nylon 6 and (a) anhydride and (b) acid functionalities.

50 cm^3 mixing head and standard rotors, operated at 240°C and 60 rev min^{-1}.

Blend morphologies were determined using a JEOL 200CX transmission electron microscope (TEM) operating at an accelerating voltage of 120 kV. Ultrathin section (15–20 nm) were cut from Izod bars perpendicular to the flow direction under cryogenic conditions (−45°C) using a Reichert–Jung Ultracut E microtome. Various staining techniques were employed to obtain phase contrast in the TEM. To stain the polyamide phase, the microtomed sections were exposed to a 2% aqueous solution of phosphotungstic acid (PTA). In other cases, osmium tetroxide (OsO_4) was used to stain the unsaturated rubber phase in ABS. This involved exposing the sections to a 2% aqueous solution of OsO_4 for at least 12 h.

3. Comparison of compatibilizers

In this section, the two compatibilizers are compared in terms of their structures, miscibility characteristics, and their potential reactions with nylon 6.

3.1. Chemical structure

Fig. 1(a) shows the chemical repeat units of the IA polymer, which was synthesized by reactive extrusion of PMMA with methyl amine [17,18]. A detailed description of the reactions that occur to form these four repeat units is provided elsewhere. The major components comprising this polymer are methyl glutarimide (55.7 wt.%) and methyl methacrylate (41 wt.%). Small amounts of glutaric anhydride (1.08 wt.%) and methacrylic acid (2.18 wt.%) groups also exist, both of which can potentially react with nylon 6, as will be discussed later in this section. The structure of the SANMA terpolymer is shown in Fig. 1(b). This material contains 33 wt.% AN and 1.3 wt.% maleic anhydride. It is important to note that these compatibilizers not only contain different amounts of anhydride functionality, but also different types of anhydrides; each of these factors may play a role in the properties of their blends with nylon 6.

3.2. Miscibility with SAN

The miscibility of these compatibilizers with the SAN phase of ABS is an important consideration in their use for blends with nylon 6. Miscibility of these blends with SAN containing 25 wt.% AN is of particular interest, since the current ABS material contains a SAN matrix of this composition. Previous work has established that the IA polymer is fully miscible with a SAN material of this composition (designated as SAN25 in Table 1), as judged by DSC [19].

The literature suggests that SAN materials of molecular weight typical of commercial products are generally immiscible with one another when their AN contents differ by more than 5 wt.% [20,21]. Thus, it would not be surprising that the SAN25 material and the SANMA compatibilizer

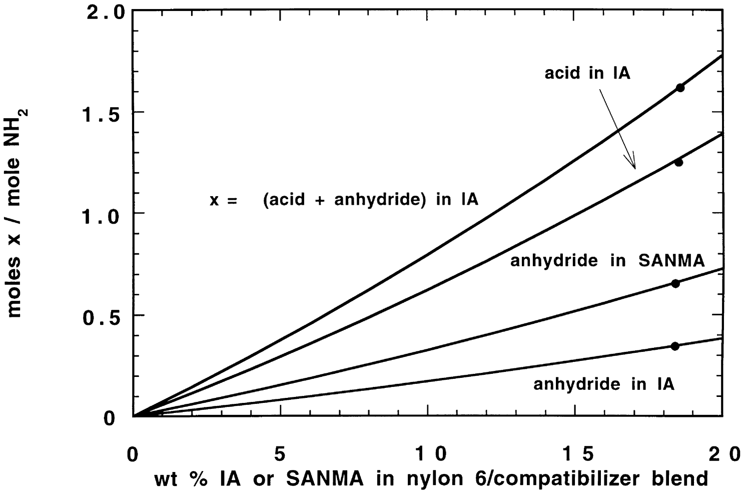


Fig. 3. Molar ratio of the number of compatibililizer functional groups to amine end groups of nylon 6 versus wt.% compatibilizer in a binary nylon 6/compatibilizer blend. The circles (●) correspond to a 45/10 ratio of nylon 6/compatibilizer, which represents the highest amount of compatibilizer used in blends in this study.

(which contains 33 wt.% AN) are not fully miscible. Limited experiments confirm this expectation. The T_gs of these materials are too close to resolve by thermal analysis; thus, visual observations were used to assess miscibility. Films of SAN25, SANMA, and a 50/50 blend of these components were cast from THF and allowed to dry for three days in a vented hood. To ensure solvent removal, the samples were slowly heated under vacuum to 150°C and annealed for several days. Thereafter, samples were removed and inspected visually. The SAN25 and SANMA films were clear, whereas the 50/50 blend appeared somewhat hazy, although not cloudy. This result suggests that the SAN and SANMA materials are indeed not completely miscible; however, there may be some partial miscibility.

3.3. Potential reactions with nylon 6

There are several potential reactions that can occur between nylon 6 and each of the compatibilizers during melt processing. Fig. 2(a) illustrates the reactions between nylon 6 and the anhydride functionalities of these compatibilizers. In this schematic, maleic anhydride (a 5-member ring) is shown; however, similar reactions may be written for the 6-membered glutaric anhydride. The literature suggests that the predominant reaction in systems containing nylon 6 and anhydride-functional polymers is between the anhydride and the amine end groups of nylon 6 (reaction I), which occurs very rapidly and results in the formation of an imide [22]. It is also possible that the anhydride could undergo interchange reactions with the amide linkages of nylon 6 (reaction II), thus forming an imide and a shorter polyamide chain. However, studies by Legras et al. have indicated that the amine/anhydride reaction proceeds much faster than the amide/anhydride reaction in polyamide-based systems [23,24]. Kinetic data from the literature tend to support this claim [25,26].

The existence of the methacrylic acid functionality in the IA polymer leads to even more reaction possibilities with nylon 6 for this compatibilizer (see Fig. 2(b)), although these reactions are expected to be quite slow relative to mechanism I shown in Fig. 2(a). Methacrylic acid can potentially react with the amine end group of nylon 6 (reaction III), or undergo interchange reactions with an amide linkage (reaction IV) [27], thereby forming a shorter polyamide chain and a polyamide-IA graft. The abundance of amide linkages along the polyamide chain, compared to the single amine chain end, certainly favors the acidolysis reaction.

In the blends examined here, it is also possible that post-condensation reactions between the acid and amine end groups of nylon 6 could occur to form longer polyamide chains; however, evidence shown later suggests that these reactions are negligible under the current melt processing conditions.

Some perspective can be gained by comparing the functional group stoichiometry for these compatibilizers in polyamide blends. Fig. 3 shows the molar ratio of functional groups on the compatibilizer (methacrylic acid or glutaric anhydride in the case of IA, maleic anhydride in the case of SANMA) to amine end groups of nylon 6 as a function of the amount of compatibilizer in binary nylon 6/compatibilizer blends. The circles on the plot denote a 45/10 ratio of nylon 6 to compatibilizer, which corresponds to the highest amount of compatibilizer used in the nylon 6/ABS/compatibilizer blends described later. For a fixed compatibilizer content, the amount of anhydride functionality for SANMA is greater than for IA. Considering only the reactions of nylon 6 with the anhydrides, one would expect a greater degree of reaction for SANMA, assuming no intrinsic

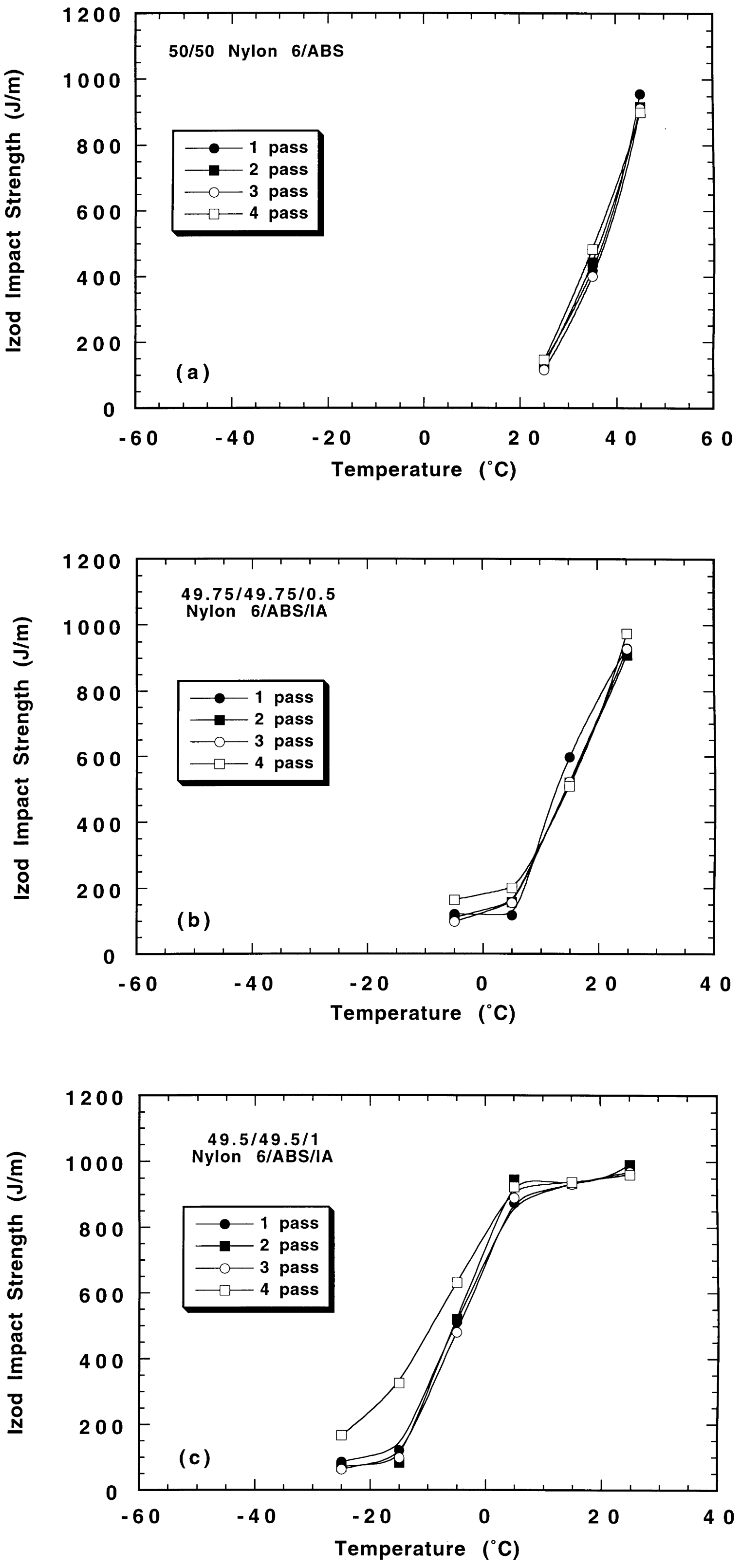


Fig. 4. Effect of temperature on the Izod impact strength of nylon 6/ABS and nylon 6/ABS/IA blends as a function of the number of extrusion passes (● = 1, ■ = 2, ○ = 3 , □ = 4 extrusions). The blends contain a 1:1 ratio of nylon 6:ABS and the following amounts of IA: (a) 0%, (b) 0.5%, (c) 1%, (d) 2%, (e) 5%, (f) 10%.

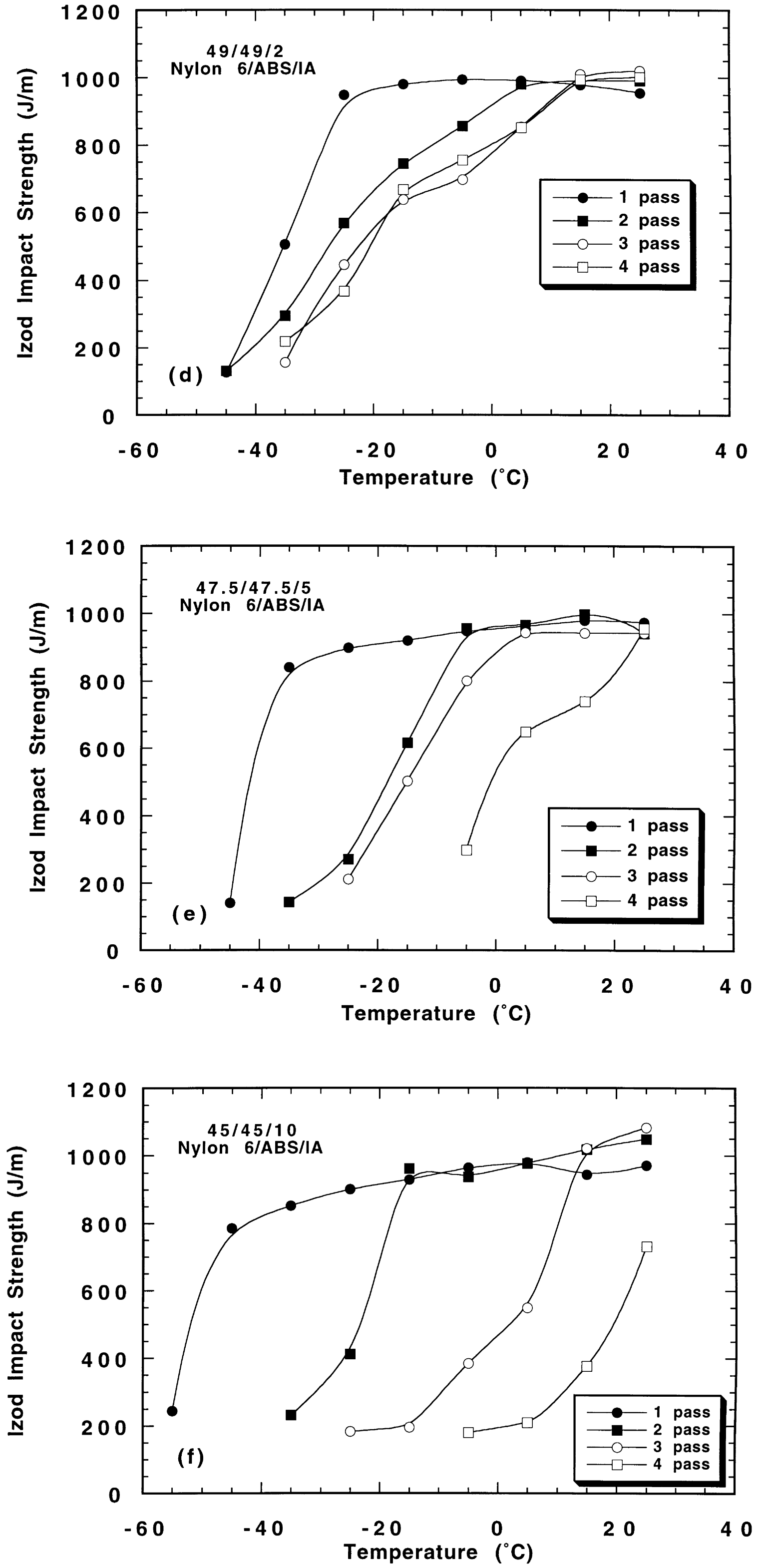


Fig. 4. (*continued*)

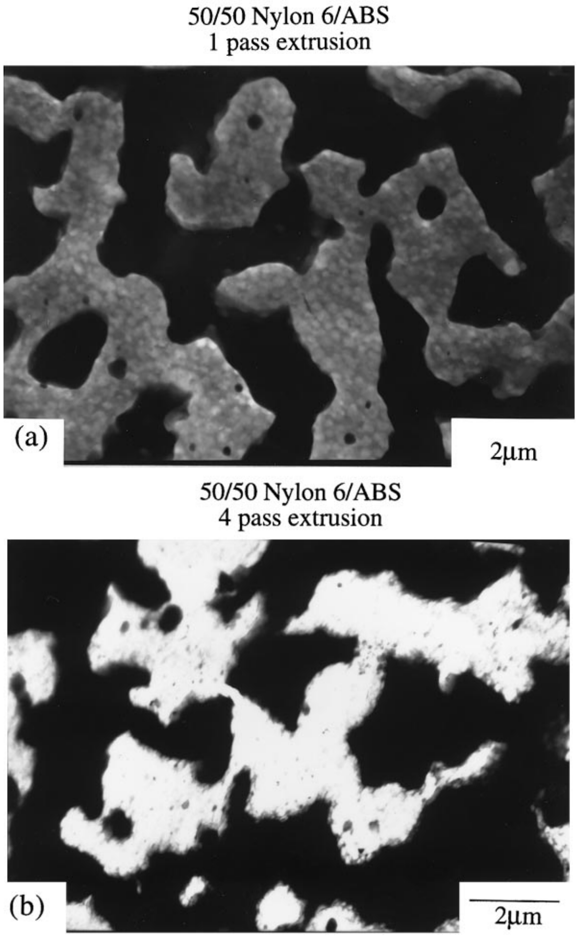


Fig. 5. TEM photomicrograph of a 50/50 nylon 6/ABS blend after (a) 1 and (b) 4 extrusions. The polyamide phase is stained dark by PTA.

difference in reactivity for glutaric versus maleic anhydride functionalities. As seen in Fig. 3, the amount of acid functionality of IA is significantly greater than the glutaric anhydride functionality. Given that there is an excess of amine end groups relative to the glutaric anhydride units over the entire composition range observed here, it is possible that the slower acid/amine reaction could take place with the remaining amine end groups even after the fast anhydride/amine reaction has proceeded towards the exhaustion of the anhydrides. When both acid and anhydride functionalities are considered, the possible extent of grafting of nylon 6 onto the compatibilizer precursor is theoretically much higher for IA than SANMA. It is important to note that the above analysis only accounts for compatibilizer reactions with the amine end groups of nylon 6; however, as mentioned earlier, grafting through amide linkages may also occur with either acid or anhydride functionalities. It is believed that amide linkages are more likely to react with the acid groups than the anhydride units. It is important to note that for polyamides like nylon 6,6, these reactions can eventually lead to crosslinking; whereas, only grafting is expected for nylon 6.

4. Blend mechanical properties and morphology

The effects of processing history and compatibilizer type on the mechanical properties and morphology of compatibilized nylon 6/ABS blends are explored here. The first subsection examines the effects of multiple extrusions on blends containing IA, whereas the next subsection focuses on similar blends containing SANMA.

4.1. Blends containing IA polymer

The effects of multiple extrusions on the morphology and mechanical properties of nylon 6/ABS/IA blends are described here. An uncompatibilized blend is used as a control. Fig. 4 shows the Izod impact strength versus temperature for a nylon 6/ABS blend and nylon 6/ABS/IA blends containing varying amounts of IA and after different numbers of extrusion passes (from 1 to 4). In each of these blends, the ratio of nylon 6 to ABS is fixed at 1:1. It is evident that the impact strength/temperature relationship is generally unaffected by the number of extrusions for blends containing 1 wt.% or less compatibilizer, as seen in Fig. 4(a)–(c). In the blend containing 1 wt.% IA (Fig. 4(c)), there is a slight reduction in the ductile–brittle transition temperature after four extrusions relative to blends with less processing history. For blends containing 2 wt.% IA, shown in Fig. 4(d), increasing the number of extrusion passes has little effect on the room temperature impact strength, but the low temperature impact strength decreases as the number of extrusion passes increases. Blends containing 5 wt.% IA have better low temperature toughness after 1 extrusion than blends containing 2 wt.% IA (compare Fig. 4(d) and (e)), but the ductile–brittle transition temperature increases more rapidly when the number of extrusions is increased. Blends containing 10 wt.% IA (see Fig. 4(f)) show an even greater increase in the ductile–brittle transition temperature as the number of extrusions is increased; after four consecutive extrusion passes, the ductile–brittle transition temperature is close to room temperature. It is evident that the low temperature ductility of these blends can be severely compromised by multiple extrusions when the compatibilizer content is above a certain level.

TEM photomicrographs of some of the blends in Fig. 4 are shown in Figs. 5–8; in each of these photomicrographs the polyamide phase is stained dark by PTA. Fig. 5 shows TEM photomicrographs for uncompatibilized nylon 6/ABS blends after 1 and 4 extrusions. The ABS phase is poorly dispersed and the morphology does not appear to change significantly with increasing number of extrusion steps; these blends are brittle at room temperature (see Fig. 4(a)). In the previous article, it was shown that the dispersion of the ABS (as well as impact properties) can be improved by incorporation of 5 wt.% of the IA polymer [15]. TEM photomicrographs of blends containing 2 wt.% IA after various extrusions are shown in Fig. 6. Surprisingly, the ABS phase is not much more efficiently dispersed than

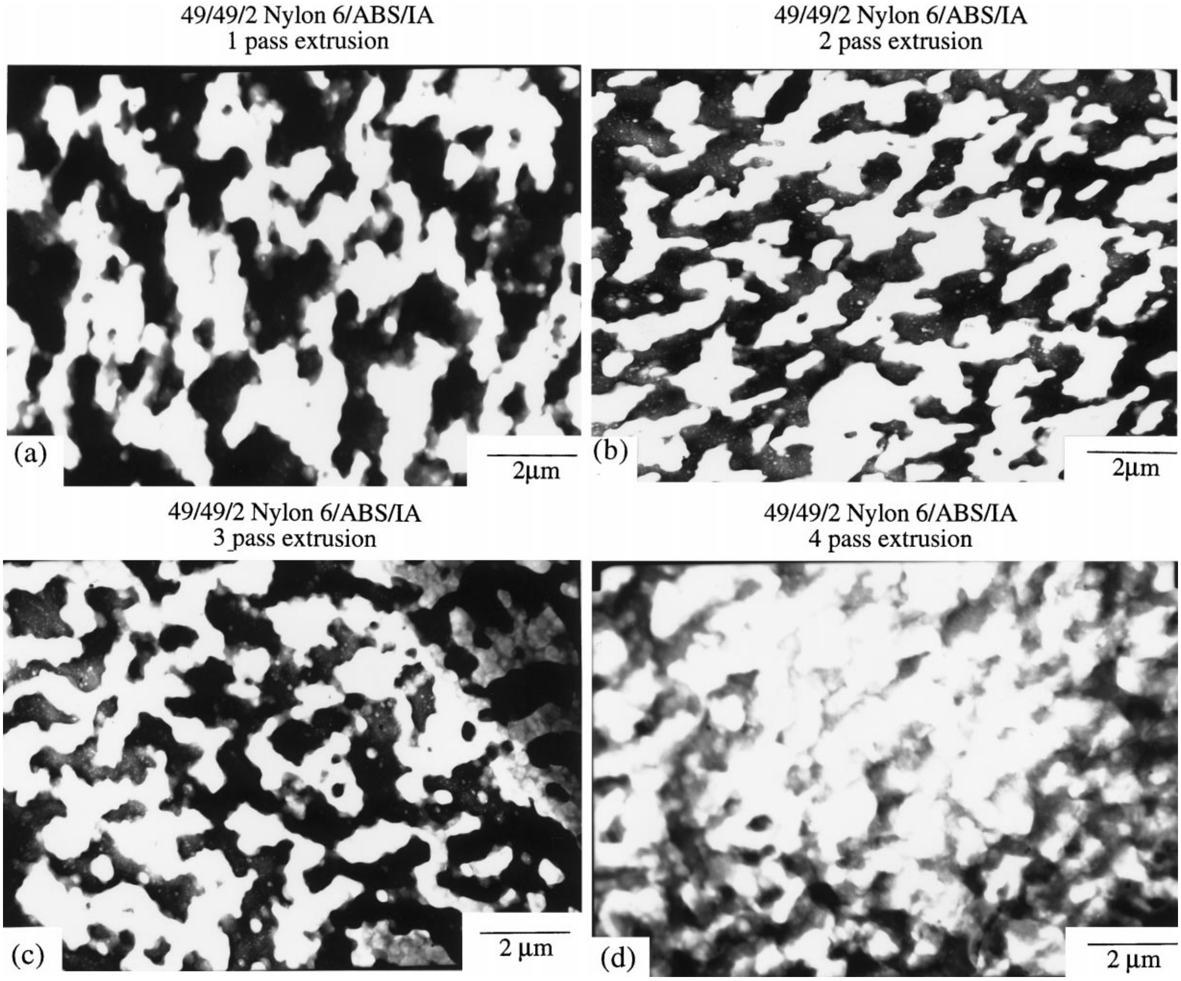


Fig. 6. TEM photomicrographs of 49/49/2 nylon 6/ABS/IA blends after (a) one, (b) two, (c) three, (d) four extrusions. The polyamide phase is stained dark by PTA.

for the uncompatibilized blend, compare Figs. 5 and 6; nevertheless, the blend with 2 wt.% IA has excellent low temperature toughness as seen in Fig. 4(d). Apparently, the impact properties can be improved substantially with only a modest improvement in dispersion of the ABS domains or simply by strengthening the interfacial adhesion between nylon 6 and ABS. A comparison of Fig. 6(a)–(d) indicates that as the number of extrusion passes increases, there are no significant changes in blend morphology.

Fig. 7 shows TEM photomicrographs of blends containing 5 wt.% IA as a function of the number of extrusion steps, corresponding to the blends in Fig. 4(e). In these blends, the morphology is not as stable (with respect to the number of extrusions) as blends containing 2 wt.% IA, and there is some morphological rearrangement as the extrusion time is increased. After three extrusions, some of the ABS domains appear somewhat enlarged and are quite large after four extrusions. It is interesting to note that all the blends represented in Fig. 7 are still super tough at room temperature, see Fig. 4(e); this morphological change only affects the low temperature toughness. Fig. 8 shows TEM photomicrographs for blends containing 10 wt.% IA, corresponding to Fig. 4(f). The ABS domains become larger as the number of extrusions is increased; after four extrusions, there are large regions where there are no ABS domains at all. There are also some isolated small domains that seem to contain no rubber particles; these may be highly grafted structures removed from the nylon 6/SAN interfacial region.

An alternative means to observe the morphological rearrangements that occur with increasing number of extrusion steps is to examine the distribution of butadiene rubber particles in the blend. The TEM photomicrographs in Fig. 9 show the rubber particles (stained dark by OsO_4) in blends containing 10 wt.% IA after one and four extrusion passes. A comparison of the photomicrographs indicates that the rubber particles are not as well dispersed in the blend after several extrusions as they are after a single

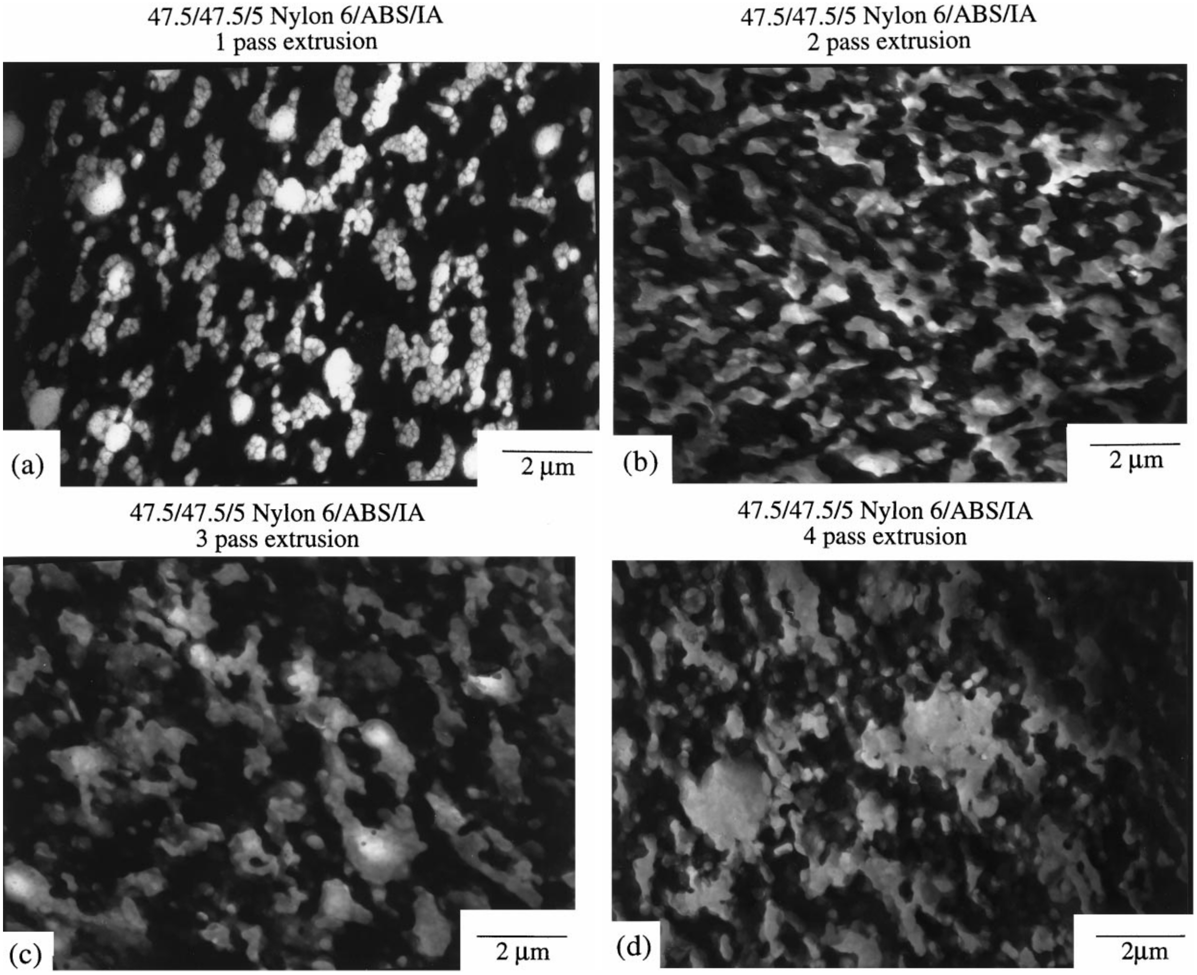
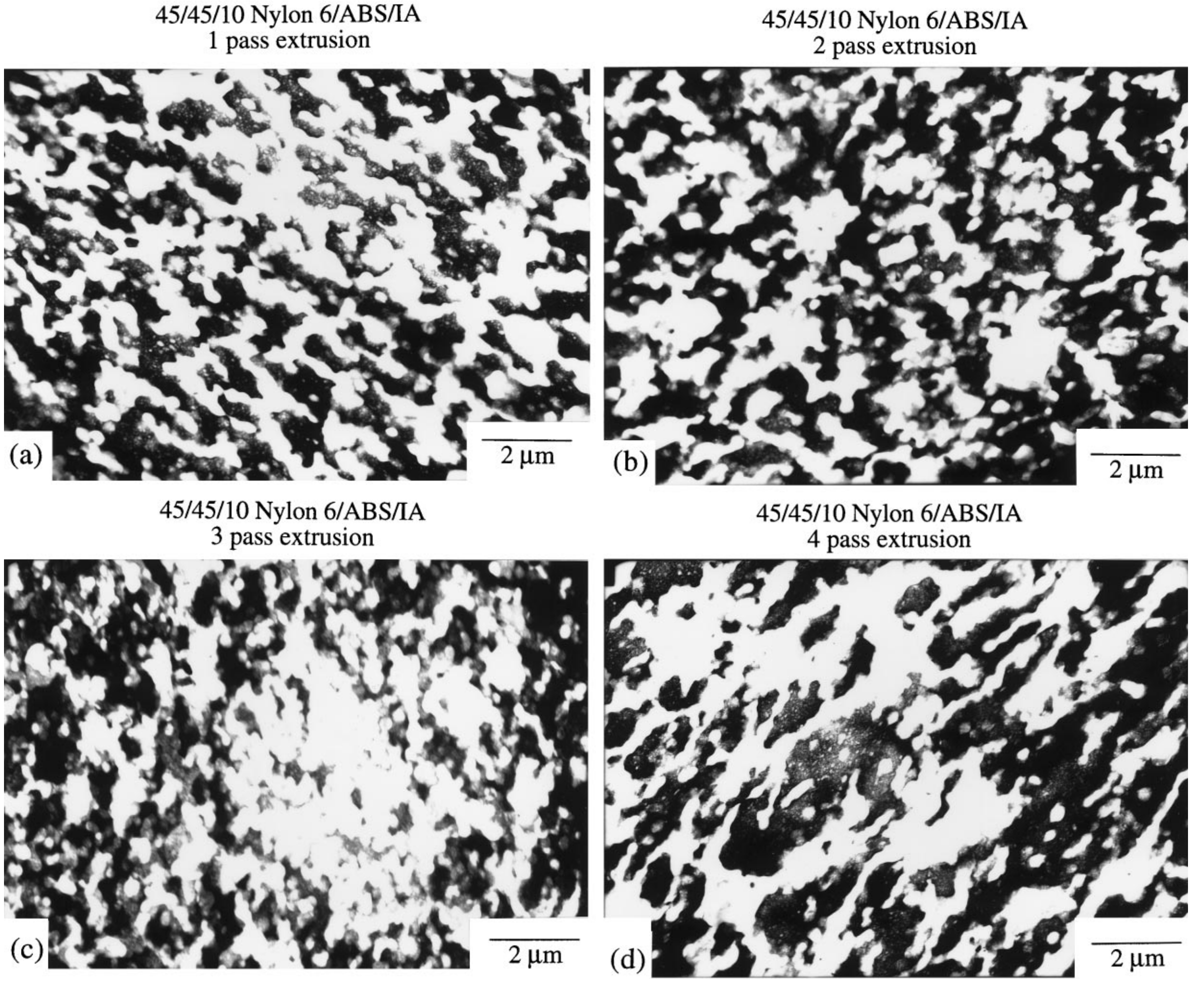


Fig. 7. TEM photomicrographs of 47.5/47.5/5 nylon 6/ABS/IA blends after (a) one, (b) two, (c) three, (d) four extrusions. The polyamide phase is stained dark by PTA.

extrusion, which no doubt limits the capacity for low temperature toughness in these blends.

Clearly, the morphology and mechanical properties of blends containing higher IA contents are strongly influenced by the number of extrusion passes during melt processing; whereas, blends with lower compatibilizer contents are much less sensitive to the processing history. A potential cause for this behavior may lie in the nature of reactions between nylon 6 and the IA polymer, as discussed in the previous section. This possibility is addressed in more detail later.

It is important to note that each of the previously examined blends contained a 1:1 ratio of nylon 6 to ABS. After a single extrusion, the morphology of these blends is near a point of phase inversion. In this region, morphological rearrangements that occur with increasing number of extrusions could alter the degree of continuity of the nylon 6 and ABS phases, which in turn could profoundly influence the blend mechanical properties. Thus, the pronounced changes in low temperature ductility with increasing number of extrusions may be unique to blends near the point of phase inversion. Blends with a higher ratio of nylon 6 to ABS will be less likely to undergo significant changes in phase continuity, and hence, may be less sensitive to the number of extrusion steps. To explore this possibility, compatibilized blends with a higher ratio of nylon 6 to ABS were subjected to multiple extrusions. Fig. 10 shows the Izod impact strength versus temperature for a 65/30/5 nylon 6/ABS/IA blend after different numbers of extrusion passes during melt processing. The impact properties of these blends are quite similar after one, two, or three extrusions, but the ductile-to-brittle transition temperature increases by about 10°C after a fourth extrusion. TEM photomicrographs of these blends after one and four extrusions are shown in Fig. 11; the polyamide phase is stained dark by PTA. A comparison of these photomicrographs indicates that their morphologies are not substantially different. While there is some dependence of impact properties on the processing history for these blends, the changes for blends that are closer to a point of phase inversion containing the same amount of compatibilizer are much more pronounced, compare Figs. 4(e) and 7.



45/45/10 Nylon 6/ABS/IA
1 pass extrusion

45/45/10 Nylon 6/ABS/IA
2 pass extrusion

45/45/10 Nylon 6/ABS/IA
3 pass extrusion

45/45/10 Nylon 6/ABS/IA
4 pass extrusion

Fig. 8. TEM photomicrographs of 45/45/10 nylon 6/ABS/IA blends after (a) one, (b) two, (c) three, (d) four extrusions. The polyamide phase is stained dark by PTA.

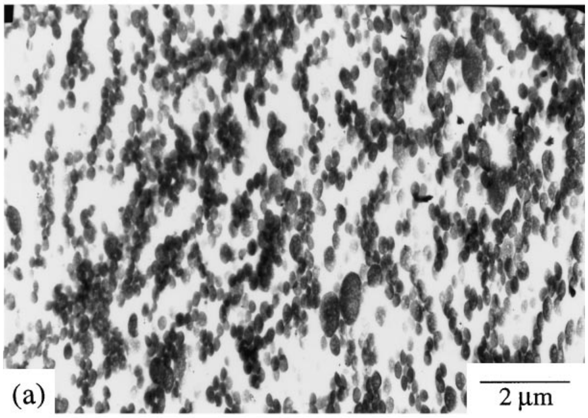
4.2. Blends containing SANMA polymer

The effects of multiple extrusions on the morphology and mechanical properties of nylon 6/ABS/ SANMA blends with the same composition as those compatibilized by the IA polymer are examined here. Fig. 12 shows the Izod impact strength versus temperature for blends (equal parts of nylon 6 and ABS) containing different amounts of SANMA after various numbers of extrusions. Fig. 12(a) shows that incorporation of only 0.5 wt.% SANMA generates super tough blends at room temperature that are insensitive to the number of extrusions. Increasing the compatibilizer content at a fixed ratio of nylon 6 to ABS reduces the ductile-to-brittle transition temperatures of these blends, and the low temperature toughness is generally unaffected by the processing history. The only exception to this trend is the blend containing 10 wt.% SANMA (shown in Fig. 12(e)). The ductile-to-brittle transition temperature of this blend is about 10°C higher after two extrusions compared to a single extrusion; however, subsequent extrusions have a negligible effect on the impact properties. For blends with higher compatibilizer contents, blends containing SANMA retain their low temperature toughness after multiple extrusions much better than analogous blends containing IA. A direct comparison of the impact properties of these compatibilized systems with respect to the processing history is provided later in this section.

TEM photomicrographs of select blends are shown in Figs. 13 and 14; the polyamide phase is stained dark by PTA. Fig. 13 shows that there is no significant morphological difference for blends containing 1 wt.% SANMA after one and four extrusions, respectively. It is evident that the ABS phase is not very well dispersed; however, the blends are super tough well below room temperature (see Fig. 12(b)). As mentioned earlier, the dispersion of ABS domains is not the sole factor governing the impact properties of these blends; interfacial adhesion may also play an important role.

The photomicrographs in Fig. 14 compare the morphology after one and four extrusions for blends containing

45/45/10 Nylon 6/ABS/IA
1 pass extrusion



45/45/10 Nylon 6/ABS/IA
4 pass extrusion

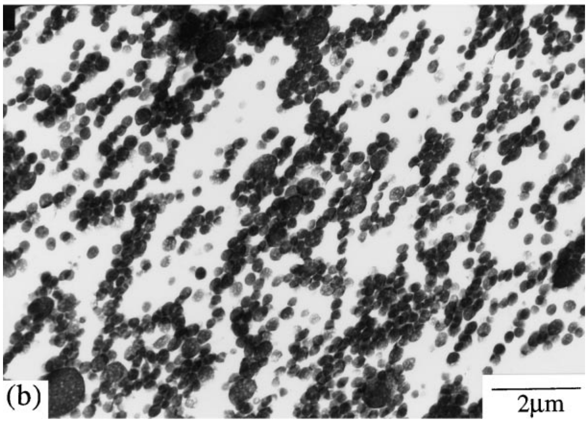


Fig. 9. TEM photomicrographs of 45/45/10 nylon 6/ABS/IA blends after (a) one and (b) four extrusions. The rubber phase of ABS is stained dark by osmium tetraoxide (OsO_4).

5 wt.% SANMA. Increasing the number of extrusions does not significantly affect the morphology of these blends. The morphological stability observed here is a stark contrast to that for blends based on IA (note Fig. 7). It is clear that increasing the compatibilizer content in blends containing SANMA can improve the dispersion of ABS domains (compare Figs. 13 and 14) as well as the low temperature ductility, independent of the processing history used here.

It is somewhat surprising that such excellent impact properties are obtained for blends containing SANMA, given that this material does not appear to be fully miscible with the SAN matrix of the ABS material. Kim et al. have noted that good interfacial adhesion between SAN and ABS materials can be achieved even when these materials are immiscible and can, thus, lead to excellent blend toughness outside of the miscible range [28]. Majumdar. et al. discussed possible configurations of the graft copolymer at the polyamide/SAN interface as a function of the interaction of the compatibilizer backbone with the SAN matrix [19].

It has been demonstrated here that the compatibilizer type, compatibilizer content, and processing history all play important roles in controlling the low temperature ductility of these blends. The effects of compatibilizer type and content on the ductile–brittle transition temperature, derived from the results in Figs. 4 and 12, of nylon 6/ABS blends are shown in Fig. 15 for four extrusion histories. Fig. 15(a) shows that after one extrusion, blends containing SANMA have better low temperature toughness at very low compatibilizer contents (0.5 or 1 wt.%); whereas, blends containing IA have superior low temperature ductility at levels of 2 wt.% or higher. After a second pass extrusion, however, the SANMA compatibilizer provides better low temperature toughness over the entire composition range examined here as seen in Fig. 15(b), since the ductile–brittle transition temperature increases beyond 2 wt.% IA. Fig. 15(c) and (d) demonstrate that after three and four extrusion passes, blends containing SANMA are clearly superior to those containing IA in terms of low temperature toughness, particularly at higher compatibilizer contents.

It is quite evident that the differences in impact properties observed above stem from fundamental differences between

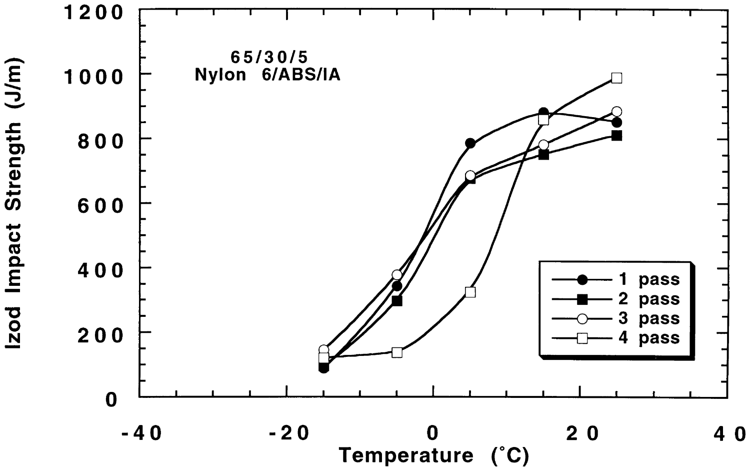
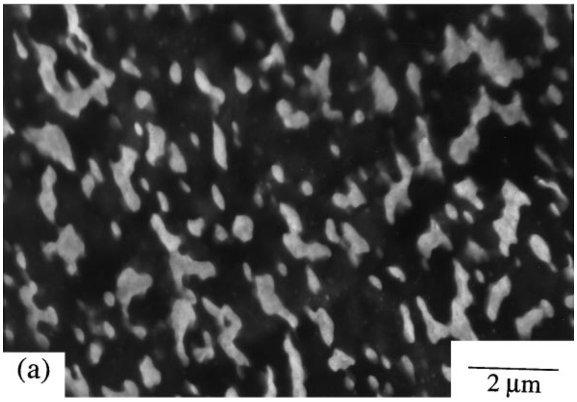


Fig. 10. Effect of temperature on the Izod impact strength of 65/30/5 nylon 6/ABS/IA blends after different numbers of extrusions.


65/30/5 Nylon 6/ABS/IA
1 pass extrusion

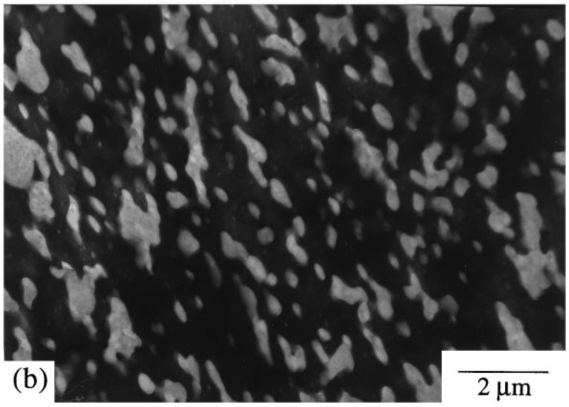

65/30/5 Nylon 6/ABS/IA
4 pass extrusion

Fig. 11. TEM photomicrographs of 65/30/5 nylon 6/ABS/IA blends after (a) one and (b) four extrusions. The polyamide phase is stained dark by PTA.

the IA and SANMA materials. The nature and extent of the reactions between nylon 6 and these compatibilizers is believed to be an important factor affecting the mechanical properties and morphology development in these blends. In the next section, Brabender torque rheometry provides some indirect evidence about the differences in the extent of grafting of nylon 6 to these compatibilizers.

5. Blend rheology

In this section, the rheological nature of ternary nylon 6/ABS/compatibilizer blends and binary nylon 6/compatibilizer blends are examined by Brabender torque rheometry. Fig. 16(a) and (b) show the Brabender torque versus melt mixing time for the blend compositions described in the previous section. The blend torque increases with increasing content of both IA and SANMA as a consequence of the grafting reactions that occur during melt processing. There are important fundamental differences in the rheological character of the blends that relate to the nature of the compatibilizer. Fig. 16(a) shows that blends containing 1 wt.% IA or lower reach a nearly constant torque after an initial fluxing period; however, the torque progressively increases with mixing time for blends with higher compatibilizer contents. A potential cause for this response could be grafting of nylon 6 to the IA backbone via the reactions of the methacrylic acid units, shown in Fig. 2(b), after the rapid anhydride/amine reaction has already occurred. As mentioned earlier, the acidolysis reaction between this acid and an amide linkage may be more likely to occur than the acid/amine reaction due to the relative amounts of amide versus amine groups. Miller has demonstrated that amide-exchange reactions in polyamide melts can involve acidolysis [29]. It is interesting to note that the blends which reach steady state torque values in the Brabender also have impact properties that are insensitive to the number of extrusions, see Fig. 4(a)–(c); whereas, blends with a progressively increasing torque response experience a loss in low temperature toughness with increasing number of extrusions, see Fig. 4(d)–(f). These changes in blend rheology with mixing time closely correlate with the deterioration of morphology and mechanical properties with increased melt processing history. For blends containing the SANMA terpolymer, shown in Fig. 16(b), each blend reaches a steady state torque after an initial fluxing period. The impact properties of these blends are generally unaffected by the number of extrusion passes during melt processing as shown in Fig. 12.

The relative degree of reaction of these compatibilizers with nylon 6 can be assessed by comparing torque values after a fixed mixing time (10 min) as shown in Fig. 17. Blends containing IA exhibit higher Brabender torques than blends containing SANMA over the entire composition range; the difference in these values becomes greater with increasing compatibilizer content. This reflects the increase in torque with mixing time for blends with higher IA contents. However, even the blends with smaller IA contents that reach a steady state torque (0.5 wt.% and 1.0 wt.% IA) have higher torques than corresponding blends based on SANMA. It was demonstrated earlier that for a fixed compatibilizer content, the number of anhydride functionalities was greater in the SANMA terpolymer than in the IA material (see Fig. 3). There may be an intrinsic difference in the reactivity between the two types of anhydrides in IA versus SANMA; however, the acid functionality in IA is believed to be responsible for a continued graft reaction between nylon 6 and IA that gives rise to this rheological behavior.

The differences in grafting between nylon 6 and these compatibilizers can be seen more clearly by monitoring their rheology in the absence of ABS. Fig. 18 shows the torque response versus time for nylon 6 blends with IA and SANMA; neat nylon 6 is used as a control. The ratio of nylon 6/compatibilizer has been set equal to the ratio for the blends described in Fig. 16, i.e. 49.5/1, 49/2, etc. in the absence of ABS. The trends in the torque versus time

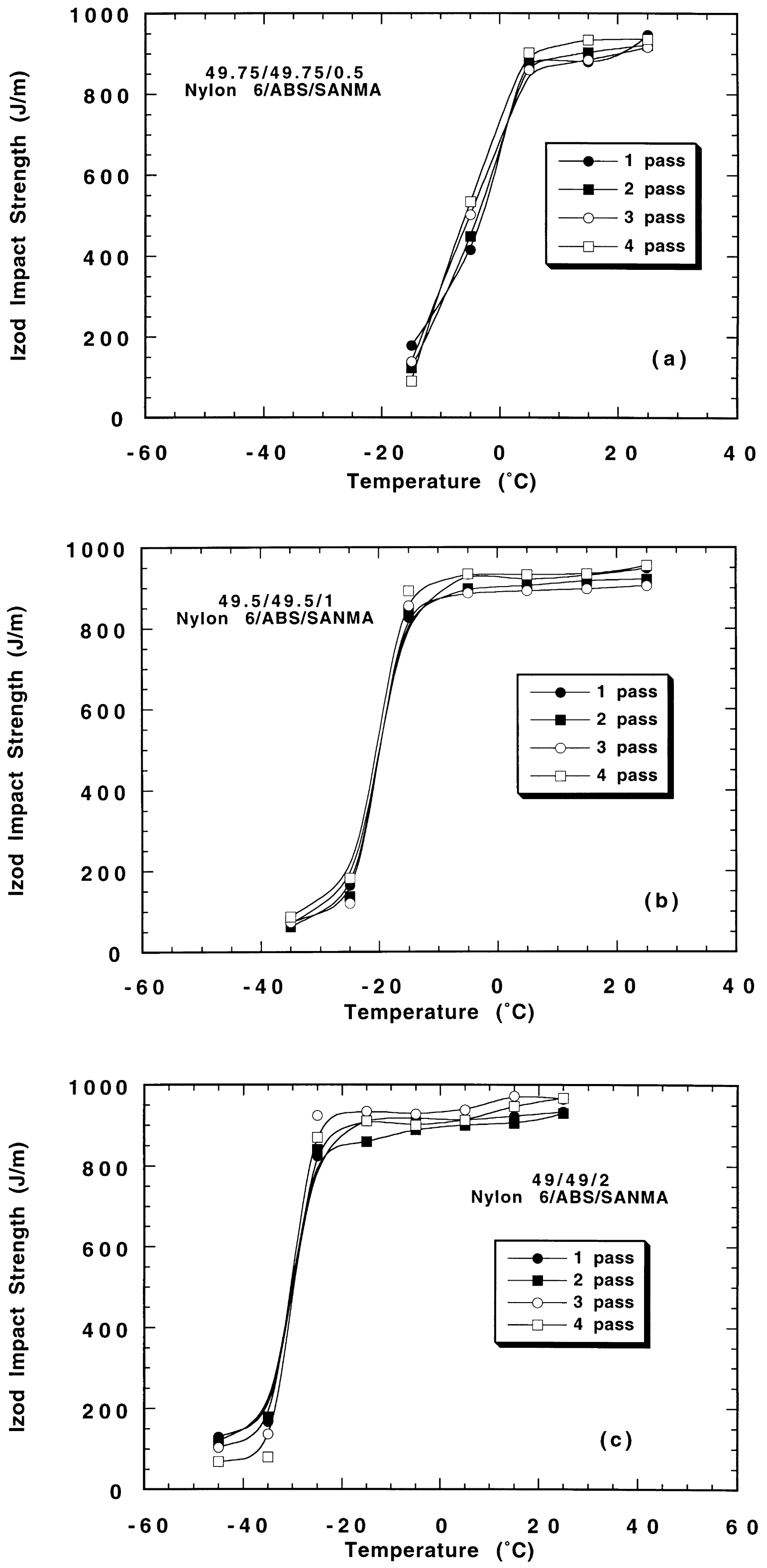


Fig. 12. Effect of temperature on the Izod impact strength of nylon 6/ ABS/SANMA blends as a function of the number of extrusion passes (● = one, ■ = two, ○ = three, □ = four extrusions). The blends contain a 1:1 ratio of nylon 6:ABS and the following amounts of SANMA: (a) 0.5%, (b) 1%, (c) 2%, (d) 5%, (e) 10%.

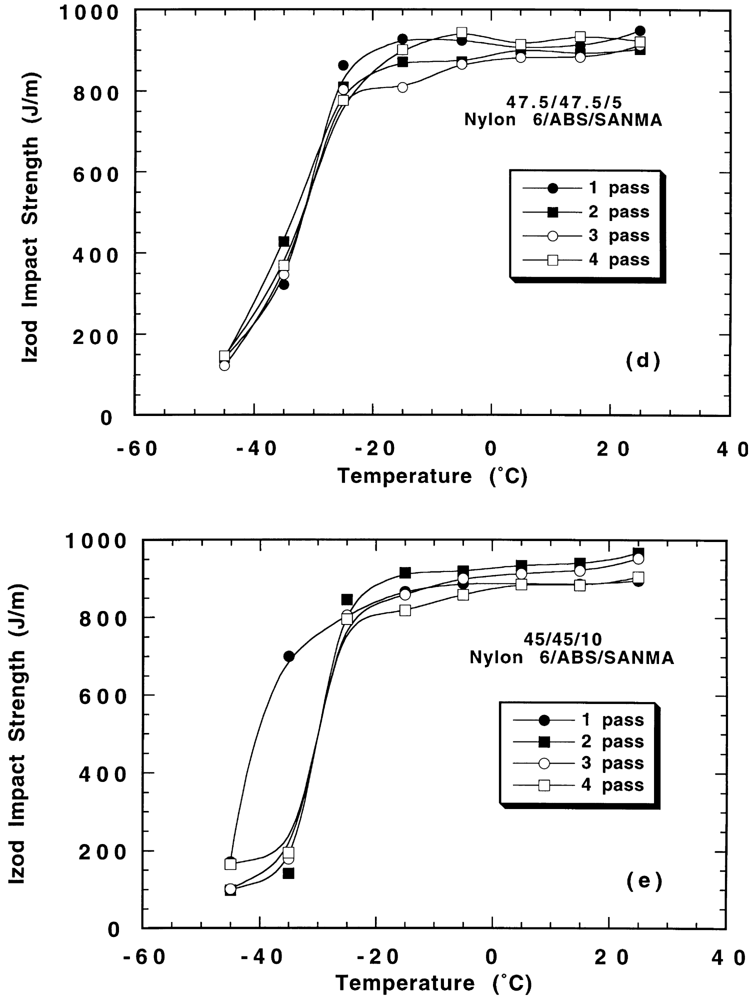


Fig. 12. (*continued*)

response of these binary blends are qualitatively similar to those shown in Fig. 16 for ternary blends containing ABS. Blends with lower IA contents tend to reach a steady state torque, whereas blends with higher IA contents exhibit a progressively increasing torque with mixing time, as seen in Fig. 18(a). Fig. 18(b) shows that all blends with the SANMA terpolymer more nearly reach a steady state torque after an initial fluxing period. It was mentioned earlier that a potential reaction in these blends are the post-condensation reactions between the acid and amine end groups of nylon 6, which would result in longer polyamide chains. However, the steady state torque response of nylon 6 indicates that these reactions are negligible under the current melt processing conditions.

A more direct comparison is shown in Fig. 19, where the torque values after 10 min of mixing is plotted versus compatibilizer content. We propose that continued grafting reactions between nylon 6 and IA, probably via the pendant acid groups, leads to the higher viscosities than observed with SANMA.

Previous investigations of nylon 6/ABS blends suggest there is an optimum level of compatibilizer functionality for maximizing impact properties. Majumdar et al. investigated a series of compatibilizers for nylon 6/ABS blends with varying levels of reactive functionality. Compatibilizers containing high levels of reactive functionality were not very effective for good low temperature toughness [9]. A styrene/maleic anhydride copolymer containing 25 wt.% MA (miscible with SAN25) has been shown ineffective for low temperature toughness of nylon 6/ABS blends; it has been speculated that this stems from the high level of reactive functionality [8]. For blends containing high IA contents, the degree of grafting may be near optimum after one extrusion step; however, it appears that the degree of grafting progressively increases with each extrusion step and may subsequently exceed the optimum level. However, the morphology of the current blends after multiple extrusions is quite different than that of the blends containing highly functional compatibilizers examined by Majumdar et al. [9]. It appears that all differences in low-temperature impact properties cannot be adequately explained in terms of simple morphological arguments at this point.

Majumdar et al. speculated that reactions that occur

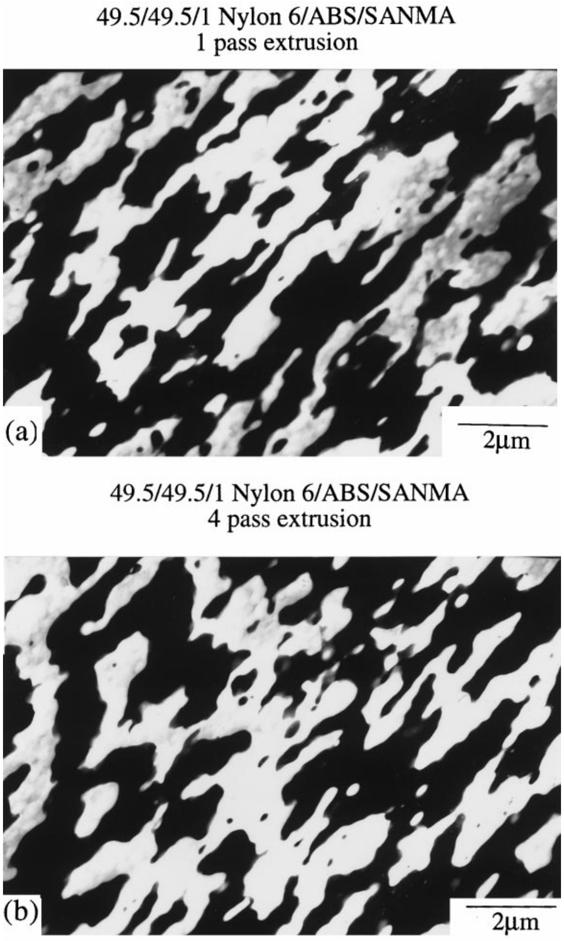


Fig. 13. TEM photomicrographs of 49.5/49.5/1 nylon 6/ABS/SANMA blends after (a) one and (b) four extrusions. The polyamide phase is stained dark by PTA.

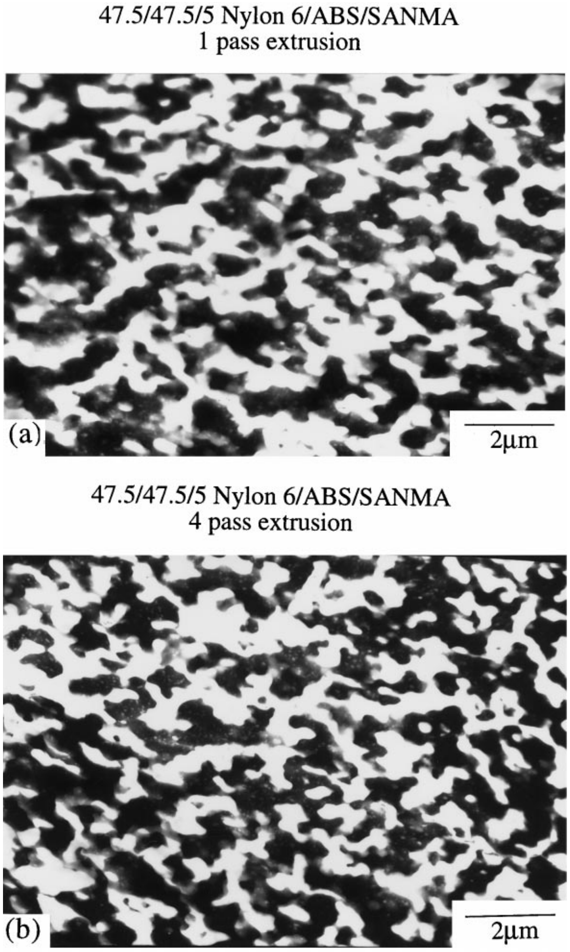


Fig. 14. TEM photomicrographs of 47.5/47.5/5 nylon 6/ABS/SANMA blends after (a) one and (b) four extrusions. The polyamide phase is stained dark by PTA.

between the compatibilizer precursor and nylon 6 during extrusion alter its molecular structure and may change the affinity of the compatibilizer precursor for SAN [19]. While the SANMA material used here is not fully miscible with the SAN matrix of ABS, it apparently has adequate affinity for the SAN to give good mechanical properties and this is not compromised by repeated extrusions. The IA material, although miscible with SAN, appears to undergo a sufficiently higher degree of reaction with nylon 6 than the SANMA material. Given the evidence that the nylon 6/IA grafting reactions continue to occur with increasing melt processing time, one could envision that the SAN/IA interaction could be altered significantly, and potentially become quite unfavorable, after multiple extrusion steps.

There are no doubt a myriad of complex chemical and physical events that could lead to the observed differences in the morphological and mechanical behavior of blends containing these two types of compatibilizers. While many of these possibilities have been addressed here in terms of chemical reactions and miscibility characteristics, further work is needed to gain a more complete understanding of the importance of each of these factors. The use of simpler model systems would provide a useful avenue to isolate some of the specific issues.

6. Conclusions

The mechanical properties, morphology, and rheology of nylon 6/ABS blends have been examined as a function of processing history using an IA polymer and a SANMA terpolymer as compatibilizing agents. The IA material is miscible with the SAN phase of this ABS material; whereas, the SANMA material is not fully miscible with this SAN. Both compatibilizers lead to blends that are super-tough at room temperature using a broad range of compatibilizer contents. However, there are key differences in the influence of multiple extrusions on the low temperature toughness of these compatibilized blends. Blends containing a 1:1 ratio of nylon 6 to ABS and IA contents above 2 wt.% exhibited a steadily increasing ductile-to-brittle transition temperature

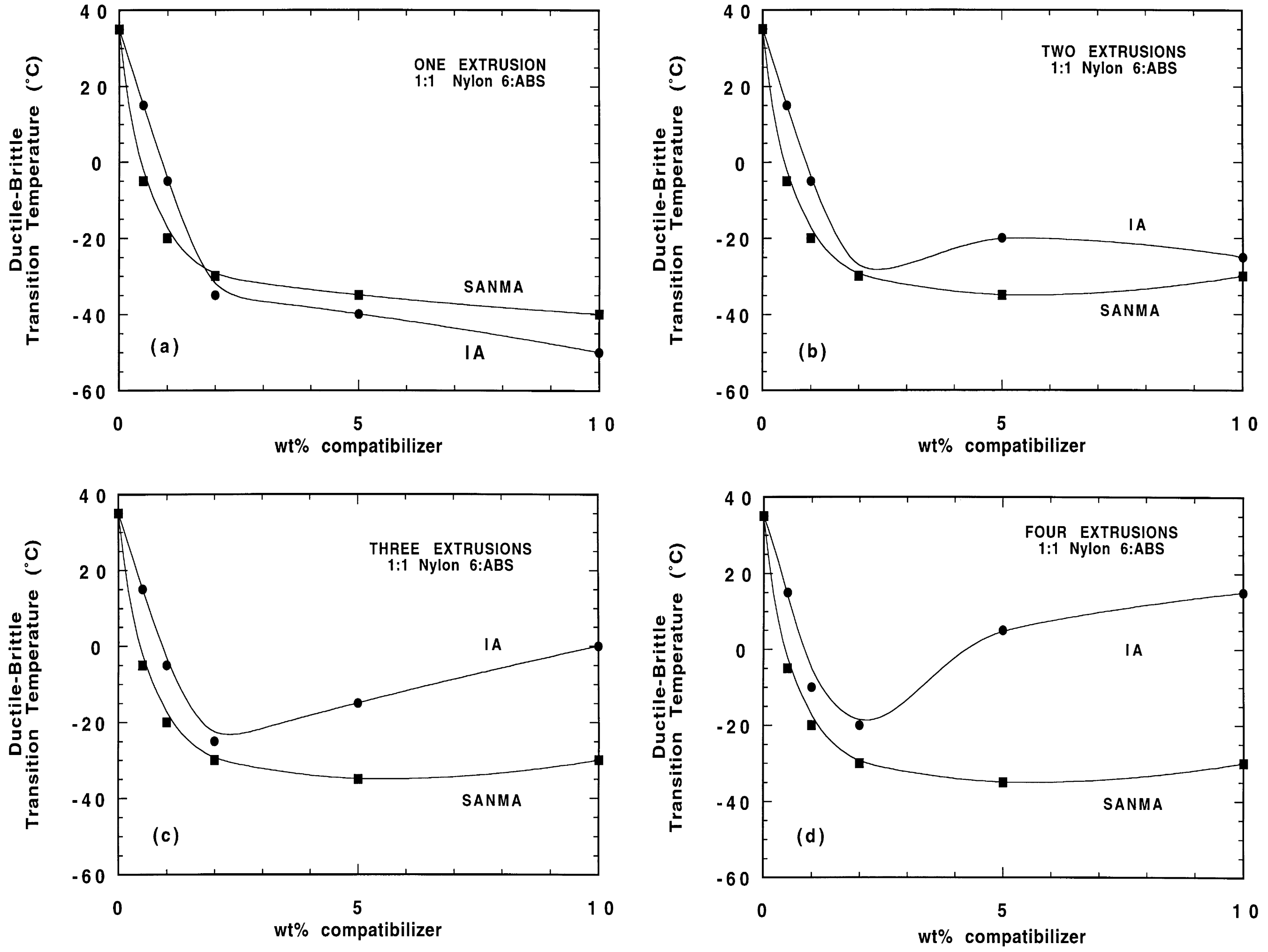


Fig. 15. Effect of compatibilizer content on the ductile-brittle transition temperature of nylon 6/ABS, nylon 6/ABS/IA, and nylon 6/ABS/SANMA blends as a function of the number of extrusion passes. The blends contain a 1:1 ratio of nylon 6:ABS and are subjected to (a) one, (b) two, (c) three, (d) four extrusions.

as a function of the number of extrusion passes; the deleterious effect on low temperature toughness becomes larger with increasing IA content. Blends with high IA contents experienced significant morphological changes as the number of extrusions increased; the ABS domains tended to become larger, leading to a poorer dispersion of the butadiene rubber particles in the blend. The morphology and low temperature ductility of analogous blends containing a SANMA terpolymer were generally unaffected by the number of extrusions. There are fundamental differences in the reactive nature of the IA and SANMA compatibilizers. Brabender torque studies revealed that the melt viscosity of blends containing high amounts of IA increases with mixing time; whereas, blends based on SANMA reach a steady state melt viscosity. These differences in rheological behavior are suggested to stem from the fact that the IA polymer contains both acid and anhydride functionalities that are capable of reacting with nylon 6; whereas, SANMA contains only anhydride functionality.

These differences in the reactive nature of these compatibilizers may be responsible for the observed differences in mechanical properties and morphologies of their blends. While potential reactions between nylon 6 and these compatibilizers have been discussed, further work is needed to gain a more complete understanding of the extent of each of these reactions during melt processing. When issues of processability and processing history are considered, blends based on the SANMA terpolymer have more desirable properties than those based on the IA polymer.

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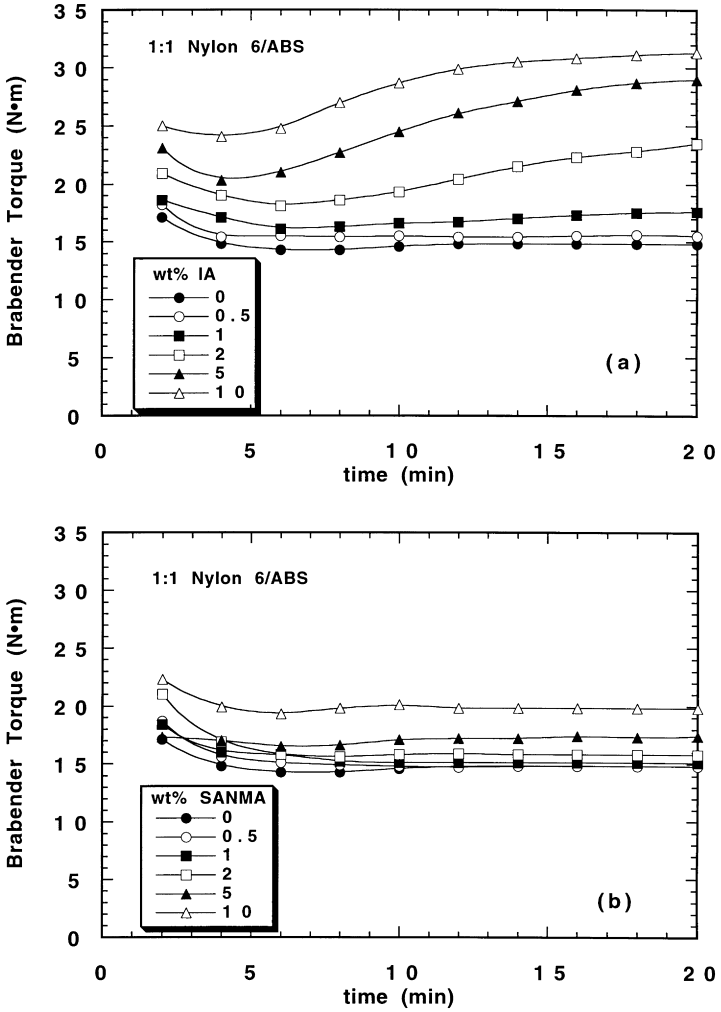

Fig. 16. Brabender torque versus time for (a) nylon 6/ABS/IA and (b) nylon 6/ABS/ SANMA blends as a function of compatibilizer content. The ratio of nylon 6:ABS is fixed at 1:1. Torque readings were taken at 240°C and 60 rev min^{-1}.

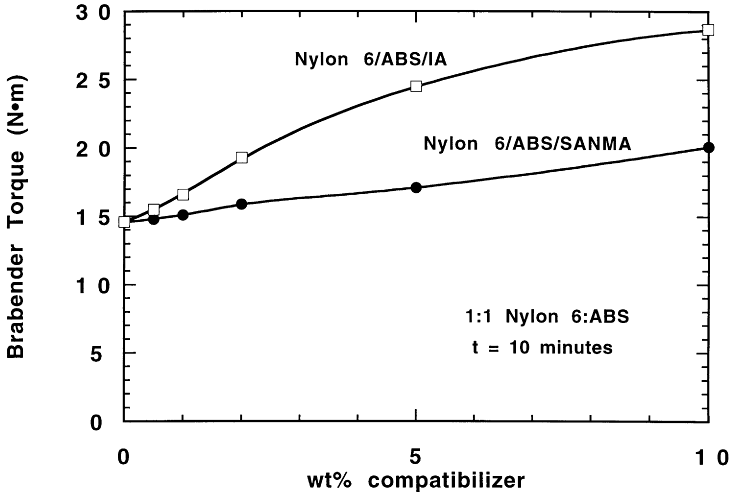

Fig. 17. Brabender torque versus wt.% compatibilizer after 10 min of mixing for a binary nylon 6/ABS blend (0 wt.% compatibilizer) and ternary nylon 6/ABS/ compatibilizer blends. These data correspond to the torque values of blends shown in Fig. 16 after 10 min of mixing. Torque readings were taken at 240°C and 60 rev min^{-1}.

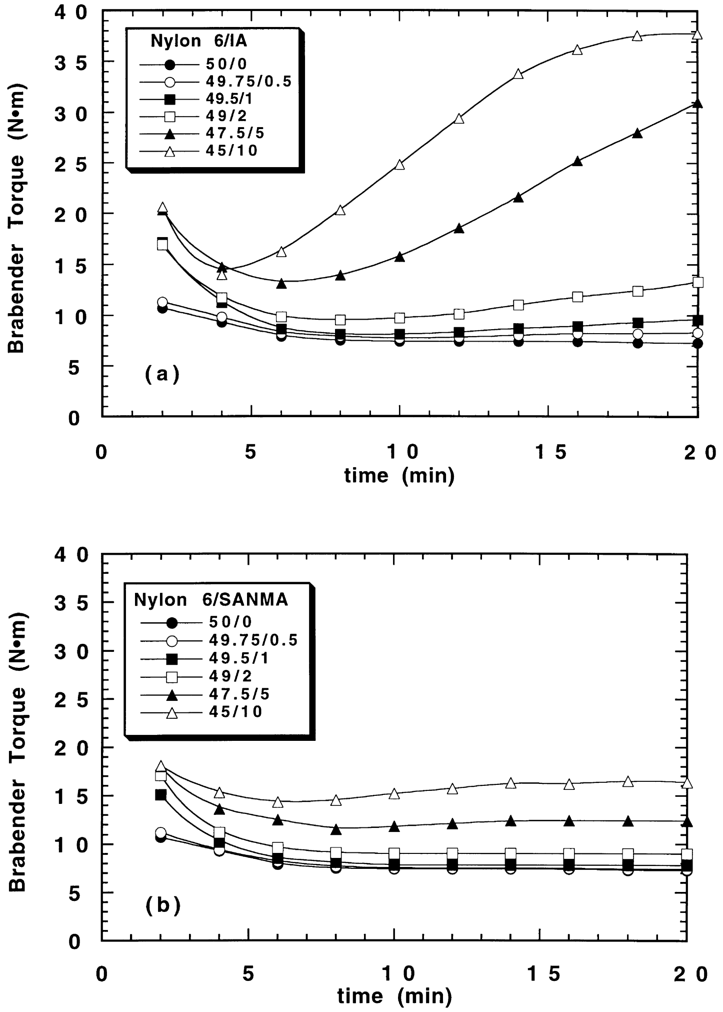

Fig. 18. Brabender torque versus time for (a) binary nylon 6/IA blends and (b) binary nylon 6/SANMA blends as a function of compatibilizer content. The ratios of nylon 6: compatibilizer are set equal to the nylon 6:compatibilizer ratios of the ternary blends shown in Fig. 16. Torque readings were taken at 240° and 60 rev min^{-1}.

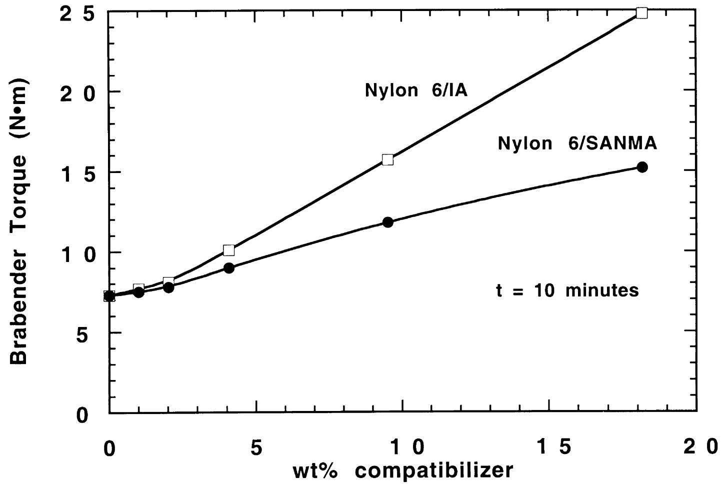

Fig. 19. Brabender torque versus wt.% compatibilizer after 10 minutes of mixing for nylon 6 and binary nylon 6/compatibilizer blends. These data correspond to the torque values of blends shown in Fig. 18 after 10 min of mixing. Torque readings were taken at 240°C and 60 rev min^{-1}.

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