On the Use of Extruders as Chemical Reactors

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ABSTRACT: Composites of polyamide-6 (PA-6) and poly(butadiene acrylonitrile) (PBAN), varying in the quantity of the elastomer and the content of its nitrile groups, were examined during extrusion in a 45-mm extruder at 225 $\pm$ 2°C and with a shear rate over 450 s^{-1}. It was established that these two incompatible polymers can be mixed and the blends display solubility in formic acid. This fact is explained by chemical transformation of the nitrile groups followed by chemical interaction between the polyamide and elastomer components. As a result, graft copolymers were most probably formed. The reaction proceeds easily if the PA-6 contains water. The extrusion leads to improved compatibility of the polymers and enhanced impact strength of the extrudates. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 871–877, 2004

Key words: reactive extrusion

INTRODUCTION

Recently, extruders have increasingly been used as chemical reactors.[1] A new trend, called "reactive extrusion," has been developed in the technology of polymers. No matter in what reactor the chemical process occurs, it is subject to the basic thermodynamic laws. The run of any reaction depends on the thermodynamic parameters—temperature, pressure, concentration, and time. The relation between them is given by the Arenius equation on the rate of chemical processes.[2] No matter whether the reaction occurs in an ordinary chemical reactor or in an extruder, the process rate is determined by the Arenius law. During the run of the chemical reaction in the extruder, however, according to the authors, there is one more factor that will influence the general rate of the process. That is the shear rate [γ].

It is well known that, in the polymer molten state, macromolecules have the shape of not quite compact globules, which is their stable conformation. When the melt starts flowing, the macromolecules stretch and become oriented in the direction of flowing. The stretching and orienting of the macromolecules depend on the shear rate of flowing. The higher the shear rate, the more the macromolecules stretch. When the macromolecules stretch, on the one hand, their functional groups become more accessible to chemical interaction, and, on the other hand, during the stretching of the macromolecules, intermolecular entropy stress emerges in them. It may increase to such an extent that the macromolecules mechanically break. This process has been known for a long time and is called "chemical flowing."[3] The entropy stresses in the macromolecules have to make the polymer functional groups more active. It is well known that if the functional groups of a substance become more accessible to a chemical reaction that it alters the preexponential multiplier on the Arenius equation. As a result, the process rate can increase even when the other thermodynamic parameters remain constant. For this reason probably, the extruder is more and more frequently used as a chemical reactor.[1]

A great number of reports about the various chemical processes during extrusion have appeared in literary sources. Our survey of literary sources, however, shows that the extrusion process in each concrete case has not been described thoroughly enough; more exactly, there are no data about the shear-rate magnitude and about where in the extruder the shear rate is high enough to accelerate the chemical process.

The theory of extrusion has been developed to perfection.[4] It enables us to get a full picture of the movement of the polymer in the extruder and of the shear rate and, respectively, the shear stresses that emerge. Also, irrespective of the well-developed theory of extrusion, the literary sources lack any data concerning the shear rate during the extrusion run of chemical reactions. It is known that during flowing the shear rate is always in equilibrium with the shear stress. But we examine mostly the shear rate, because it gives a clearer idea about the mechanism by which the macromolecules stretch, making their functional groups accessible. The shear rate, perpendicular to the cross section, leads to different speeds at the two ends of the molecular globule. The logical result of this is the stretching and orienting of the macromolecules. The

rheological properties of the polymers are a proof of that. The non-Newton flowing and the validity of the power law are the result of the changing conformation of the macromolecules during flowing. In this respect, it is necessary to point out that the so-called mixing screws actually do not increase the shear rate of the processed materials considerably.[5]

The compatibilization of polyamide–elastomer blends has gained particular attention in recent years due mainly to technological applications of these materials. In the area of engineering plastics, reactive blending is usually used to compatibilize immiscible polymers.[6,7] The presence of functional groups along the polymer chains can lead to specific interactions with the other blend constituents and the formation of a copolymer (graft or block). The latter can act as a compatibilizer for the blend, thus improving the physical and mechanical properties of the system. A successful approach is the blending of polyamide with maleated rubber. The maleic anhydride groups grafted onto the elastomer chains can react with polyamide amine end groups and form a graft copolymer which reduces the interfacial tension.[8] A phase morphology study of nonreactive and reactive polyamide blends with a styrene–acrylonitrile copolymer showed significant differences in the evolution of the blend morphology.[9] Reactive blending was achieved by introduction of an imidized acrylic polymer which is miscible in the styrene–acrylonitrile phase and had functional groups which were capable of reacting with the amine end groups in the polyamide phase.

Severyanova et al. reported that a chemical interaction proceeded between polyamide-6 (PA-6) and poly(butadiene acrylonitrile) (PBAN) during extrusion without discussing the mechanism of the reaction.[10] Mehrabzadeh and Delfan studied the dynamic crosslinking of the system PA-6 and PBAN as the best way to produce thermoplastic compositions with improved mechanical properties, resistance to attack by fluids, etc.[11]

Binary polymer blends containing a single crystallizable component have become a subject of our investigations. In a previous study, we established that during the extrusion of PA-6 and PBAN-40 the nitrile groups in the elastomer undergo chemical changes.[12] It is an interesting fact giving rise to the application of the reactive extrusion for compatibilization of the system without grafting of new reactive groups onto the elastomer chains or introduction of a compatibilizer.

The initial PBAN-40 is soluble in dichlorethane, but it does not dissolve in formic acid (HCOOH). This makes it fairly easy to determine to what extent the chemical reaction during extrusion has proceeded. It has been established the nitrile groups ($-C\equiv N$) are transformed into amide groups ($-CO-NH-$) and carboxyl groups (COOH) and the process runs more easily if the polyamide contains water. It was found

that a high shear rate (over 450 s^{-1}) is needed for the chemical transformation and blending of the polymers.

It was interesting to check if the same relations would be observed when butadiene–acrylonitrile copolymers, varying in nitrile group content, were used. We focused our investigation on the crystallization behavior and mechanical properties of the blended compositions as indicators of the nature and the extent of the interaction between the blend components.

EXPERIMENTAL

The work was carried out using the following polymers:

1. Polycaprolactam (PA-6), named "Vidlon," produced by the firm Vidachim (Bulgaria). The polymer has a molecular mass M of 23,000.
2. Polybutadiene–acrylonitrile elastomer CKH-40, produced in Russia. Its average molecular mass is 250,000. The elastomer that we used contains 40% acrylonitrile.
3. Polybutadiene–acrylonitrile elastomer CKH-26, produced in Russia. The elastomer that we used contains 26% acrylonitrile.
4. Polybutadiene–acrylonitrile elastomer CKH-18, produced in Russia. The elastomer that we used contains 18% acrylonitrile.
5. Polybutadiene–acrylonitrile elastomer, named "Perbunant," produced in France. The elastomer that we used contains 40% acrylonitrile.

A single-screw extruder was used with a diameter $D = 45$ mm, a channel depth in the feeding zone of 8 mm, and a channel depth in the end of the compression zone of 2.5 mm. The extruder was equipped with a head of changeable dies that also altered the shear rate. Extrusion at high shear rates (475 s^{-1}) was carried for the composites shown in Table I.

TABLE I
Composites Extruded at a Shear Rate of 475 s^{-1}

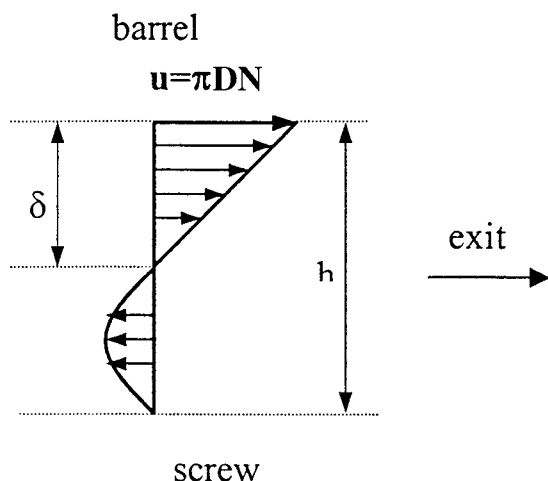| No.	CKH-18 (%)	CKH-26 (%)	CKH-40 (%)	Perbunan (%)	PA-6 (%)
1	10				90
2	20				80
3	30				70
4		10			90
5		20			80
6		30			70
7			10		90
8			20		80
9			30		70
10				30	70

Figure 1 Profile of the rate in the screw channel.

^{13}C-NMR spectra were measured on a Bruker D RX 500-MHz instrument in the solid state. The IR spectra were recorded on a Bruker IFS 113V spectrometer with a resolution of 2 cm^{-1}. The DTA analysis was performed on an Erdey (Paulik &Paulik, Hungary) instrument with scanning rate of 5°C/min.

The tensile strength was determined using a "Schopper" dynamometer according to the ISO 6239/1996 standard with a constant crosshead speed of 50 mm/min. The notched impact strength was measured according to standard BDS 2991.

RESULTS AND DISCUSSION

Selecting the regime for reactive extrusion

Knowing that the shear rate in the extruder is of decisive importance for the run of the process, we had to develop a methodology for carrying out the process at a defined shear rate. The theory of McKelvey[4] about extrusion provides an excellent description of the process. The profile of the rate in the screw channel in the most common case is shown in Figure 1.

In the upper part, the polymer melt moves toward the screw outlet, whereas in the lower part, it moves at a certain angle in the opposite direction. A higher average shear rate emerges in the upper part of the flowing polymer. The shear rate (γ) is determined by the formula

$$\gamma = \frac{\pi DN}{\delta}, \text{ s}^{-1} \tag{1}$$

where D is the screw diameter (mm); N, the screw revolutions (s^{-1}); and δ, the distance from the zero line to the barrel (mm).

As the channel depth varies along the screw length, the shear rate increases toward the extruder outlet. We established that it does not exceed 150 s^{-1} and it is insufficient for the complete run of the chemical process.[13] It is interesting to point out that when mixing parts are worked out in the screw channel the shear rate does not change considerably. At a low shear rate, only the so-called distributive mixing occurs, not dispersive mixing.[14]

This necessitated the development of a method for maintaining a higher shear rate in the extruder's head. As known,[4] grids and nets are usually placed there. The grids are massive metal parts, with round orifices, through which the polymer melt flows. Grids with a different number of orifices and different diameters of the same could be worked out, which is shown in Figure 2. The rate in each orifice is determined by the formula

$$\gamma = \frac{4Q}{\pi R^3}, \text{ s}^{-1} \tag{2}$$

where Q is the volumetric flow rate of the polymer flowing through each separate channel (mm^3/s), and R, the radius of the orifices (mm).

The cutting stress (σ), which emerges during flowing, depends on the geometric dimensions and the pressure of the polymer melt:

$$\sigma = \frac{PR}{2L} \tag{3}$$

where P is the pressure at the extruder's end (Pa), and L, the length of the orifice in the grid (mm). The stress itself depends on the shear rate by the power law:
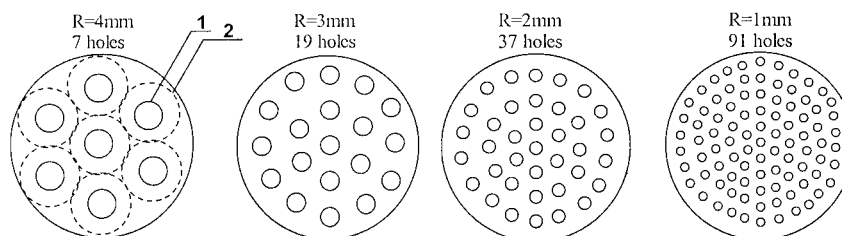

Figure 2 Scheme of the grates used in the extruder's die: (1) holes of the grate; (2) conical entrance of the holes.
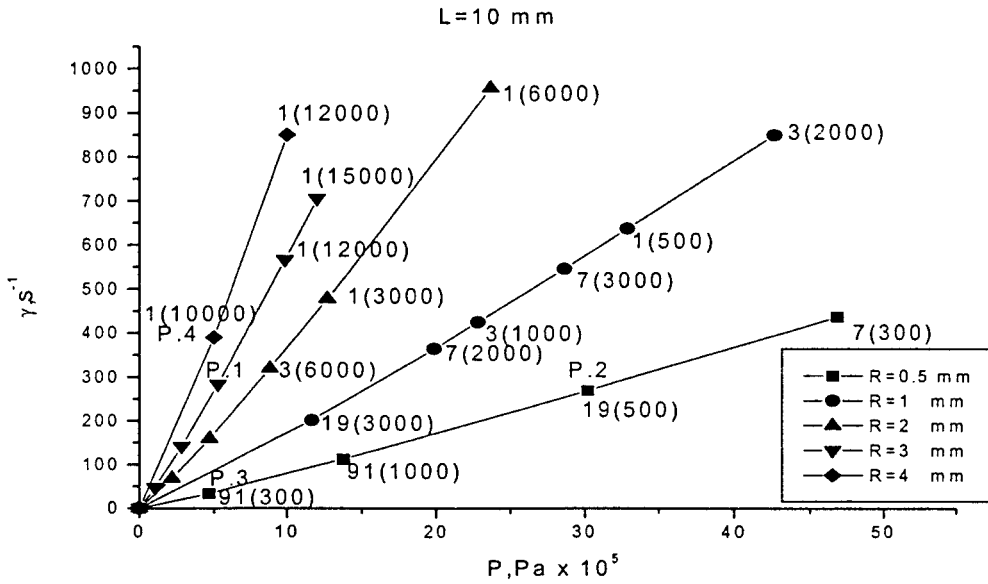
Figure 3 Dependence of the pressure (P) at the end of extruder on the shear rate (γ) in the die for grates with different radii (R); data are labeled A(B000), where A is the number of the orifices and B000 is the flow rate (mm^3/s).

$$\sigma = k\beta^n \qquad (4)$$

where k is the coefficient of proportionality, called the "coefficient of consistency"; β, the true shear rate (s^{-1}); and n, the index of flowing. When instead of the true shear rate (β) the average one (γ) is used, then k_R is the Rabinovich corrector:

$$\sigma = \kappa_R \gamma^n \qquad (5)$$

By introducing the value of σ in eq. (3), we obtain at constant length (L)

$$P = \frac{2L}{R}\gamma^n K_R = \frac{\text{const}}{R}\gamma^n \qquad (6)$$

For polyamide and its composites with PBAN, the index of flowing n is over 0.9 (very close to 1). This dependence explains why, when the shear rate is calculated depending on the pressure before the grid with a constant length, the dependencies, shown in Figure 3, are obtained.

Irrespective of the number of the orifices in the grid, the shear rate depends only on the pressure and, respectively, on the debit. For each radius, this is a separate
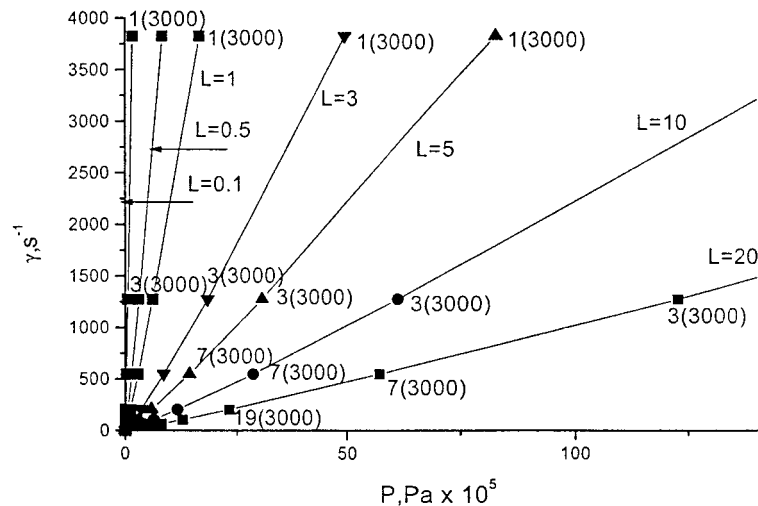

Figure 4 Dependence of the pressure (P) at the end of extruder on the shear rate (γ) in the die for grates with different lengths of the channels and constant radius $R = 1$ mm; data are labeled A(B000), where A is the number of the orifices and B000 is the flow rate (mm^3/s).
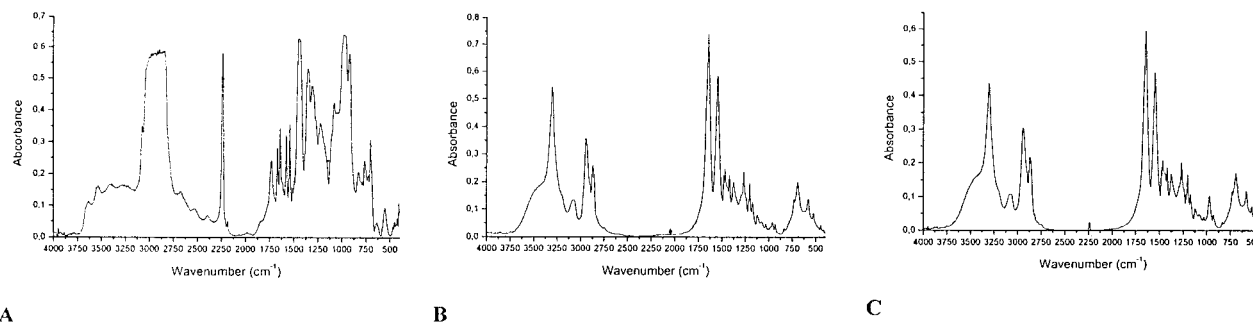
Figure 5 IR spectra of (A) PBAN-40, (B) PA-6, and (C) extrudate from 70% PA-6 and 30% PBAN-40.

independent straight line. This makes possible the construction of grids, in which the desired shear rate emerges, which gradually can be adjusted depending on the melt-flow rate, which, in turn, depends on the revolutions of the screw. If we keep R and the flow rate constant, then the dependence shown in Figure 4 is obtained. Consequently, the shear rate can be adjusted within broad limits and depending on the length of the channels (thickness of the grid).

Solubility in formic acid

All extrudates are soluble with the exception of composite no. 3 from Table I. It was found that when the content of nitrile groups in the elastomer is high they not only transformed into amide groups, but participated in exchange reactions with the amide groups in PA-6. We suppose that three-dimensional molecular crosslinking occurs.

In all composites, 5–7% of the mixture remains, which dissolves in the acid colloidally, and after a certain stay, it becomes liberated upon the surface of the solution. We suppose that it is the copolymer, containing mainly the polybutadiene polymer.

Analysis of the product

Analyses of the obtained product and of the initial polymers were carried out using infrared spectros-

copy. Figure 5 shows IR spectra of PA-6, CKH-40, and the product. The spectrum of the extrudate containing 30% w/w of the elastomer component and that of PA-6 are very similar. Nevertheless, a change in the peak intensity of the nitrile group (2238 cm^{-1}) is observed. A semiquantitative estimation was done by the comparison of the ratios between the peak absorbances at 2238 and 970 cm^{-1} (*trans* RCH=CHR) recorded in the spectrum of the CKH-40 and that of the blend calculated to be 1.08 against 0.31. This considerable decrease in the ratio (more than three times) for the characteristic bands of PBAN shows that the nitrile groups of the rubber change chemically.

A nuclear magnetic spectrum of the extrudate precipitated from the formic acid solution into water was taken. As visible from the spectrum (Fig. 6), the signal for the nitrile groups at 120 ppm shows only traces, while at 248 ppm, there is a peak, characteristic for a carbonyl group, different from the amide group, which gives a peak at 173 ppm.

These results led us to the conclusion that the nitrile groups of rubber during extrusion with PA-6 hydrolyze to amide groups, and if there is enough humidity, even to carboxyl groups. Between the amide and the carboxyl groups of the elastomer and the amide groups of PA-6, salt and hydrogen bonds are probably formed, resulting in durable polymer complexes:
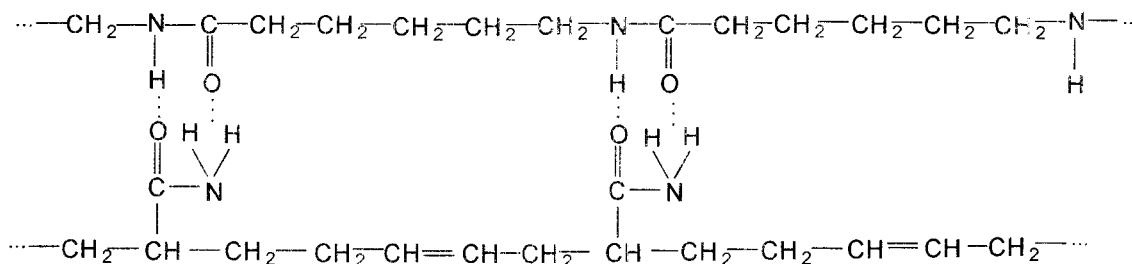
It has been reported[15,16] that polyamide macromolecules can graft onto other polymer chains if the latter

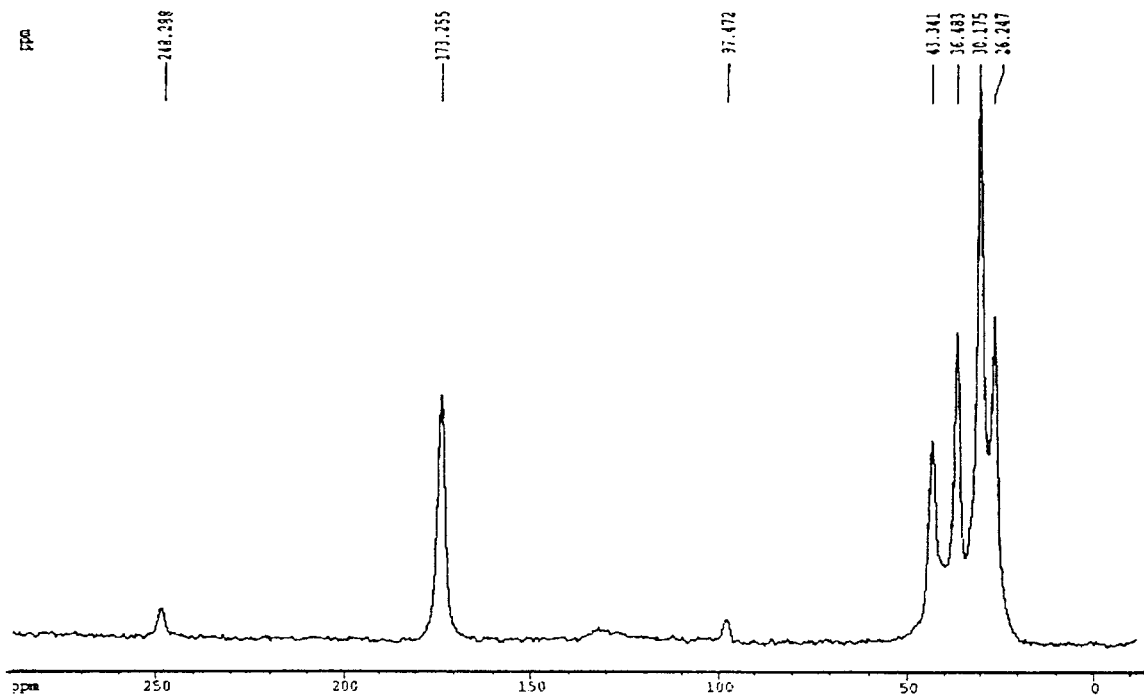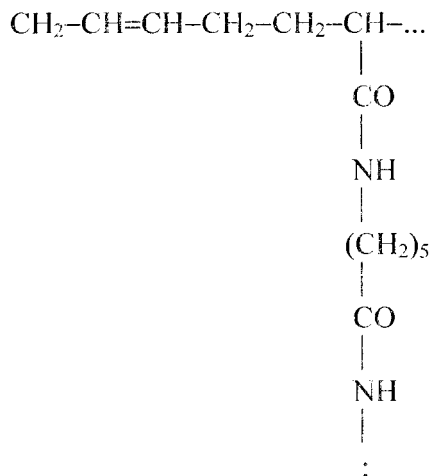bear carboxylic or amide groups. Considering the above during the extrusion of PA-6 and PBAN,

Figure 6 ^{13}C-NMR spectrum of extrudate from 70% PA-6 and 30% PBAN-40.

grafted macromolecules are probably formed with the following structure:

$$CH_2-CH=CH-CH_2-CH_2-CH-...$$
$$|$$
$$CO$$
$$|$$
$$NH$$
$$|$$
$$(CH_2)_5$$
$$|$$
$$CO$$
$$|$$
$$NH$$
$$|$$
$$:$$

Crystallinity

It has been found that the degree of crystallinity of the obtained products drastically decreases. Even composition nos. 5, 6, 8, 9, and 10, containing high concentrations of nitrile groups in the initial mixture, are optically entirely amorphous. In a polarized microscope at crossed polarizers, complete extinction of the light is observed.

During DTA, however, a slight endothermic deviation is observed, corresponding to the temperature of the melting of PA-6. This means that very small crys-

tals are formed, invisible with a polarized microscope. The percentage of crystals in mixture no. 9 is 14.8% of the crystallinity of the pure PA-6 (Fig. 7).

Mechanical indices

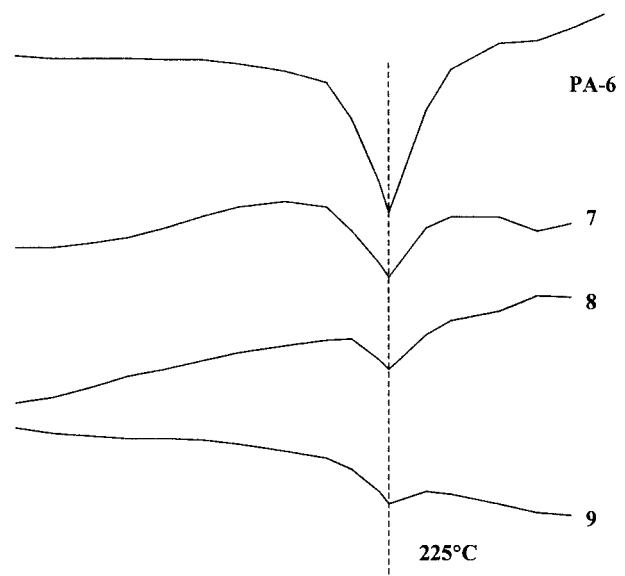The tensile strength and impact strength of the mixtures (given in Table I) were determined after their

Figure 7 Variation of the endothermic peak at 225°C in the DTA thermograms of PA-6 and composites nos. 7, 8, and 9 (listed in Table I).
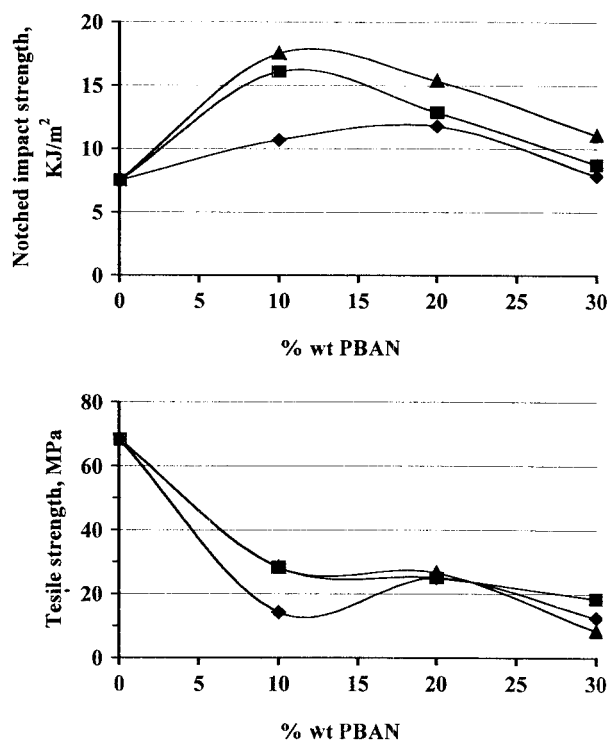
Figure 8 (A) Notched impact strength and (B) tensile strength of extrudates consisting of PA-6 with different percentages of PBAN: (♦) CKH-18; (■) CKH-26; (△) CKH-40.

extruder processing. The results are shown in Figure 8 and the mechanical behavior of the blends can be explained by supramolecular structure formations. The high content of nitrile groups in PBAN favors its chemical modification and, consequently, the compatibility with PA-6, which is displayed in higher values for the notched impact strength.

CONCLUSIONS

The results show that during the extrusion of composites of PA-6 and the PBAN elastomer chemical transformation of the nitrile groups occurs. Both polymers become more compatible and mainly amorphous. This can be used for producing polyamide products with increased impact strength.

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