Effects of Processing Parameters on the *In Situ* Compatibilization of Polypropylene and Poly(butylene terephthalate) Blends By One-step Reactive Extrusion

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SYNOPSIS

This paper concerns the effects of processing parameters on the *in situ* compatibilization of polypropylene (PP) and poly(butylene terephthalate) (PBT) blends by one-step reactive extrusion in a corotating intermeshing twin screw extruder. This *in situ* compatibilization process was characterized by a sequential arrangement for the free radical grafting of glycidyl methacrylate (GMA) onto PP and the interfacial compatibilization reaction between the GMA functionalized PP and the terminal carboxylic group of the PBT. Among the processing parameters examined were feed rate (Q), screw speed (N), and specific throughput (Q/N). Their effects were evaluated by the associated mechanical properties of final blends in terms of elongation at break and impact strength. Results showed that elongation at break and impact strength increased virtually linearly with decreasing Q or N. Moreover, for a particular Q/N, they increased with decreasing Q with a concomitant decrease in N. Further analysis of these results showed that it is through residence time that these parameters affect the performance of the above mentioned *in situ* compatibilization process. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Mechanical properties of a polymer blend are directly associated with its morphology and interfacial adhesion between the various phases. When a polymer blend is made in a modular corotating intermeshing twin screw extruder, for example, processing parameters which affect the blend morphology include temperature profile, screw configuration, screw speed, and feed rate. On the other hand, as large as the effects of these processing parameters are, a desired and stabilized morphology of an immiscible polymer blend with sufficiently strong interfacial adhesion can be obtained only when an appropriate interfacial agent (compatibilizer) is present. Well-known compatibilizers are block or graft copolymers that locate preferentially at the interface. As a result, they tend to reduce interfacial tension, strengthen the interfacial adhesion, and prevent coalescence.[1] However, if a particular compatibilizer had to be synthesized separately for a particular pair of immiscible polymers, "polymer blend" would have been nothing else but an academic term. This is due to difficulties in designing and synthesizing these particular molecules at an industrial scale.

Recently, increasing effects have been directed towards *in situ* compatibilization of immiscible polymer blends by reactive extrusion[2,3]: Instead of synthesizing compatibilizers as a separate step, they are created during extrusion through interfacial reactions between selected functional polymers. Not all polymers contain functional groups. When a polymer bearing functional groups is to be mixed with another polymer which is chemically inert with respect to these functional groups, the latter ought to be functionalized. Free radical grafting of a monomer bearing desired functional groups is employed the most for functionalizing chemically inert polymers. In this case, two reactive blending processes are conceivable: (a) the chemically inert

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Table I   Selected Properties of the PP and PBT Used in This Study

	$\bar{M}_n$ (kg/mol)	$\bar{M}_w$ (kg/mol)	Melting Point (°C)	Viscosity at 260°C and 450 s^{-1}	Carboxylic Group (eq/kg)	Hydroxyl Group (eq/kg)
PP	141	654	165	290	—	—
PBT	28	65	223	200	0.040	0.032

polymer is functionalized as a separate extrusion step, and the polymer thus functionalized is then blended with the functional polymer in a second extrusion step; (b) both the functionalization and blending steps are executed in the same extrusion process. For example, functionalization can be carried out in the first part of the extruder, followed by subsequent interfacial reaction between the functional and functionalized polymers. Process (a) is called *in situ* compatibilization of immiscible polymers by two-step reactive extrusion and process (b) is called one-step reactive extrusion. The feasibility and advantages of the latter process have been demonstrated by our recent work.[4,5]

The objective of this study was to investigate the effects of processing parameters on the *in situ* compatibilization of polypropylene (PP) and poly(butylene terephthalate) (PBT) blends by one-step reactive extrusion in a co-rotating intermeshing twin screw extruder. Those processing parameters were feed rate (Q), screw speed (N), and specific throughput (Q/N). Their effects were evaluated by the mechanical properties of the final blends in terms of elongation at break and impact strength. A bifunctional monomer, glycidyl methacrylate (GMA), which bears a double bond and an epoxy group, was chosen to functionalize PP by free radical grafting.

EXPERIMENTAL

Materials

The PP used in this study was a commercial grade of Himont (Valtec CL101D). It was in the form of

porous pellets which were capable of absorbing larger amounts of liquid monomers and peroxides than normal PP pellets. The PBT was a commercial grade of DSM (Arnite T08-200). Selected characteristics of those two polymers are gathered in Table I.

The functional monomer, GMA, was purchased from Aldrich and used as received. Styrene was used for assisting the free radical grafting of GMA. It was also purchased from Aldrich and used without further purification. The free radical grafting of GMA was initiated by 1,3-bis(*tert*-butylperoxy-isopropyl)benzene, a commercial grade of Akzo (Perk-14; purity: 90%). Its half lifetime is about 30 sec at 200°C and about 2 sec at 240°C.

An intermeshing co-rotating twin-screw extruder (Werner & Pfleiderer ZSK-30) was used (screw diameter D = 30 mm; screw length-to-diameter ratio L/D = 42). The screw and temperature profiles used are shown in Figure 1. Basically, the extruder was divided into two functional zones: the free radical grafting of GMA onto PP in the first part of the extruder, and the interfacial compatibilization reaction between PP-g-GMA and the carboxylic group of the PBT for the rest of the extruder.

The PP, the monomers, and peroxide were fed together through the first hopper, located at the rear of the extruder. This mixture was conveyed first with regular right-handed screw elements and then melted and homogenized with the help of combined kneading block (KB90/5/28) and a left-handed screw element (−20/10). It was shown in a previous work[6] that the free radical grafting of GMA onto

PP + Reagents   PBT

|——————— 200°C ———————|——————————— 240°C ———————————|

Solids conveying,   PBT melting   Mixing and reaction   Devol.   Pumping
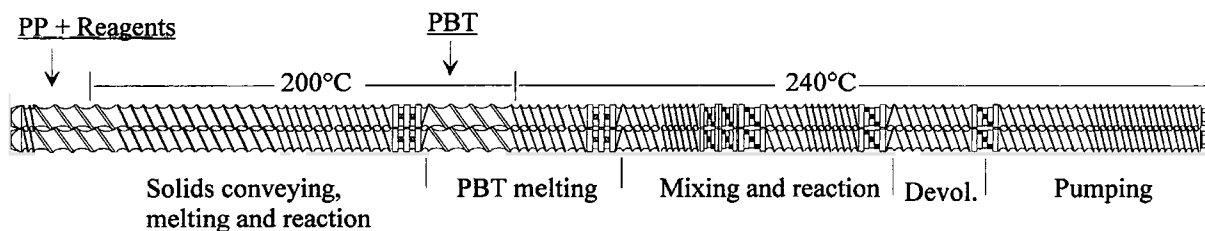melting and reaction

Figure 1.   Screw and temperature profiles used for the PP/PBT blending.

PP almost went to completion when the reacting mixture passed through the melting zone. The PBT was fed thereafter through a second hopper. The barrel temperature was raised to 240°C in order to melt the PBT and to promote the subsequent interfacial reaction between the GMA grafted PP and the carboxylic group of the PBT. Several kneading blocks were placed after the feeding point of the PBT in order to melt the PBT and to ensure sufficient mixing for the interfacial reaction. A devolatilization zone was created in the last zone of the extrusion process to remove volatile products before the blend exited the die. The vacuum in that devolatilization zone was about 25 mm Hg.

As the focus of this study was on the processing aspect of the problem, the composition of the PP/PBT blends was fixed at 70/30 by weight. The initial concentrations of the monomers and peroxide were $[GMA]_i = 1.40$ phr (gram per 100 grams of PP); $[styrene]_i/[GMA]_i = 1.40$ mol/mol; $[Perk-14]_i = 0.30$ phr. Appropriate amounts of the liquid monomers and the peroxide were mixed with the porous PP pellets at room temperature for about an hour before being fed to the extruder. The PBT pellets were dried at 105°C under a hot air circulation overnight. The extrusion process was carried out under a constant nitrogen purge. Extrudates were cooled in water and then pelletized for further analyses.

GMA Grafting Yield Measurement

The amount of the GMA grafted onto the PP was measured just before the feeding point of the PBT. Samples were taken therefrom and then quenched immediately in liquid nitrogen. They were dissolved in hot xylene and precipitated in a large amount of acetone at room temperature so that residual monomers and possible homo- and/or copolymers of GMA and styrene were washed out. Those extruded samples were also dissolved in hot xylene and then precipitated in methanol. In this way, the total amounts of the homo- or copolymers of GMA and styrene were obtained.[7] Purified PP samples were pressed into films and then passed through a Fourier-Transform infrared spectrometer to determine GMA grafting yields.

Morphological and Mechanical Characterization

The effects of the aforementioned processing parameters on the *in situ* compatibilization of the PP/PBT blends were evaluated by their morphology and mechanical properties (elongation at break and impact strength).

The morphology of selected PP/PBT blends was examined by scanning electron microscopy (SEM) on the fresh fractured and gold-sputtered surface of the specimens to be used for tensile testing. The middle part of the cross section of the specimens was chosen as being representative of the morphology.

The tensile test (ASTM 638-71A) provided the values of Young's modulus (M), yield strength (σ_y), and elongation at break (ε_b) of the blends, while the impact test (ISO 6603/2) gave those of impact strength. The specimens for the tensile and impact tests were made with an injection-molding machine of type Billion 50. The temperatures in all zones of the injector were at 240°C, and that in the mold was 80°C. Prior to injection molding, the pellets of the polymer blends were dried at 105°C under a hot air circulation overnight. Before the tensile or impact testing, the specimens stood at room temperature for at least three days.

The tensile test was carried out with a mechanical testing machine of type Instron 8031 at room temperature. The tensile rate was 50 mm/min. Five specimens were tested for each blend sample, and the average was taken as the final value. The impact test was done at 0 and -20°C with a Rosand falling weight impact tester (IFWI-5). The inner diameter of the support was 40 mm, and that of the hemispherical striker was 10 mm. The striker weighed 25 kg. The diameter and thickness of specimens were 50 and 3 mm, respectively. Here again, five specimens were tested for each blend sample, and the average was taken as the final value.
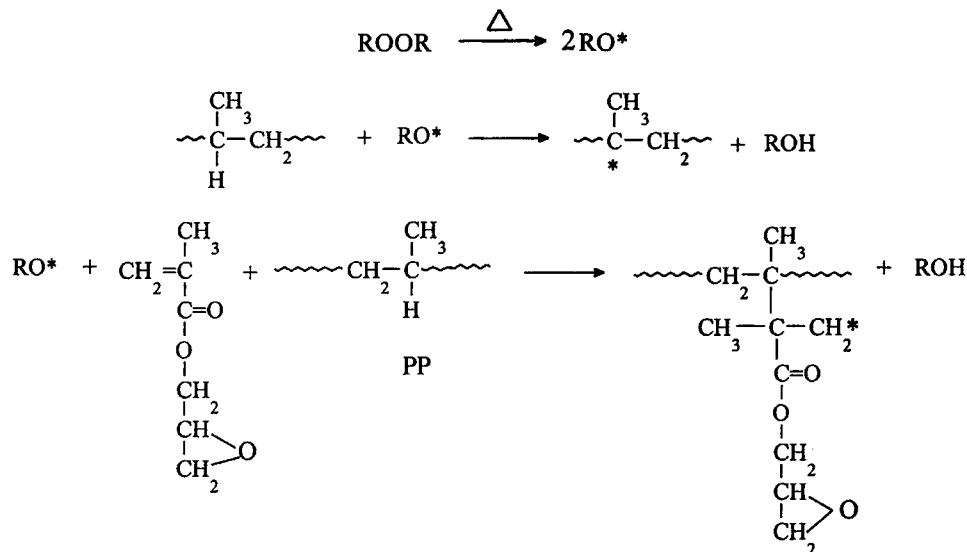
Residence Time Distribution Measurement

Being a measure of macromixing, the residence time distribution (RTD) is an important parameter for reactive extrusion processes. Because the PP/PBT blend is a rheologically complicated system, a polystyrene (1240H of Atochem) was chosen as a model polymeric fluid, which allowed us to appreciate the effects of selected processing parameters on the RTD. A UV-sensitive substance, 1-aminoanthraquinone, was used as a tracer. The RTD measurements were done with the same screw configuration as that used for making the PP/PBT blends, except that the barrel temperature profile was now set at 200°C all along the screw length. The tracer (1 wt %) was dispersed in the PS in a Haake batch mixer at 200°C and then pelletized into small particles having a similar

size of the PS pellets. Those concentrate pellets were injected into the extruder through the hopper as a pulse after the extrusion process was steady. Samples were collected at the die at chosen time intervals and cut in the direction perpendicular to that of the flow. The tracer concentrations were determined by UV spectrophotometry. The reproducibility of the RTD measurements was found to be good by comparing repeated experiments. Further experimental details can be found elsewhere.[8]

RESULTS AND DISCUSSION

The underlying chemistry used for compatibilizing the PP/PBT blend involves free radical grafting of GMA onto PP (free radical reactivity), followed by interfacial reaction between the functionalized PP and PBT (functional reactivity). The intended chemistry for the PP/PBT system can be represented as follows:

Free radical reactivity: grafting of GMA onto PP[6,7]:

$$ROOR \xrightarrow{\Delta} 2RO*$$

$$\underset{\substack{| \\ H}}{\overset{\substack{CH_3 \\ |}}{\sim\sim C}}-CH_2\sim\sim + RO* \longrightarrow \underset{*}{\overset{\substack{CH_3 \\ |}}{\sim\sim C}}-CH_2\sim\sim + ROH$$

$$RO* + \underset{\substack{| \\ C=O \\ | \\ O \\ | \\ CH_2 \\ | \\ CH_2}}{\overset{CH_3}{CH_2=C}}\!\!\!\!\!>O \quad + \quad \sim\sim\sim CH_2-\underset{\substack{| \\ H}}{\overset{CH_3}{C}}\sim\sim\sim \; (PP) \longrightarrow \sim\sim CH_2-\underset{\substack{| \\ CH_3-C-CH_2* \\ | \\ C=O \\ | \\ O \\ | \\ CH_2 \\ | \\ CH_2}}{\overset{CH_3}{C}}\!\!\!\!\!>O \sim\sim\sim + ROH$$

Functional reactivity: formation of the PP-g-PBT copolymer through interfacial reaction between the GMA grafted PP and the PBT[4,5]:

$$\underset{\substack{CH_3-C-CH_2* \\ | \\ C=O \\ | \\ O \\ | \\ CH_2 \\ | \\ CH_2}}{\overset{CH_3}{\sim\sim\sim CH_2-C}}\!\!\!\!\!>O \quad + \quad HOOC\sim\sim\sim OH \;(PBT) \longrightarrow \underset{\substack{CH_3-C-CH_2* \\ | \\ C=O \\ | \\ O \\ | \\ CH_2 \\ | \\ CH-OH \\ | \\ CH_2 \\ HO\sim\sim\sim C-O}}{\overset{CH_3}{\sim\sim\sim CH_2-C}} \;(PBT)$$
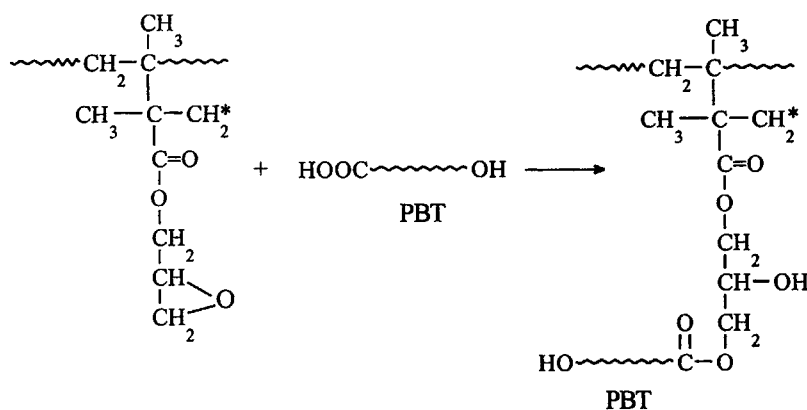
As shown in Figure 1, these two chemical reactions are arranged in a sequential manner. Early work[4,5] showed that they are very efficient for compatibilizing PP/PBT blends. This is also confirmed by the change in morphology of the PP/PBT blend with and without compatibilization. As shown in Figure 2, while the particle size of the dispersed phase (PBT) in the mechanical blend is large and the cohesion between the PP and PBT phases is
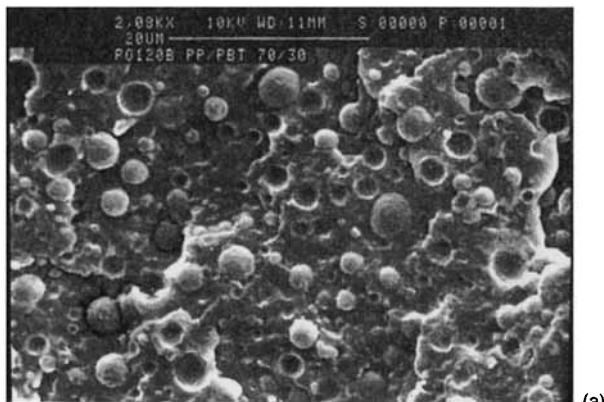
(a)
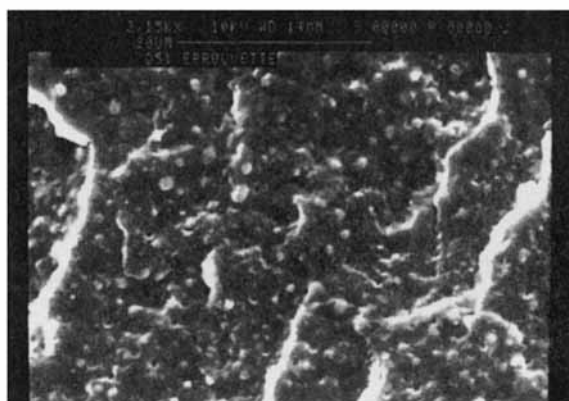
(b)

Figure 2 Photographs of the mechanical and compatibilized PP/PBT (70/30) blends: (a) mechanical blend; (b) compatibilized blend.

weak, it is greatly reduced in the compatibilized blend, and the interfacial adhesion is improved. Below, we will discuss how processing parameters (Q, N, and Q/N) affect the compatibilization performance in terms of mechanical properties.

Effect of Feed Rate

The elongation at break and the impact strength of the compatibilized PP/PBT blend as a function of feed rate (PP + PBT) are shown in Figures 3 and 4, respectively. Very interestingly, both the elongation at break and the impact strength (at two testing temperatures: 0 and $-20°C$) decrease almost linearly with increasing feed rate.
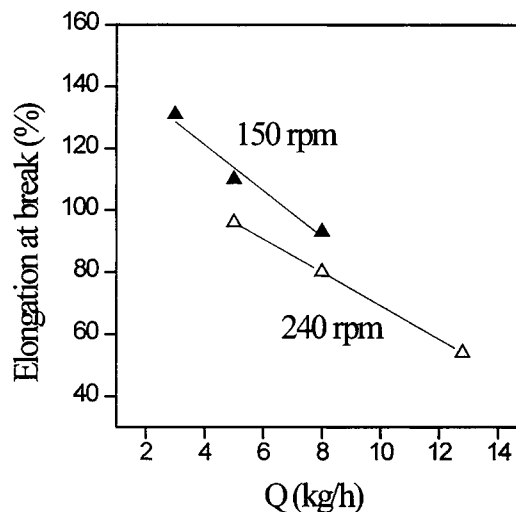
Figure 3 Variation of the elongation at break of the compatibilized PP/PBT blend as a function of feed rate (PP + PBT) at given screw speeds (150 and 240 rpm).

An increase in Q reduces residence time and probably spatial mixing as well. When Q increases, the residence time the material has experienced should decrease both in the first part of the screw length (free radical grafting of GMA) and in the second part (formation of the PP-g-PBT copolymer through interfacial reaction). Thus, both the GMA grafting yield and the rate of formation of the PP-g-PBT copolymer would decrease. Indeed, a previous work showed[6] that the GMA grafting yield at the
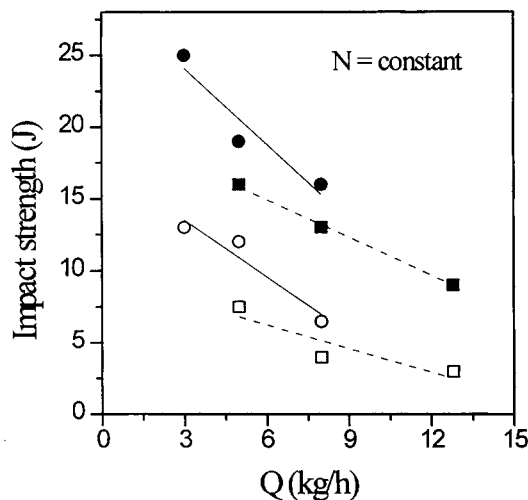
Figure 4 Variation of the impact strength of the compatibilized PP/PBT blend as a function of feed rate (PP + PBT). ●, 150 rpm and 0°C; ○, 150 rpm and $-20°C$; ■, 240 rpm and 0°C; □, 240 rpm and $-20°C$.

feeding point of the PBT decreased with increasing Q. As for the rate of formation of the PP-g-PBT copolymer, it was appreciated indirectly using a model reacting system. The latter was composed of

a copolymer of ethylene, ethyl acrylate and GMA, and 1-naphthylacetic acid. As reported in a previous work,[9] the main reaction of this system should be as follows:
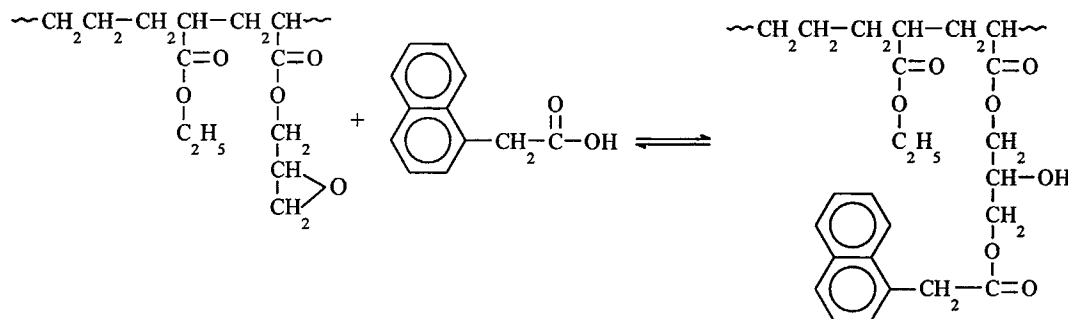
The three monomers involved in the copolymer (ethylene, ethyl acrylate, and GMA) weighed 68.0, 24.0, and 8.0 wt %, respectively. This copolymer had a number molecular weight of about 10,000 g/mol with a melting temperature ranging from 36 to 80°C. In order to best simulate the reaction between the GMA grafted PP and the carboxylic group at the chain end of the PBT, the model reaction was carried out in the extruder with the same screw and temperature profiles as those used for making the PP/PBT blends (Figure 1) and with the screw speed set at 150 rpm. Before being fed to the extruder, the copolymer pellets and the acid were premixed. Shown in Figure 5 is the conversion of the acid along with the screw length. It reached 78.5% at the exit of the die when the feed rate of the copolymer and

the acid was 3.0 kg/h. When the total feed rate was raised to 5.0 kg/h, the conversion was reduced to 73.4%. Clearly, the decrease in conversion with increasing Q is attributed mainly to a reduced residence time. Thus, the PP/PBT blend should be better compatibilized with decreasing Q.

Effect of Screw Speed

An increase in N reduces residence time and enhances mixing intensity. The outcome of these two opposing effects is that the elongation at break and impact strength of the compatibilized PP/PBT blend decrease with increasing N (Figs. 6 and 7).
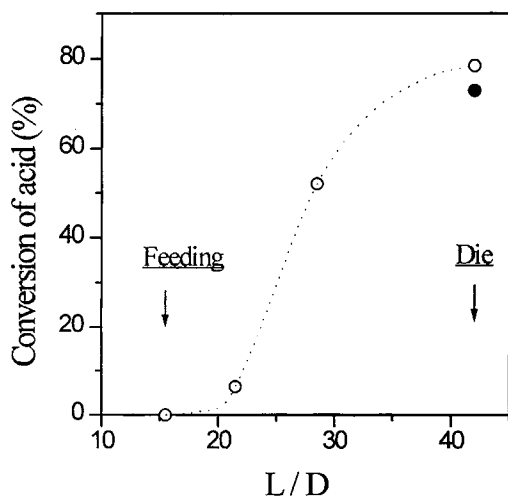
Figure 5 Acid conversion along the screw length: $\bigcirc$, Q = 3 kg/h; $\bullet$, Q = 5 kg/h. N = 150 rpm; the acid concentration is 5 phr with respect to the copolymer.
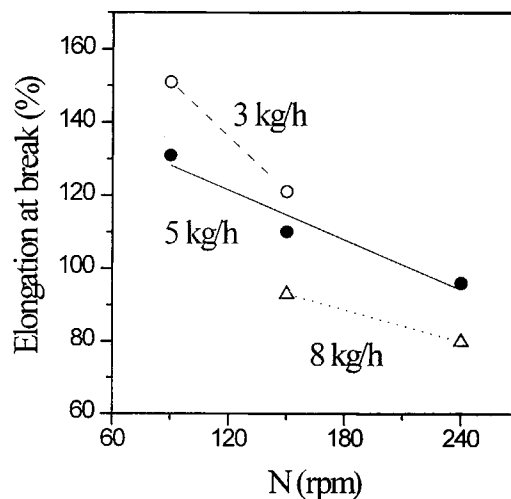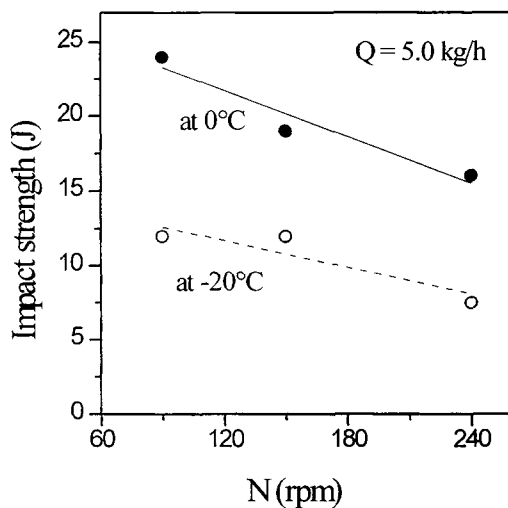
Figure 6 Variation of the elongation at break of the compatibilized PP/PBT blend as a function of screw speed for three different feed rates.

Thus, increasing N amounts to increasing Q in terms of a decrease in the elongation at break and impact strength of the compatibilized PP/PBT blend.
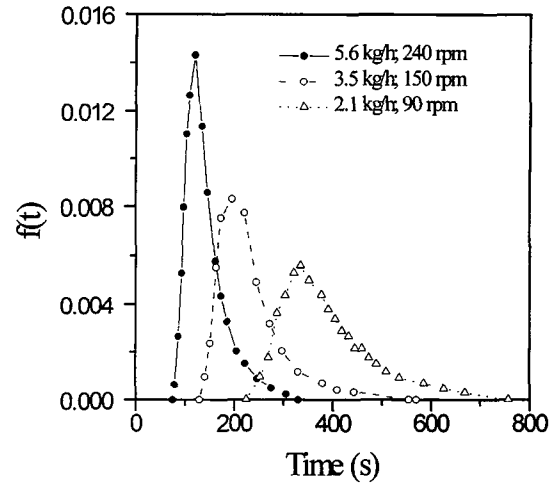
As discussed above, an increase in Q or N shortens the residence time. On the other hand, an increase in N enhances mixing intensity, whereas an increase in Q reduces it. Thus, the fact that increasing Q or N has the same effect on the elongation at break and impact strength should be related only to residence time. In other words, residence time should be the primary parameter that governs the performance of this *in situ* compatibilization process.
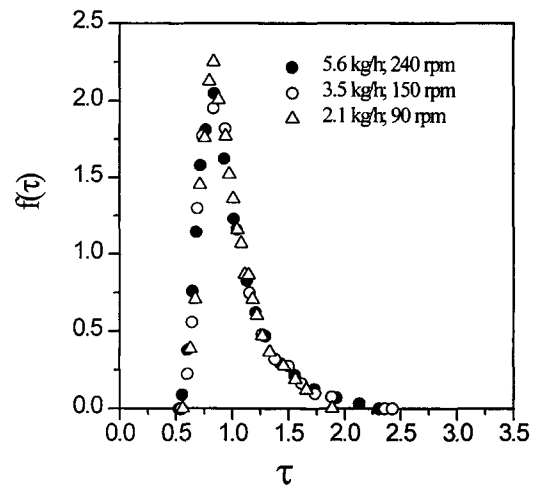
Effect of Specific Throughput

In order to further support the fact that it is through residence time that Q or N affects the mechanical properties of the *in situ* compatibilized PP/PBT blend, the effect of specific throughput is examined. Specific throughput is defined as the ratio of throughput over screw speed, Q/N, with a unit of (kg/h)/rpm. As discussed elsewhere,[10,11] Q/N measures, to some extent, the pumping capacity of a particular twin screw extruder (the amount of material each turn of screw can pump). It also characterizes the degree of fill of a twin screw extruder in partly filled zones. The reverse of this ratio, N/Q, has a unit of rpm/(kg/h). It can be viewed as being the number of screw turns a unit amount of material has experienced before it exits from the extruder. Thus, it measures the mixing intensity the material has experienced in the partly filled zones.
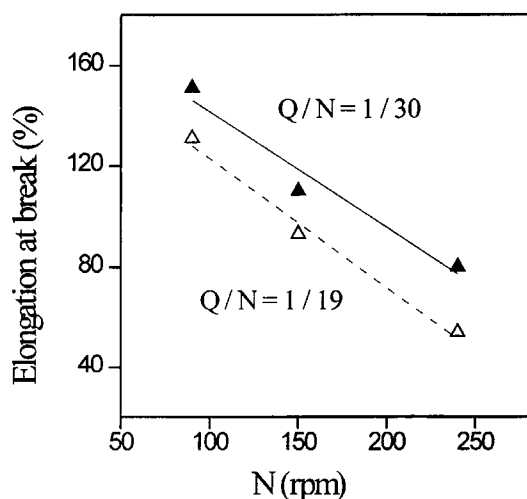
Figure 8 Residence time distribution density function as a function of time for three different feed rates and screw speeds with a particular Q/N (1/43): (a) $f(t)$ versus t; (b) $f(\tau)$ versus τ. Polymeric fluid was polystyrene ($Q = 3.5$ kg/h).
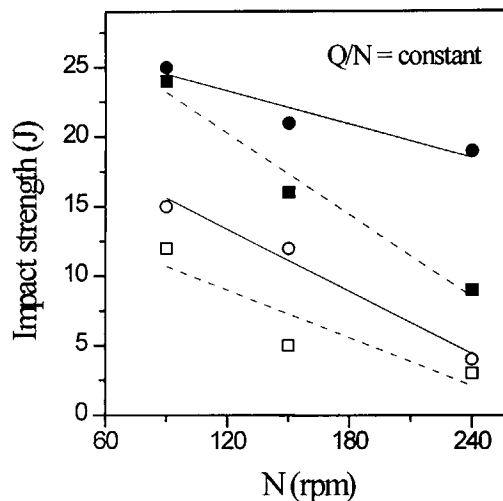
If pressure flow in a twin screw machine due to the die resistance and/or other pressure consumers (kneading blocks, left-handed screw elements, etc.) is unimportant with respect to drag flow, Q/N and N/Q then characterize the average degree of fill and the mixing intensity of the extruder, respectively. If this is true, unlike a change in Q or N, which affects not only residence time but also mixing intensity, variations in Q and N at the same time with the same proportion for a particular Q/N will change residence time distribution only.

Figure 7 Variation of the impact strength of the compatibilized PP/PBT blend as a function of screw speed for a particular feed rate ($Q = 5.0$ kg/h).

The residence time distribution density function $f(t)$ as a function of time for a given Q/N (1/43 kg/rpm) is shown in Figure 8(a) for three different feed rates and screw speeds. The corresponding dimensionless residence time distribution density function $f(\tau)$ as a function of dimensionless time τ ($\tau = t/\bar{t}$ with $\bar{t}$ being the mean residence time) is shown in Figure 8(b). The $f(t)$ curve is shifted to a shorter time domain when Q and N are increased concomitantly [Fig. 8(a)]. Interestingly, the three $f(t)$ curves in Figure 8(a) superimpose well when they are converted to the $f(\tau)$ curves [Fig. 8(b)]. This means that when Q/N is fixed, a variation in Q with a concomitant change in N changes only the residence time, while the longitudinal mixing remains unchanged.

Shown in Figures 9 and 10 are the variation of the elongation at break and that of the impact strength of the compatibilized PP/PBT blend as a function of N for two particular specific throughputs (Q/N = 1/30 and 1/19 kg/h/rpm). Keep in mind that for a given Q/N, an increase in N corresponds to a concomitant increase in Q, and vice versa. It is seen that the elongation at break and impact strength decrease virtually linearly with increasing N, which in turn reduces residence time. Thus, it can be concluded that residence time controls the *in situ* compatibilization performance of the PP/PBT blend by the one-step reactive extrusion process chosen in this study.

Figure 10 Variation of the impact strength of the compatibilized PP/PBT blend as a function of screw speed for two particular specific throughputs (Q/N = 1/30 and 1/19 kg/h/rpm), ●, 0°C; ○, -20°C; ■, 0°C; □, -20°C.

CONCLUSIONS

In this study, the effects of processing parameters on the *in situ* compatibilization of PP and PBT blends by one-step reactive extrusion have been investigated in a corotating intermeshing twin screw extruder. Among the processing parameters examined are feed rate (Q), screw speed (N) and specific throughput (Q/N). Their effects have been evaluated by the associated mechanical properties of the PP/PBT blends in terms of elongation at break and impact strength. Results have shown that the latter increases virtually linearly with decreasing Q or N. Moreover, for a particular Q/N, they decrease almost linearly with a concomitant increase both in Q and N. Further analysis of these results have led to the conclusion that the effects of these processing parameters are dictated primarily by residence time (macromixing).

Figure 9 Variation of the elongation at break of the compatibilized PP/PBT blend as a function of screw speed for two particular specific throughputs (Q/N = 1/30 and 1/19 kg/h/rpm).

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