Ultrasonic Treatment of Polypropylene, Polyamide 6, and Their Blends

Heng Lin, A. I. Isayev

Institute of Polymer Engineering, University of Akron, Akron, Ohio 44325-0301

ABSTRACT: The mechanical and rheological properties of polypropylene (PP), polyamide 6 (PA6), and their blends treated by high-intensity ultrasound during extrusion were investigated. A lower head pressure was achieved in the extrusion of these thermoplastics. The mechanochemical and sonochemical effects of ultrasound led to simultaneous ionic condensation reactions and degradation in a homogeneous melt of PA6, with a prevailing effect of enhanced polycondensation reactions. The observed improvements in the mechanical properties of ultrasonically treated PA6 were attributed to condensation reactions, which yield a higher molecular weight, a higher crystallinity, and a more uniform crystal size distribution. At high ultrasound amplitudes, for PP, the degradation of polymer chains was observed with little deterioration of the mechanical properties. For ultrasonically treated PP/PA6 blends, a competition between the degradation and partial *in situ* compatibilization effect was found. At certain blend ratios, the tensile toughness and impact strength of the treated blends were almost double those of the untreated blends. However, full compatibilization was not achieved, possibly because of the low coupling selectivity of highly reactive radicals. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2643–2653, 2006

Key words: blending; compatibilization; polyamides; polyolefins; rheology

INTRODUCTION

Polypropylene (PP) and polyamide 6 (PA6) are among the most widely used general-purpose and engineering thermoplastics, respectively. The cost of products made from these materials could be cut significantly if a faster process could be designed to increase the output by reducing the die-head pressure during the extrusion. Ultrasound-aided extrusion may render an opportunity to achieve this objective. Although ultrasound-assisted extrusion offers some additional advantages, such as the reduction of die-lip buildup, the elimination of melt fracture, the improvement of extrudate surface quality, and the reduction of cell sizes in thermoplastic foams, little information can be found in the open literature on the use of high-intensity ultrasonic waves for the continuous melt processing of thermoplastics.[1–6] There is also limited information available concerning the impact of this process on the final product properties. On the other hand, considerable efforts have been devoted to ultrasonically devulcanize and recycle different kinds of crosslinked elastomers.[7–10] A more recent development is the application of ultrasound to compatibilize polymer blends.[11–16] However, the molecular underpinning of this compatibilization is virtually unknown.

Significant advances have been made and a deeper understanding has been obtained with respect to the use of ultrasound in the preparation of small organic molecules, metal particles, and other inorganic materials.[17–20] For polymer solution systems, fundamental work has been conducted to understand and evaluate the sonochemical effects.[21] Ultrasound under static conditions has also been applied to obtain *in situ* block copolymers in solutions of polymer blends.[22,23] However, for polymer melts, sonochemical concepts are not well established yet.

This article describes a further effort to understand the effects of ultrasonic waves on polymer melts. The study is based on a detailed analysis of the rheological and mechanical properties of ultrasonically treated samples of PP, PA6, and PA6/PP blends. It is well known that good material performance cannot generally be obtained from polymer mixtures, which are often thermodynamically immiscible. As a result, many investigations have been devoted to improving the compatibility of polymer blends via *in situ* compatibilization.[24,25] *In situ* compatibilization has advantages over adding premade block or graft copolymer compatibilizers, which may have difficulty landing themselves on interfaces during the mixing processes.[26] Ultrasound-assisted extrusion may provide a pathway for the *in situ* compatibilization of immiscible polymer blends. Another advantage is that there is no need to do any chemical modification on the base materials before their compounding. From this aspect, sonochemical compatibilization is similar to mechano-

chemical methods, such as solid-state shear pulverization,[27–29] cryogenic mechanical alloying,[30] and CO_2 high-energy ball milling.[31] The outcome of these technologies could be crucial for the efficient recycling of rapidly growing plastic waste. In fact, sonochemical and mechanochemical concepts not only possess the same practical advantages in reactive blending but also may share a similar mechanism when applied to solids or highly viscous liquids.[32] This study may provide an interesting example revealing a link between sonochemistry and mechanochemistry. Although most other studies on compatibilization through radical mechanisms are based on morphological or spectroscopic observations with indirect evidence, some advances in the direct detection of *in situ* formed copolymers with fluorescence-detection gel permeation chromatography (GPC) have been made recently.[27] However, little information on rheological and mechanical properties is reported in the literature for mechanochemically compatibilized thermoplastic blends. In one case, inferior mechanical properties were reported,[30] despite the achievement of a nanosize dispersion in an immiscible blend obtained by cryogenic mechanical alloying. In efforts to further understand these intriguing facts, this study emphasizes the mechanical properties of PP/PA6 blends treated by high-intensity ultrasound.

Furthermore, for reactive blending processes, a diffusion-reaction theory has been developed.[33] However, this theory has not yet been proven by experiments, and the most recent experimental data[34] have indicated that the diffusion-reaction theory is not justified. This inconsistency has been attributed to the low reactivity of the functional groups used in common experiments. It has been suggested that the theory may still be suitable to describe highly reactive radical species used in reactive blending processes.[35] The results obtained in this study may indicate that there is an intrinsic obstacle to performing a direct test of the diffusion-reaction theory by the use of highly reactive radical species.

Overall, the purpose of this study is to investigate the effects of high-intensity ultrasound on the rheological and mechanical properties of PP, PA6, and their blends. The results are evaluated and compared with literature data from the mechanochemical/sonochemical point of view and in the light of the earlier proposed diffusion-reaction theory. We illustrate the advantages and drawbacks of sonochemical methods by revisiting the fundamentals of radical chemistry.

EXPERIMENTAL

Materials

The materials used in this study were PA6 (Capron B135W, Honeywell, Morristown, NJ) and PP (Profax 6823, Basell, Elkton, MD). PP was an extrusion-grade resin with a melt flow index (MFI) of 0.51 g/10 min (230°C/2.16-kg load cell, ASTM D 1238). PA6 was a high-viscosity-grade homopolymer for casting films. Its MFI was 1.2 g/10 min (230°C/2.16-kg load cell, ASTM D 1238). PA6 was dried at 80°C in a vacuum oven for 12 h before use.

Preparation of the PP/PA6 blends

The blending of PP and PA6 was carried out in a Farrell FTX-80 (Ansonia, CT) corotating twin-screw extruder. Because the single-screw extruder was not a good mixer, this compounding stage was necessary to obtain uniformly mixed blends before they were passed through the single-screw extruder equipped with the ultrasonic unit. The temperature of the feeding zone was kept at 200°C for the twin-screw extruder. The other eight zones were kept at 250°C. The feeding rate was 5 kg/h for all compositions. The diameter of the screw was 37 mm. The extrudates were pelletized and dried at 80°C in a vacuum oven for 12 h before use.

Ultrasound treatments of PP, PA6, and their blends

The homopolymers and polymer blends obtained from the twin-screw extruder were treated by high-intensity ultrasonic waves during extrusion in a single-screw extruder (KL100, Killion, Pawcatuck, CT) with a 20-kHz ultrasonic slit die attachment. The horn vibration was perpendicular to the flow direction. Water-cooling channels inside the horn removed extra heat from the ultrasound dissipation and thus stabilized the temperature during the extrusion. Two thermocouples were installed immediately before and after the ultrasonic horn, respectively, to monitor the melt temperature. The cooling channels were efficient enough so that the temperatures before and after the ultrasonic horn were both in the range of 245 ± 2°C. The clearance between the horn and lower die surface was 2 mm. The details of the ultrasonic extrusion system can be found in an earlier article.[12] Although this equipment allowed for the use of two horns in these experiments, only one horn was activated. For every composition, the amplitudes of the ultrasonic waves for treatment were 0, 5, 7.5, and 10 μm, unless the machine was overloaded. The processing temperature was 245°C. The average flow rate of the polymer was 45 g/min.

Mechanical tests and characterization

The injection-molded bars were prepared in a Boy 15S (Exton, PA) 24-ton injection-molding machine for mechanical tests. The melt temperature was 230°C. An Instron 5567 tensile tester (Norwood, MA) was used to obtain the mechanical properties. The crosshead speed was 50 mm/min for homopolymers and 5 mm/min
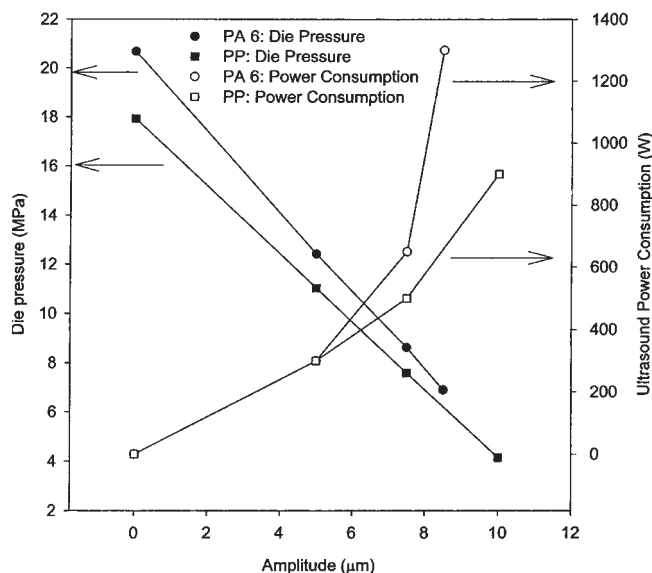
Figure 1 Die pressure and ultrasound power consumption versus the ultrasound amplitude for PP and PA6.

for polymer blends. The experimental procedures followed ASTM D 638-00. Five to six specimens were tested for every sample. The unnotched impact strength was obtained by the specimens being hit from the backside of the notch according to ASTM D 256-00. Seven to nine specimens were used. A rheometer (ARES, Rheometrics, New Castle, DE) was used to obtain the rheological properties at 230°C with a shear-strain amplitude of 4%. Differential scanning calorimetry (2920, TA instruments, New Castle, DE) was used for the study of the melting behavior. The samples were several thin pieces and weighed 6–7 mg. The heating rate was 10°C/min. Three to five specimens were used for every sample.

Morphological studies

A morphological study of the blends was carried out on extrudates exiting the single-screw extruder with and without ultrasonic treatment. A Hitachi S-2150 scanning electron microscope (Tokyo, Japan) was used. The samples were broken in liquid nitrogen. They were etched in boiling xylene for 12 h when PA6 was a major component. When PP was a major component, they were etched in formic acid for 8 h. Then samples were dried and sputter-coated with silver.

RESULTS AND DISCUSSION

Processing characteristics

Figure 1 shows the die pressure as a function of amplitude during the extrusion of PP and PA6. The die pressure decreased linearly with the amplitude. Because of the acoustic cavitation in the melt, both permanent and thixotropic changes in viscosity could take place.

Typically, cavitation can cause degradation of a polymer, leading to a reduction of the viscosity. However, in the case of PA6, as shown in the next paragraph, the viscosity of the treated sample was higher than that of the untreated one. Therefore, the reduction of the die pressure seen in Figure 1 cannot be explained just on the basis of degradation. The drop of the die pressure under the action of ultrasound was most likely due to the thixotropic effect. It has also been suggested that the reason for this behavior is the shear thinning of the melt caused by ultrasound waves and a possible detachment of the polymer melt from the solid surface during the ultrasonic treatment.[3–5] Figure 1 also shows the ultrasonic power consumption as a function of the amplitude for PP and PA6. The power consumption increased with the amplitude of the ultrasonic waves for both PP and PA6. The power consumption of PA6 was higher than that of PP, especially at high amplitudes. For both PP and PA6, at the highest amplitude, the die pressure was about 4 times lower than that in the extrusion without the application of ultrasound. This makes ultrasonic-aided extrusion a potentially valuable process to achieve faster extrusion. However, the speed of extrusion can be limited by the power output capacity of an ultrasound generator at high amplitudes and the ability to efficiently remove heat generated by the dissipation of ultrasound energy.

Rheological characterization

Figure 2 depicts the dynamic complex viscosity as a function of the ultrasonic amplitude at a frequency of $1.19 \, s^{-1}$ for PA6 and PP. At low amplitudes, no significant change in viscosity in PP was found. However, at a higher amplitude, 10 μm, the viscosity was lower
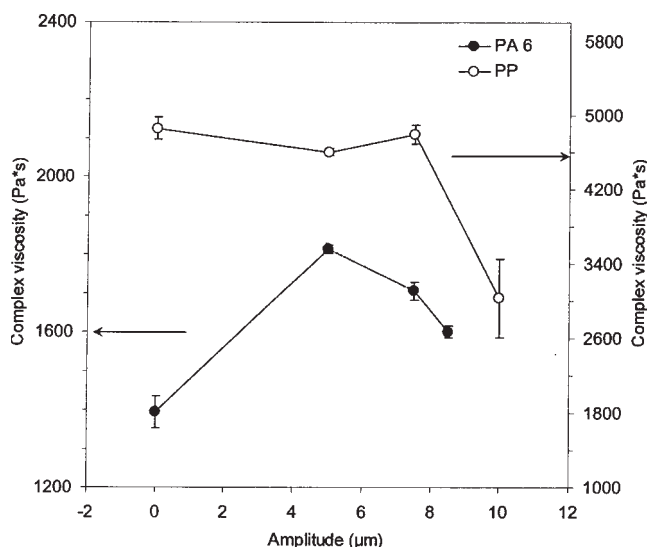

Figure 2 Complex viscosities at a frequency of $1.19 \, s^{-1}$ for untreated and treated PP and PA6 versus the ultrasound amplitude.

than that of the untreated sample. Clearly degradation prevailed at this point. From Figure 2, it seems that no degradation occurred during the ultrasonic treatment of PA6, as also indicated by an initial visual inspection. Samples treated by ultrasound had higher viscosity than the control. However, the viscosities did not continuously increase with the amplitude of the ultrasound. At 5 μm, the viscosity was the highest. This observation suggests that during the ultrasonic treatment, the polymerization and degradation of PA6 chains occurred simultaneously. Because IR spectra of treated and untreated PA6 did not show differences, the increase in the viscosity could be attributed to two possible reactions: (1) polycondensation among the PA6 chains and (2) radical reactions causing sparse long-chain branches (LCBs). Under most circumstances, especially in a homogeneous system such as an organic solution, ultrasound is known only to promote free-radical reactions. This category of sonochemical reactions has been identified by organic chemists as a Luche type I system.[19] However, the mechanism of polycondensation reactions is well known as a class of ionic reactions. Therefore, the question arises if free-radical reactions were involved in ultrasonic treatments of PA6, generating a branched polymer with a few branch points, so that the IR spectrum was not sufficiently sensitive to show the difference. Typically, there are two popular methods used to distinguish branched polymers from their linear analogues. One of them, ^{13}C-NMR, which is analytical, can precisely determine the percentage of LCBs for a polymer. The detection limit is around 0.1 LCB/1000C.[36] Knowing the chemical structure around the branching point is the prerequisite for using NMR to calculate the percentage of LCBs. Another widely adopted method is dynamic rheological measurement, which is more sensitive and suitable for comparative studies than NMR. Studies have shown that even 0.01 LCB/1000C has a profound impact on rheological properties and often provides sufficient data to indicate the existence of LCBs.[37] Although there are many ways to detect LCBs by means of dynamic rheological measurements, Cole–Cole plots [dependence of the storage modulus (G') vs the loss modulus (G'')] were adopted here. It has been suggested[38] that these plots are a very efficient tool for detecting the presence of branching.

In Figure 3, the data for both PP and PA6 obtained at several different treatment conditions and temperatures fall into two master curves corresponding to each polymer. This immediately eliminates the possibility of the formation of LCBs induced by a free-radical process in the ultrasonic treatment. In other words, in the homogeneous polyamide melts, our experiments show that the increase in the viscosity most likely resulted from condensation reactions among the PA6 chain ends. These reactions would indicate that the ultrasonic treatment promoted an ionic pathway. This
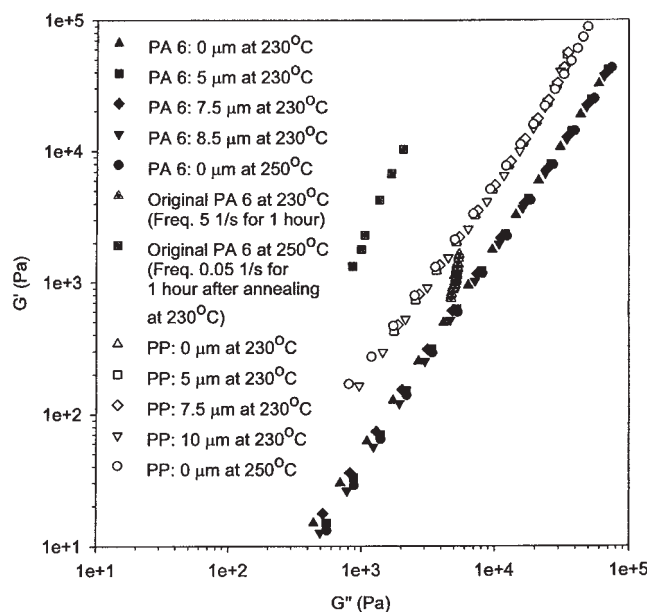

Figure 3 G' versus G'' for the untreated and treated PA6 and PP in comparison with annealed virgin PA6.

may not be unique for polyamides, as it has been found[39] that high-intensity ultrasound enhances the reaction in the preparation of polyurethanes. This effect can be attributed to the mechanochemical effects of ultrasonic waves, which are usually involved in many reactions.[40] In fact, these mechanochemical effects are far more complex than those created by agitation effects and are not completely understood yet. It is known only that mechanochemical effects are extremely localized, and they are significantly different from mechanophysical effects, such as the enhancement of mass diffusion by convection in mixers. Indeed, polycondensation reactions of PA6, which must obey the equivalence of reactivity,[41] cannot be just enhanced by a faster diffusion of polymer chains. In this case, mechanochemical effects produced by ultrasound can act as a catalyst and help the reactants to overcome the activation barrier.[32] However, earlier observations[40] have indicated that the mechanochemical effect can assist the ionic pathway in the heterogeneous system only. These reactions are categorized as the Luche type II systems. Interestingly, the polymer melt in our experiments was a homogeneous phase. It was noticed that the earlier experiments involving the mechanochemical effects of ultrasound solely focused on small molecules, in which the effect of elasticity was negligible. On the other hand, it is also known that performing mechanochemistry by shear is not possible in an ideally viscous state. However, for viscoelastic polymer melts under high-frequency shear forces, mechanochemical effects can be observed.[39] Therefore, the existence of elasticity in polymer melts solves the seemingly conflicting findings by us and Luche.[40] In other words, not the heterogeneity
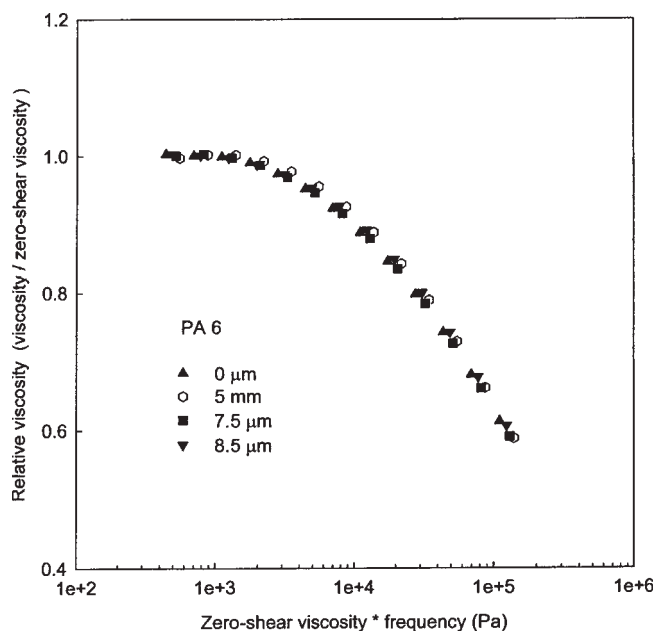
Figure 4 Vinogradov–Malkin plot of untreated and ultrasonically treated PA6.

but the elasticity is the essential requirement for Luche type II reactions to happen.

Moreover, heat generated by sonication is unlikely the explanation for our results. In the experiments, the sonicated area was sufficiently cooled by water-cooling lines, and the temperature before and after the area was sonicated were identical and stable throughout the process. It is known that heat-induced degradation results in a broad molecular weight distribution (MWD) of the final product because every link of the chain is subject to a similar probability of breaking under heat. In our study of PA6, the competition between condensation reactions and chain scissions was observed as the molecular weight first reached a maximum at 5 μm and then decreased with the intensity of the ultrasound, as is evident from the viscosity data (Fig. 2). If chain scissions are totally random, like those in thermal degradation, the MWD usually broadens.[42] A direct proof of this effect requires the MWD of PA6. Unfortunately, the MWD measurement of PA6 with a common GPC solvent, such as tetrahydrofuran or CH_2Cl_2, is not possible because of the existence of strong hydrogen bonds and other polar–polar interactions in PA6. Over the years, a number of dissolution schemes for polyamide have been proposed, involving highly polar solvents or high-temperature measurements. However, because of issues such as possible degradation or possible interactions between the solute and the stationary phase or the involvement of special columns, an accurate GPC analysis of PA6 remains either highly expensive or complicated. Recently, there was even evidence showing that the common universal calibration procedure for GPC is

only applicable for benzyl alcohol with high-temperature GPC.[43] Alternatively, a simple and inexpensive rheological method, the Vinogradov–Malkin plot,[44,45] can be used to determine if MWD changes occur. Hence, the Vinogradov–Malkin plot was adopted here in the absence of GPC measurements of PA6. The plot is shown in Figure 4. The lower viscosity of PA6 treated at 10 μm in comparison with that at 5 μm signified more severe degradation at 10 μm. If heat indeed played a role, a broad MWD at 10 μm would have been observed. However, the dependence of the relative viscosity (viscosity/zero-shear viscosity) on the product of the zero-shear viscosity times the frequency falls into a master curve in Figure 4, which indicates that the polydispersity of our samples virtually did not change. Therefore, during the ultrasonic treatment, the random scission of PA6 did not occur.

To gain a better understanding of the reaction mechanisms, the complex viscosities of the PA6 melts were measured in an ARES rheometer at 230 and 250°C at a constant frequency after prolonged heating. The data were added to Figure 3. The viscosity was relatively stable at 230°C but increased to the level of the sample sonicated at 5 μm after 10 min of heating at 250°C. The calculated average residence time in the sonicated area was about 3 s. Consequently, for achieving the same increase in the viscosity, the time needed in the heating experiments was on the order of minutes, whereas in ultrasonic extrusion, this time is only a few seconds. In Figure 3, an analysis based on G' versus G'' shows more interesting results for the samples subjected to heating for an hour. At both temperatures, these data do not fit into the master curve of PA6 but lie beyond the master curve. This is a typical rheological behavior indicating branching or crosslinking,[38] which agrees with the observation of nylon gelation under the heat.[46] This also suggests that the higher viscosity observed with the heating of the samples in air was actually caused by a different mechanism (branching) than that observed in the ultrasonically treated samples (condensation). The facts again indicate that not heat but a mechanochemical effect, which is not well understood so far,[47] dominates in ultrasound-assisted extrusion. The viscosity data for PA6 in Figure 2 also imply that there were two competing reactions occurring simultaneously, that is, polycondensation and

TABLE I
Thermal Properties of Untreated and Ultrasonically Treated PA6

Amplitude (μm)	Melting completion temperature (°C)	Melting point (°C)	Heat of fusion (J/g)
0	227.3	221.0	52.2
5	227.4	221.2	58.5
7.5	229.8	221.8	52.2
8.5	229.6	221.7	52.8

TABLE II
Thermal Properties of Untreated and Ultrasonically Treated PP

Amplitude (μm)	Melting completion temperature (°C)	Melting point (°C)	Half-peak width (°C)	Heat of fusion (J/g)
0	181.4	164.4	8.7	79.6
5	181.9	164.8	8.23	83.6
7.5	182.3	163.9	9	81.0
10	182.3	163.6	8.5	83.0

mechanochemical degradation. Clearly, polycondensation reactions are prevalent in the ultrasonic treatment of PA6.

Thermal and mechanical properties of the homopolymers

Table I shows that with increasing ultrasound amplitude, the melting point of treated PA6 shifted to a slightly higher temperature. This may suggest the existence of bigger crystals in the treated samples. The temperature corresponding to melting completion was clearly higher for the samples treated at the higher amplitudes. The melting peak at 5 μm was the narrowest in comparison with the other samples. A narrow peak usually suggests a narrow crystal size distribution. Also, as shown in Table I, the heat of fusion reached the highest value for the sample treated at 5 μm. Thus, we can suggest that the sample treated at 5 μm had the highest crystallinity and narrowest crystal size distribution. Interestingly, Table II shows that PP treated at 5 μm also had the narrowest melting peak by a comparison of the half-peak widths of all the samples. As indicated by the heat of fusion, this sample
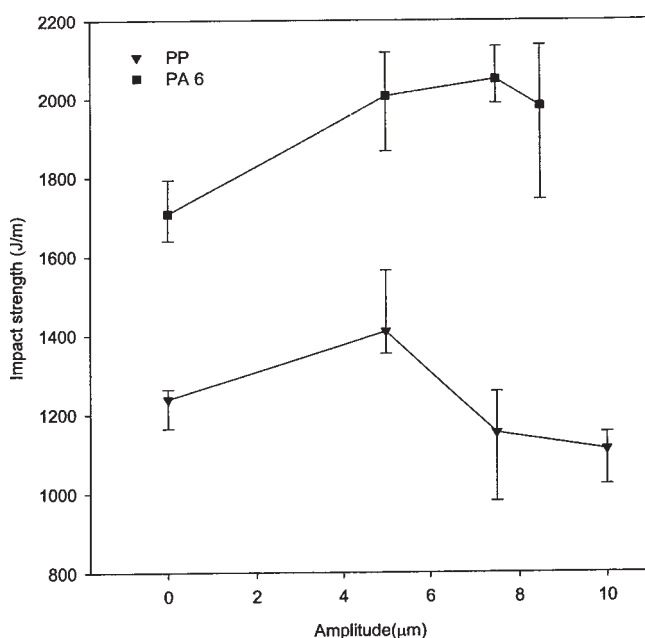
exhibited the highest crystallinity, too. It is intriguing that both PP and PA6, treated at 5 μm, had their melting behavior affected similarly by ultrasound. Obviously, although rheological tests and IR spectra were unable to reveal differences in the structure before and after the treatment, some subtle changes indeed happened.

In principle, the uniform crystal size and high crystallinity could improve the mechanical properties. The results shown in Figure 5 indicate that both PP and PA6 treated at 5 μm had higher impact strength than untreated samples. Figure 6 shows that for both PP and PA6, the tensile strength and Young's modulus were well maintained at 5 μm compared with those of the untreated samples. In Figure 7, the toughness of both PP and PA6 samples treated at this amplitude was maintained as well, although it dropped at higher amplitudes. It was found that the change in the elongation at break was insignificant for both polymers. Overall, the mechanical properties of both PP and PA6 samples treated at 5 μm were at least as good as those of the controls. At this amplitude, the power consumption of ultrasonic units was low (200–300 W), whereas the die-head pressure was reduced by half in comparison with that without ultrasound (see Fig. 2). Our results indicate that ultrasonic-aided extrusion has
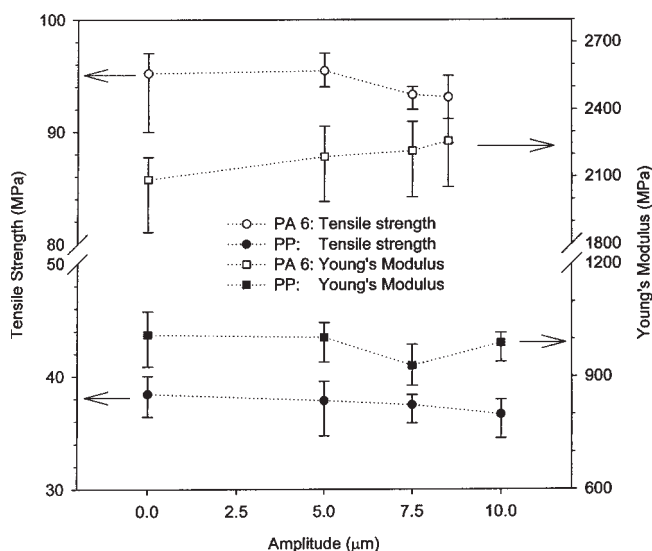

Figure 5 Impact strength of PP and PA6 versus the ultrasound amplitude.

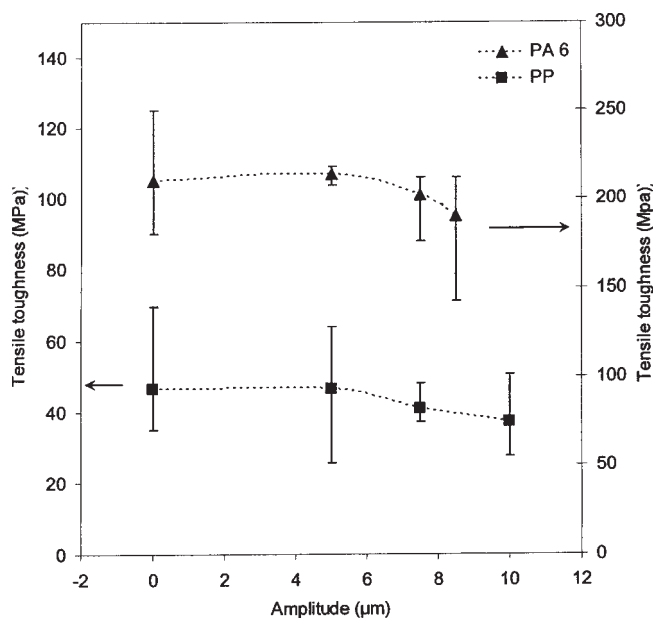**Figure 6** Tensile strength and Young's modulus of PP and PA6 versus the ultrasound amplitude.

Figure 7 Tensile toughness of untreated and ultrasonically treated PP and PA6 versus the ultrasound amplitude.

great potential to become a powerful industrial process for increasing the output without invoking melt fracture by reducing the head pressure during extrusion. Best of all, the final mechanical properties can also be enhanced in the process.

Polymer blends

It is well known that the mechanical properties of polymer blends are the most sensitive measure of compatibilization. Unlike scanning electron microscopy and transmission electron microscopy, which only focus on an extremely localized region, mechanical tests can help us to view a much big picture. An indicator of full compatibilization is that all mechanical properties of blends fall into or near the additive line of individual components.[48] Figure 8 shows that after the ultrasonic treatments, the tensile strength and Young's modulus of the polymer blends did not show clear differences. In particular, the modulus of treated and untreated PP/PA6 blends versus the blend ratios fell close to the line of additivity, whereas their tensile strength (indicated by the yield stress) showed a negative deviation from this rule. However, they should not be regarded as a measure of compatibilization. The additivity of some mechanical properties, especially the modulus, is typically observed in both compatible and incompatible polymer blends because Young's modulus is usually measured at a very low strain, which is not critical for interfacial debonding in polymer blends.[49] For the same reason, the yield stress is not a sensitive indicator of the compatibilization either. The benchmarks of compatibilization, which may

indicate interfacial debonding occurring at either high strains or high strain rates, are the toughness and impact strength, respectively. They are directly dictated by interfacial adhesions for polymer blends. Therefore, the toughness and impact strength are used here to evaluate the effect of ultrasonic treatments. In our results, the curves of the toughness and impact strength versus the blend ratios show a significant negative deviation from the additive line, which generally indicates that full compatibilization has not been achieved. However, this is not convincing evidence that compatibilization did not occur. The evaluation of the ultrasonic effects is conducted with the following statistical analysis for individual compositions. In Figures 9 and 10, error bars show the maximum and minimum values of the toughness and impact strength obtained in all the experiments. As a result, the vertical asymmetric error bars depicted in these figures give longer error bars than those of the standard deviation. In a sense, these error bars are more like statistical box plots. To make the error bars more clearly visible and overlapping, the data points of the same PA6 concentration treated at different amplitudes were slightly shifted from their original positions. Figure 9 shows, that, on average, the treated samples showed higher toughness. However, using the error bars of the data, one should be careful drawing a conclusion about differences between the untreated and treated blend samples. This led us to perform a one-way analysis of variance hypothesis test with 95% confidence intervals for each composition. The result showed that statistically the toughness of the sample containing 40% PA6 treated by ultrasonic waves was significantly higher than that of the untreated sample. The sample treated
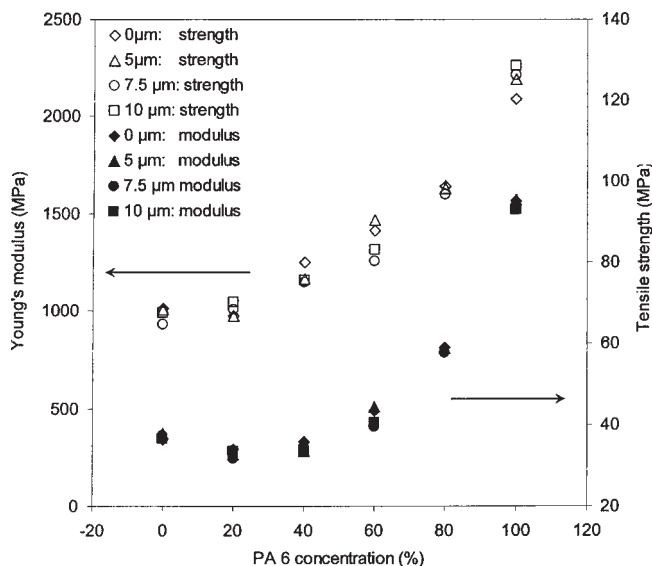

Figure 8 Tensile strength and Young's modulus versus the PA6 concentration for untreated and ultrasonically treated PP/PA6 blends.
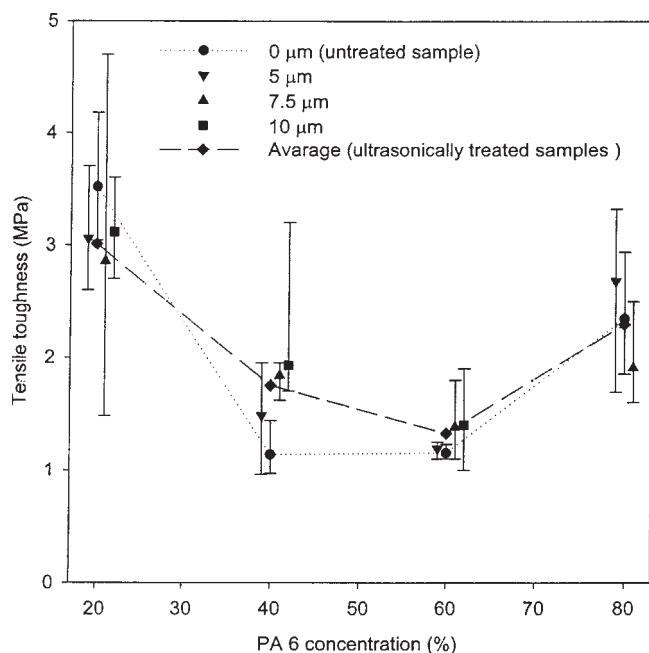
Figure 9 Tensile toughness versus the PA6 concentration for untreated and ultrasonically treated PP/PA6 blends. The data, along with error bars, at the same concentration but at different ultrasound amplitudes have been shifted for clarity.

at 10 μm showed an almost 100% increase in toughness compared to the untreated sample. This increase in toughness was even higher than that of some of the PP/PA6 blends compatibilized with 5% maleic anhydride grafted PP.[50] The toughness of the samples at other concentrations did not fall within the 95% confidence, as indicated by the *p* value of *F* tests. Hence statistically there was not sufficient evidence to assert the improvements for the rest of the compositions. Meanwhile, as shown in Figure 10, the ultrasonically treated blend at 7.5 μm containing 60% PA6 showed an increase in impact energy by 50%. One-way analysis of variance testing agreed with this finding. The two sample *T* tests showed that at a 95% confidence interval, the sample treated at 7.5 μm had at least 35% higher impact strength than the untreated sample. However, these values for the 40 and 60% PA6 blends were still well below those of pure PA6 and PP.

A morphology investigation was performed,[51] as shown in Figure 11. The samples were directly taken from the extrudates without any further annealing because the samples had passed through the die located after the ultrasonic treatment zone and were naturally annealed after the treatment. As shown in Figure 11, the material remaining after the etching process was PP, and the holes represent PA6. For the case of the blend containing 20% PA6, the morphology was not very different for the samples with and without ultrasound treatment. This coincided with results of mechanical tests. However, for the 40% PA6 blend, the

morphology became more complicated. Because of the different melting points, PP melted first in the extruder and then formed a continuous phase, whereas PA6, still being solid, was a dispersed phase. However, after both PP and PA6 melted, the rheological effect was such that the viscosity ratio started to play a role, in that less viscous PA6 tended to also form a continuous phase. Therefore, phase inversion occurred. Compatibilization could slow down the phase-inversion process significantly because of adhesive interactions between PP and PA6. In particular, Figure 11 shows that without ultrasound treatment, a bicontinuous phase was formed. However, with ultrasound treatment, although a portion of PA6 came out of the PP matrix and formed a secondary continuous phase, a significant amount of PA6 remained in the PP continuous phase. This indicates that the phase-inversion process was incomplete because of a compatibilization effect. This is a reason that mechanical tests showed that the treated sample exhibited significantly higher toughness than the untreated sample. A more stable structure was formed in this composition during the treatment.

The increase in the toughness and impact strength was probably due to a small amount of *in situ* formed copolymers acting as binding agents between the two phases. High-intensity ultrasound is known for being capable of producing radicals and then causing degradation of the polymers.[52] It has been shown in dilute solutions that different radical species can combine together, forming block copolymers.[22] It has been sug-
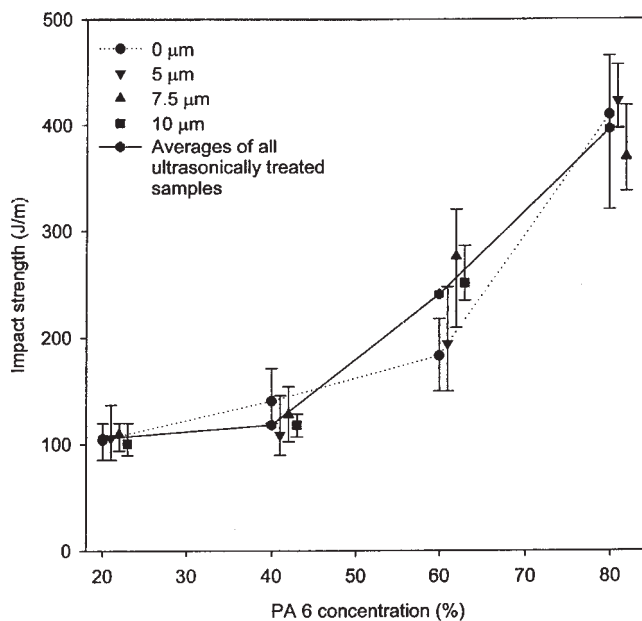

Figure 10 Impact strength versus the PA6 concentration for untreated and ultrasonically treated PP/PA6 blends. The data, along with error bars, at the same concentration but at different ultrasound amplitudes have been shifted for clarity.
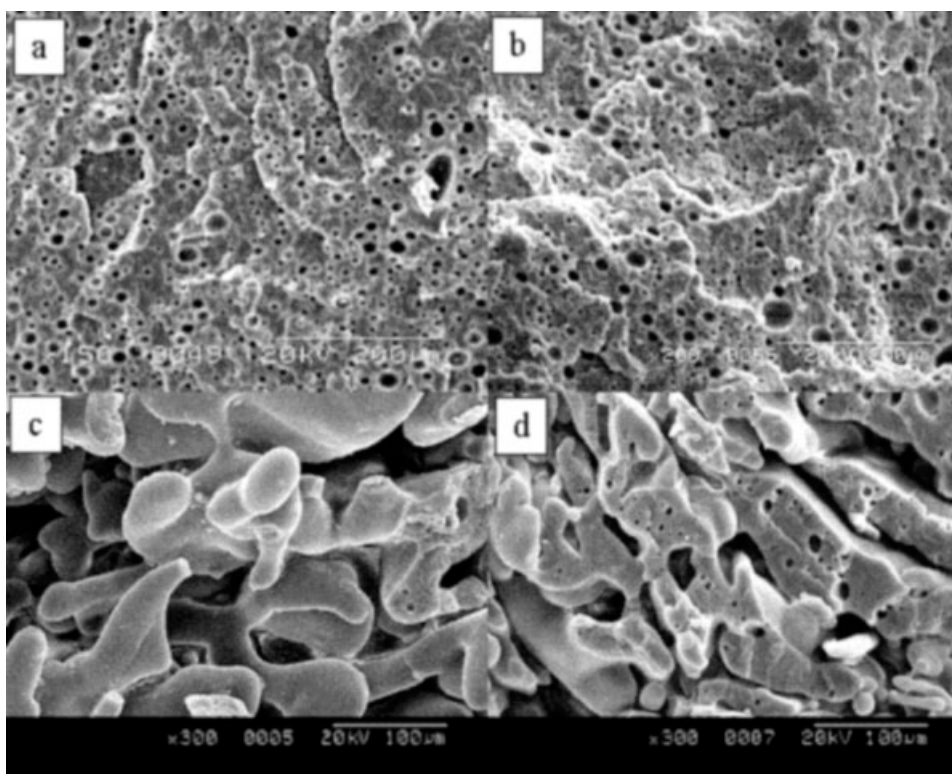
Figure 11 Morphology of the polymer blend extrudates containing (a,b) 20% PA6 (untreated and treated at 10 μm, respectively) and (c,d) 40% PA6 (untreated and treated at 10 μm, respectively).

gested that block copolymers can also be formed in polymer melts because of coupling termination of radicals from chain segments of different polymers.[53] However, the coupling reaction involving two different radical species at the interface subjected to shear during the extrusion is extremely complicated. The rheology, mass transfer, and interfacial reaction kinetics are coupled together in a complex fashion. Therefore, it is extremely difficult to treat this problem vigorously. A diffusion-reaction process describes the radical reactions inside the polymer melt, and this theory has also been extended to diffusion-controlled reactions at polymer–polymer interfaces.[33] Although this theory has been found inconsistent with reactive blending experiments of low reactive species,[34] it may still be a viable theory for reactive blending involving highly reactive radical species.[35] According to the theory, in the diffusion-controlled coupling process, the reaction constant on polymer interfaces is not only proportional to the diffusion coefficient but also proportional to the interfacial area generated by mixing. This may be the reason that better properties were more easily obtained in blends containing 40–60% PA6 or PP because more interfacial area was created dynamically in these blends than in blends of other concentrations. The interfacial couplings may play more important roles in these cases than in those blends with less interfacial area containing smaller amounts of PP and PA6.

Despite the better mechanical properties after the ultrasonic treatments of certain compositions, overall the ultrasonic treatment did not reach full compatibilization. Experiments with longer residence times were conducted, but no further improvements were seen. It is believed that the underlying reason is the chemistry. The reactions among these highly reactive radical species are very complex. For PP alone, besides the desirable coupling reactions, other known competitive pathways include chain scissions, disproportions, β scissions, intermolecular hydrogen abstractions, and intermolecular hydrogen transfers.[54] Presently, the mechanism of radical behavior of polymer blend interfaces, analogous to that in PP melts, is not available. However, it can be assumed that the behavior will be similar to or even more complicated than that in the bulk state. It seems that in our case, at least for PP, intermolecular hydrogen abstraction and disproportionation reactions dominate coupling reactions at interfaces. Indeed, the more reactive, the less selective is a rule of thumb in the radical chemistry. In addition to the reactions at interfaces, the scission and hydrogen abstraction of PP occur in the bulk state simultaneously at high amplitudes, and this implies that even if ultrasound-induced reactions generate a small amount of copolymer at the interface, they may lead to much more degradation in the bulk phases. From a material property point of view, this may largely cancel the effect of stronger interfacial bonding on the toughness

and impact strength. It is known that one of the most important aspects of reactive blending with radical species is the specific chemical structures of selected polymer components. In fact, from the observation of earlier mechanochemical experiments, much more chain scission than chain coupling has been seen on many polymers, including PP.[55] Furthermore, in the commercial resins used in this study, various ingredients including antioxidants are typically added to capture the radicals. In the presence of oxygen, carbon radicals can be easily transformed into active peroxy radicals too.[56] Experiments carried out decades ago showed that mechanoradicals react with oxygen even more efficiently than added monomers.[57] This is probably the reason that CO_2 milling in the absence of oxygen achieved relatively good mechanical properties among reactive blending processes involving mechanochemical methods.[31]

Although many competitive reactions exist, in principle, it is still possible to selectively boost a coupling reaction or specific chain-transfer reaction leading to the grafting process. Because each reaction has a different activation energy, it is a common practice to adjust the temperatures to facilitate one desired reaction process. For example, at temperatures lower than its melting point, PP favors radical grafting instead of chain scission in processing.[58] However, it is not universally true for all polymer materials. For example, in the mechanical alloying process using liquid nitrogen,[30] poly(methyl methacrylate) experiences severe degradation in liquid nitrogen, whereas polyisobutylene can be crosslinked in the same batch. Clearly, the material chemistry must dictate the results of the reactive blending processes. As long as the reactivity between the radicals of different species at the interfaces is not much lower than that of the same species in the bulk state, it is still possible to discover the right materials and right processing conditions to selectively promote the coupling reactions at the interfaces to achieve the full compatibilization. From this point of view, more investigations will be required to provide further and adequate grounding for a reactive blending process involving sonochemistry and mechanochemistry.

CONCLUSIONS

With a little power consumption, the die pressure has been reduced by at least half in the extrusion of PP and PA6 by ultrasound-assisted extrusion. Ultrasonically treated PA6 and PP samples at 5 μm showed even better mechanical properties than untreated samples. A new scenario for a faster extrusion of common thermoplastics is envisioned. In a homogeneous system of PA6 melts, ultrasound promotes an ionic reaction, which cannot be categorized into traditional sono-

chemical reactions caused by radicals. This reaction is also intrinsically different from the one due to only heating of the sample, which leads to a gelation reaction. It is proposed that mechanochemical effects by ultrasound assist ionic reactions. However, elasticity is required for this purpose because without it mechanochemical reactions will not take place. Products made from ultrasonically heated PA6 possess a higher molecular weight, higher impact strength, higher crystallinity, and more uniform crystal morphology. Blends of PP and PA6 have also been investigated by ultrasound-assisted extrusion. At certain blend ratios, compatibilization effects were achieved with a 50–100% increase of the tensile toughness or impact strength in blends. However, full compatibilization could not be achieved within these systems. This is attributed to the lack of selectivity of highly reactive radicals for coupling reactions.

References

1. Rauwendaal, W. Plast Addit Compd 2002, 4, 24.
2. Peshkovski, S. L.; Friedman, M. L.; Tukachinsky, A. I.; Vinogradov, G. V.; Enikolopian, N. S. Polym Compos 1983, 4, 126.
3. Isayev, A. I.; Wong, C. M.; Zeng, X. Soc Plast Eng Annu Tech Conf 1987, 33, 207.
4. Isayev, A. I. Proceedings of the 23rd Israeli Conference on Machanical Engineering, Technion, Haifa, Israel, 1990; Paper 5.2.3, p 1.
5. Isayev, A. I.; Wong, C. M.; Zeng, X. Adv Polym Technol 1990, 10, 31.
6. Isayev, A. I.; Mandelbaum, S. Polym Eng Sci 1991, 31, 1051.
7. Hong, C. K.; Isayev, A. I. J Appl Polym Sci 2001, 79, 2340.
8. Diao, B.; Isayev, A. I.; Levin, V. Y. Rubber Chem Technol 1999, 72, 152.
9. Yushanov, S. P.; Isayev, A. I.; Kim, S. H. Rubber Chem Technol 1998, 71, 168.
10. Tukachinsky, A.; Schworm, D.; Isayev, A. I. Rubber Chem Technol 1996, 69, 92.
11. Feng, W. L.; Isayev, A. I. Polymer 2004, 45, 1207.
12. Oh, J. S.; Isayev, A. I.; Rogunova, M. A. Polymer 2003, 44, 2337.
13. Isayev, A. I.; Hong, C. K. Polym Eng Sci 2003, 43, 91.
14. Isayev, A. I.; Hong, K. J. Rubber Chem Technol 2003, 76, 923.
15. Isayev, A. I.; Hong, C. K. U.S. Pat. 6,528,554 (2003).
16. Chen, Y. Z.; Li, H. L. Polym Eng Sci 2004, 44, 1509.
17. Suslick, K. S.; Price, G. J. Annu Rev Mater Sci 1999, 29, 295.
18. Suslick, K. S. Science 1990, 247, 1439.
19. Luche, J. L. Synthetic Organic Sonochemistry; Plenum: New York, 1998.
20. Einhorn, C.; Einhorn, J.; Luche, J. L. Synthesis 1989, 11, 787.
21. Price, G. J.; Smith, P. F. Polymer 1993, 34, 4111.
22. Price, G. J.; West, P. J. Polymer 1996, 37, 3975.
23. Lebovitz, A. H.; Gray, M. K.; Chen, A. C.; Torkelson, J. M. Polymer 2003, 44, 2823.
24. Polymer Blends; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000.
25. Two-Phase Polymer Systems; Utracki, L. A., Ed.; Hanser: New York, 1991.
26. Sundararaj, U.; Macosko, C. W. Macromolecules 1995, 28, 2647.
27. Lebovitz, A. H.; Khait, K.; Torkelson, J. M. Macromolecules 2002, 35, 8672.
28. Lebovitz, A. H.; Khait, K.; Torkelson, J. M. Macromolecules 2002, 35, 9716.

29. Furguiele, N.; Lebovitz, A. H.; Khait, K.; Torkelson, J. M. Macromolecules 2000, 33, 225.

30. Smith, A. P.; Ade, H.; Balik, C. M.; Koch, C. C.; Smith, S. D.; Spontak, R. J. Macromolecules 2000, 33, 2595.

31. Cavalieri, F.; Padella, F.; Bourbonneux, S. Polymer 2002, 43, 1155.

32. Boldyrev, V. V. Ultrason Sonochem 1995, 2, 143.

33. Fredrickson, G. H. In Theoretical Challenges in the Dynamics of Complex Fluid; McLeish, T. C., Ed.; Kluwer Academic: Dordrecht, 1997.

34. Schulze, J. S.; Cernohous, J. J.; Hirao, A.; Lodge, T. P.; Macosko, C. W. Macromolecules 2000, 33, 1191.

35. O'Shaughnessy, B.; Vavylonis, D. Europhys Lett 1999, 45, 638.

36. Gabriel, C.; Kokko, E.; Lofgren, B.; Seppala, J.; Munstedt, H. Polymer 2002, 43, 6383.

37. Graebling, D. Macromolecules 2002, 35, 4602.

38. Han, C. D. Rheology in Polymer Processing; Academic: New York, 1976.

39. Price, G. J.; Lenz, E. J.; Ansell, C. W. G. Eur Polym J 2002, 38, 1531.

40. Luche, J. L. Ultrasonics 1992, 30, 156.

41. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.

42. Casale, A.; Porter, R. S.; Johnson, J. F. Rubber Chem Technol 1971, 44, 534.

43. Nguyen, T. Q. J Liq Chromatogr Relat Technol 2001, 24, 2727.

44. Isayev, A. I. J Polym Sci Polym Phys Ed 1973, 11, 2123.

45. Minoshima, W.; White, J. L. Polym Eng Sci 1980, 20, 1166.

46. Nylon Plastics Handbook; Kohan, M. I., Ed.; Hanser: Cincinnati, 1995.

47. Gilman, J. J. Science 1996, 274, 65.

48. Han, C. D. Multiphase Flow in Polymer Processing; Academic: New York, 1981.

49. Kolarik, J. Eur Polym J 1998, 34, 585.

50. Tseng, F. P.; Lin, J. J.; Tseng, C. R.; Chang, F. C. Polymer 2001, 42, 713.

51. Lin, H.; Isayev, A. I. Soc Plast Eng Annu Tech Conf Pap 2003, 49, 1518.

52. Price, G. J. In New Methods of Polymer Synthesis; Ebdon, J. R.; Eastmond, G., Eds.; Chapman & Hall: New York, 1995.

53. Isayev, A. I.; Hong, C. K. Soc Plast Eng Annu Tech Conf Pap 2002, 48, 1334.

54. Kruse, T. M.; Wong, H. W.; Broadbeld, L. J. Macromolecules 2003, 36, 9594.

55. Sohma, J. Prog Polym Sci 1989, 14, 451.

56. Sakaguchi, M.; Yamakawa, H.; Sohma, J. J Polym Lett 1974, 12, 193.

57. Sakaguchi, M.; Sohma, J. J Appl Polym Sci 1978, 22, 2915.

58. Ratzsch, M.; Arnold, M.; Borsig, E.; Bucka, H.; Reichelt, N. Prog Polym Sci 2002, 27, 1195.