

# Microstructural Changes in Homopolymers and Polymer Blends Induced by Elastic Strain Pulverization

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## SYNOPSIS

A novel polymer processing technique known as elastic strain pulverization (ESP) involves the simultaneous effects of high pressure and shear deformation to pulverize polymers. Homopolymers and blends of commercially important postconsumer plastics, including high-density and low-density polyethylene (HDPE, LDPE), polypropylene (PP), and polystyrene (PS) are studied by several characterization techniques to determine the effects of ESP on the microstructure. Electron spin resonance spectroscopy confirms that free radicals are generated by the mechanical rupture of main chain carbon bonds during pulverization by ESP. The possibility of these free radicals terminating by heterogeneous combination to form compatibilizing block or graft copolymers in coprocessed polymer blends establishes the potential of ESP in commingled plastics recycling. Differential scanning calorimetry (DSC) and polarized light microscopy of homopolymers and blends indicate that crystalline structure is drastically altered by ESP processing. Spherulite size reduction is also observed in both crystalline/crystalline and crystalline/amorphous blends after ESP. These results are consistent with homogenization that may be due to the formation of compatibilizing copolymers by heterogeneous macroradical combination. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The incompatibility of polyolefin blends poses a significant obstacle in postconsumer plastics recycling technology.<sup>1</sup> Most current recycling methods sidestep this problem with sortation and separation steps, which are both time consuming and expensive; further, the recycled products are often of lower quality and value than the original materials, even after segregated processing.<sup>2</sup> Alternative techniques such as addition of compatibilizing agents to the commingled wastestream are limited by the prohibitive cost of the compatibilizing additives (usually block copolymers).<sup>3,4</sup> We have studied a processing technique known as elastic strain pulverization (ESP) or, synonymously, solid-state shear extrusion

or elastic deformation grinding. Discovered by Russian scientists in the early 1980s,<sup>5-9</sup> ESP is a solid-state mechanochemical process in which polymers are pulverized in the barrel of a specially designed extruder by a combination of high pressure, large shear strains, and thermoelastic stresses. The mechanism of this process is not well understood, but data and physical observations of the originators of ESP<sup>5,6,8,9</sup> indicate that the polymers are pulverized by a sudden and catastrophic rheological explosion-type mechanism, not unlike that reported by early investigations of high pressure and shear effects performed with Bridgman anvils.<sup>10,11</sup>

The motivation for our study of ESP-processed materials is the possibility of *in situ* compatibilization of polymer blends induced solely by the mechanochemical reactions that occur in the extruder without any external addition of compatibilizing agents. It has been reported that powders of incompatible polymer blends produced by ESP show degrees of homogenization not ordinarily achievable with existing mixing equipment.<sup>9,12,13</sup> It is also plau-

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sible that homogenization is effected by the presence of compatibilizing copolymers mechanochemically formed during extrusion, as reported in a recent study of polypropylene/high-density polyethylene (PP/HDPE) blends extruded in the *melt* state under high shear.<sup>14</sup> It has been documented in two extensive reviews of polymer mechanochemistry that block or graft copolymers may be formed by heterogeneous recombination of macroradicals that are generated when C—C bonds are ruptured during vibromilling, cryogenic grinding, and other types of solid-state mechanical processing of polymer-polymer blends.<sup>15,16</sup>

We performed a comparative analytical study of a variety of polymers and polymer blends to examine differences in physical properties, microstructure, and morphology of samples before and after pulverization by ESP. Because we are interested in the application of this process to recycling, we studied polymers that are common in the postconsumer wastestream, using virgin materials only when necessary to clarify ambiguities that are presented by unknown additives and impurities that may be present in "real" plastics. Results from electron spin resonance (ESR) spectroscopy, differential scanning calorimetry (DSC), and optical microscopy are reported here. Macroscopic properties obtained by mechanical testing have been published previously.<sup>17</sup> In each experiment, we observe significant and often striking differences between the original and the ESP processed samples that are consistent with partial mechanochemical compatibilization. Our results suggest that ESP has potential for development as a plastics recycling technique that warrants further investigation.

## EXPERIMENTAL

### Materials

Postconsumer low-density polyethylene (LDPE), HDPE, PP, poly(ethylene terephthalate) (PET), and polystyrene (PS) were obtained from commercial recyclers in a sorted, washed, and chopped flake form. Because of the nature of recycled materials, information was not available regarding the original properties of these samples, many of which contain dyes, stabilizers, and other proprietary additives. To eliminate experimental artifacts caused by these additives, virgin samples of PP (Quantum 8020-GU homopolymer) and PS (Amoco R5) were also studied.

### Elastic Strain Pulverization

All samples were pulverized in a pilot-scale, 40-mm corotating twin screw extruder with a specially designed screw configuration (Berstorff Corporation, Charlotte, NC).<sup>7,18</sup> Plastics were fed as individual components and as dry blends at various ratios. The extruder has kneading elements that provide the pressure and high shear strains necessary to pulverize the polymers. After passing through a hot zone where the plastic is softened, it enters an externally quenched cooling zone where the combination of pressure, shear strain, and thermal stresses pulverize the material. The hot zone of the extruder was kept at temperatures greater than the melting temperatures ( $T_m$ ) of the sample, but the pulverization occurs in the cooling zone, in which the temperatures typically are below  $T_m - 70^\circ\text{C}$ . Each sample was pulverized in a single pass through the extruder.

Process parameters such as the cooling water temperature, shear rate, and feed rate were varied until the material pulverized. No optimization of process parameters was performed during this study.

### ESR Spectroscopy

ESR spectra were obtained with a modified X-band Varian E-4 spectrometer. Solid polymer samples loaded in precision quartz tubes (5-mm ID) were studied at room temperature. The samples were kept under ambient conditions for several months prior to the experiments. For quantitative accuracy, great care was taken to maintain consistent arrangement of the samples both within the tubes and within the spectrometer cavity. Spectra were recorded digitally by an on-line computer.

Because the prepulverized blend samples in ESR studies are merely mixtures of solid flakes of each component placed together in a tube, their ESR spectra were obtained by the addition of the spectra of each individual component of the polymer blend weighted by the appropriate mass fraction representative of the blend. Similarly, the ideal spectra of the pulverized blends were simulated by spectral addition of the individual pulverized homopolymers. In this manner, we were able to compare the actual ESR spectra of coprocessed blends with spectra that would be expected if the pulverization were simply a noninteractive physical mixing of the pulverized components.

### DSC

DSC measurements were obtained with a Perkin-Elmer DSC-7. Sample masses ranged between 4 and

10 mg. The pre- and postpulverized samples that are compared were made of comparable masses in standard aluminum DSC pans to eliminate any thermal lag effects that might cause spurious inconsistencies. All crystalline samples were melted at temperatures well above  $T_m$  (see Results section for details pertinent to each sample), held isothermally for 5 min, then cooled at 10°C/min to erase any thermal history differences caused by processing. Melting endotherms were obtained by subsequent heating at 10°C/min. Nitrogen gas was continuously fed into the sample chamber throughout each experiment. In order to completely eliminate discrepancies in thermal histories, some polyolefin DSC samples were made after being dissolved in boiling xylene and dried for 1 week at 50°C *in vacuo*.

### Optical Light Microscopy

Samples of pre- and postpulverized polymers were dissolved in boiling xylene then dried for 1 week in a vacuum oven at 50°C. Thin films of the polymers were hot pressed onto microscope slides and studied with a Nikon Optiphot2-Pol optical microscope. All specimens were melt-crystallized at 10°C/min from at least 35°C above  $T_m$  in a Mettler FP82 HT hot stage before examination under cross-polarized light.

## RESULTS AND DISCUSSION

### Free Radical Generation by Chain Rupture

The ambient temperature ESR spectra of all plastics exhibited either a significant increase in peak in-

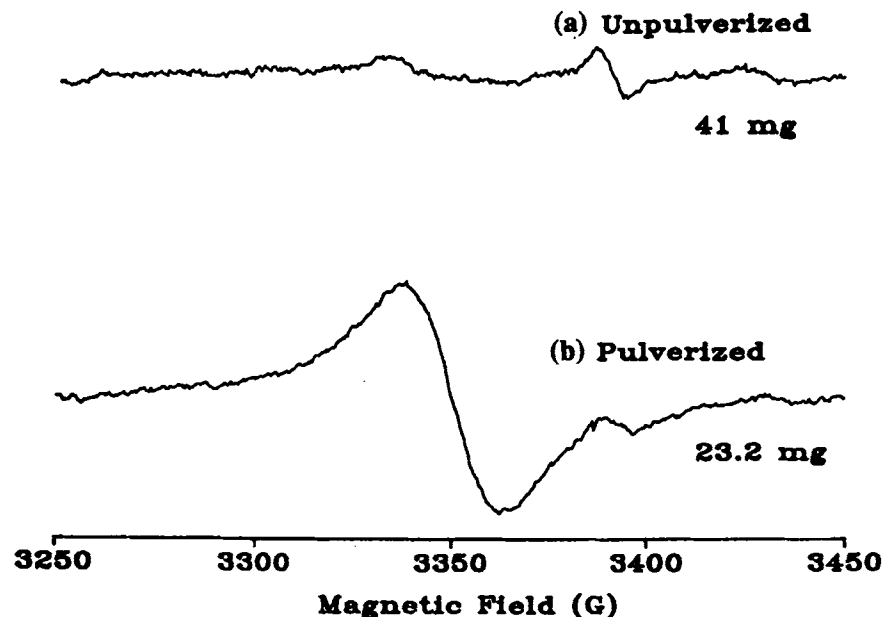
tensity after pulverization by ESP or no detectable peaks at all in the organic radical frequency range; a decrease in the signal after processing was never observed. To quantify these results, the peaks were integrated twice and compared with the spectrum of a known standard [ $\alpha, \alpha'$ -diphenyl- $\beta$ -picrylhydrazyl (DPPH) in KBr] to obtain the number of spins per gram of sample,  $N_s$ , that indicates the number of free radicals present in the sample. The  $N_s$  values of pre- and postpulverized samples are shown in Table I. Figure 1 shows the room temperature first derivative spectra of postconsumer PP, (a) before and (b) after pulverization by ESP, in which  $N_s$  is increased nearly a 100-fold by ESP. The peaks range from a minimum  $g$ -value of 2.000 up to 2.035, which is in the region typical of organic radicals [ $g_{\perp} \approx 2.002$  and  $g_{\parallel} \approx 2.035$  for thermally oxidized peroxy radicals (ROO·)].<sup>18</sup> The broad and slightly asymmetric line shape appears to originate from a combination of a number of different species. The absence of hyperfine splitting prevents us from identifying the contributing species. Because the samples were kept in ambient air for several months prior to study, the large number of stable free radicals detected at room temperature is quite unexpected.<sup>19</sup> The conspicuous absence of any detectable signal in the virgin PP samples, as well as in all single component HDPE and PET samples, causes us to eliminate the explanation that macroradicals are stabilized in regions of high crystallinity.

It is possible that certain additive molecules present in postconsumer PP and LDPE, but not in HDPE and PET, act as radical scavengers and stabilize the radicals as they are formed. An alternative

Table I Number of Spins/g Sample

Sample	$N_s$ ( $g^{-1}$ )		$N_s$ (After Pulv.)/ $N_s$ (Before Pulv.)
	Before Pulv.	After Pulv.	
LDPE	$1.9 \times 10^{16}$	$5.7 \times 10^{16}$	3.0
HDPE	$< 10^{11}$	$< 10^{11}$	—
PP	$7.2 \times 10^{14}$	$6.7 \times 10^{16}$	93
Virgin PP	$< 10^{11}$	$< 10^{11}$	—
PET	$< 10^{11}$	$< 10^{11}$	—
70/30 HDPE/PP			
Physical mixture	$2.2 \times 10^{14}$	$1.6 \times 10^{16}$	73
Copolymerized	NA	$2.1 \times 10^{16}$	95
40/60 HDPE/LDPE			
Physical mixture	$1.1 \times 10^{16}$	$3.4 \times 10^{16}$	3.0
Copolymerized	NA	$4.4 \times 10^{16}$	4.0

$N_s$ , for various postconsumer plastics before and after pulverization by ESP as determined by room temperature ESR.



**Figure 1** ESR spectra of (a) unpulverized and (b) pulverized postconsumer PP at room temperature.

explanation is that PP and LDPE form similar types of primary radicals that are more reactive with the scavenging additives than the HDPE and PP primary radicals. This is plausible because PP is known to rupture at the tertiary carbons, which are also present in a lesser degree in low density PEs (from chain branching), to form  $\cdot\text{C H}(\text{CH}_3)\text{—CH}_2\text{—R}$  radicals.<sup>20</sup> In contrast, linear PEs such as HDPE are known to rupture to form primary radicals  $\cdot\text{C H}_2\text{—R}$  that tend to transform into the secondary  $\text{R—CH}_2\text{—}\dot{\text{C}}\text{H—CH}_2\text{—R}$  radicals.<sup>20</sup> PET obviously will form very different radicals because of its unique chemical structure.<sup>15</sup>

Many commercial dyes are of low molecular weight (and therefore relatively mobile), and contain amines, aromatic, and highly conjugated groups,<sup>21</sup> which are typical of radical scavenging molecules. The reactions of mechanically created macroradicals of various polymers with radical scavengers is extensively reviewed elsewhere.<sup>16</sup> Because information about commercial polymer additives is largely proprietary and the original sources of the recycled materials are unknown, we cannot readily pinpoint the origin of the signal. However, the drastic increases observed in  $N_s$  after pulverization, particularly in the case of PP, are consistent with the data of many investigators<sup>15,16,19,20,22</sup> that have shown that free radicals are generated by the rupture of mainchain C—C bonds by mechanical forces.

Further analysis of the secondary reactions by ESR requires studying primary radicals that have

been trapped in liquid nitrogen before they can react, a feat complicated by the need to keep the powders in a cryogenic, inert atmosphere during sample transfer, loading, and experimentation. At this time, our ambient ESR studies have simply confirmed that mainchain C—C bonds are ruptured during the ESP process.

#### ESR Study of Polyolefin Blends

It has been reported that under sufficient mechanical action, reactions in some polymer blends proceed to copolymer formation despite the presence of radical scavengers.<sup>16</sup> Because the combination of pressure and shearing strain imposed on polymer chains during ESP is significantly higher than that of traditional mechanical grinding techniques,<sup>7</sup> we believe that there is a reasonable chance that either block, graft, or random copolymers may be formed in unpurified polymer blends. Compatibility is induced by the presence of block copolymers known to migrate to the interfacial regions of polymer blends and act as emulsifiers by reducing interfacial tension.<sup>3,4,23,24</sup> The presence of graft or random polymers should also promote homogenization, although not to the same extent as would block copolymers. In a “domino effect” scenario, the initial formation of a small amount of copolymer would propagate further copolymerization by promoting more thorough physical mixing of the blend components, that would in turn provide a more supportive environment for

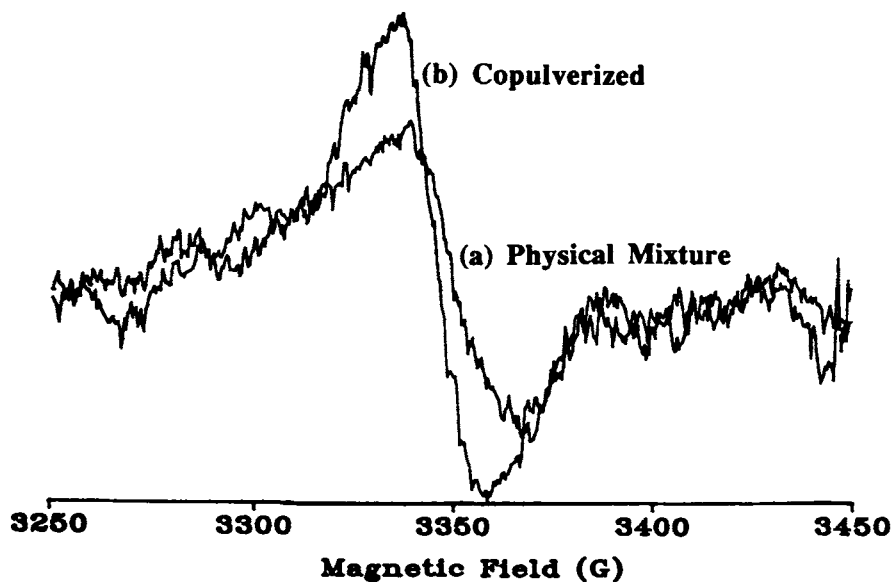
heterogeneous combination of macroradicals. In order for ESP to be practical in recycling of commingled postconsumer plastics, it is important that copolymer formation, or any other means of compatibilization, can occur despite the presence of radical scavenging additives. Otherwise, the process would be limited by costly purification steps.

As expected, the ESR spectra of both a 70/30 (mass %) HDPE/PP blend and a 40/60 HDPE/LDPE blend show a significant increase in  $N_s$  after ESP due to chain breakage. Furthermore, the copulverized samples of both blends show a 30% increase in  $N_s$  over what is expected of a physical mixture of the same polymers that have been individually pulverized. Figure 2 illustrates this effect for the 70/30 HDPE/PP blend. This supports a previous observation<sup>9</sup> that pulverization by ESP is enhanced by the presence of a second polymer. We can further trace this behavior back to the mechanism of rheological rupture. In any type of viscoelastic rheological rupture, the mechanical moduli of the polymer must be sufficiently large for elastic strains to build up to the critical point of bond rupture without being released by viscous flow. Experiments of several investigators<sup>25-27</sup> have shown a positive synergism in the tensile moduli of blends of HDPE and PP. For a 70/30 HDPE/PP blend, the enhancement in tensile modulus is 12%.<sup>25</sup> Thus, we believe that the enhancement in  $N_s$  that occurs in polyolefin blends

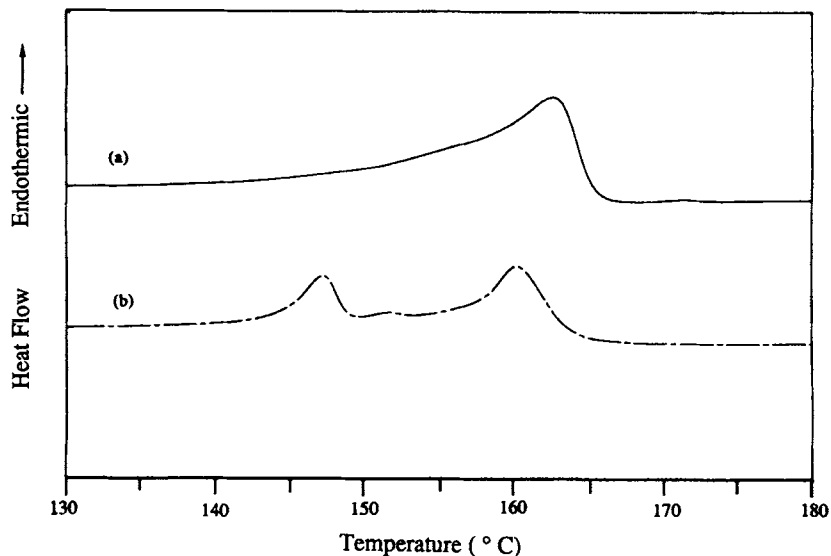
is due to the underlying enhancement of tensile modulus by blending. This increase in mechanically generated free radicals should improve the chances of copolymer formation by recombination during ESP.

### Melting Behavior and Morphology of PP after ESP

Consistent with the ESR data that show a drastic increase in spin density only in the postconsumer PP, the DSC thermograms of pulverized samples of HDPE and LDPE homopolymers did not show any noticeable differences from the unpulverized samples, but a striking difference in the melting peaks of postconsumer PP samples is shown in Figure 3. A heating rate of 10°C/min was used in both cases. Prior to the melting scan, both samples were kept at 200°C for 5 min, then cooled at 10°C/min, so the changes are not due to discrepancies in thermal history, and the result has been reproduced in other samples. Both of the corresponding crystallization exotherms obtained by cooling at 10°C/min are monomodal and are centered around 122°C. In the unpulverized PP, we see a single broad peak that melts at 162°C, while the pulverized sample is fractionated into three peaks at 148, 152, and 162°C. Multiple melting peaks are not uncommon in PP and have been attributed to a variety of different causes, including the presence of different types of



**Figure 2** (a) ESR spectrum of a noninteracting physical mixture of pulverized postconsumer 70/30 HDPE/PP obtained by spectral addition. (b) Actual spectrum of the copulverized 70/30 HDPE/PP blend at room temperature. Both spectra are normalized to the same mass.



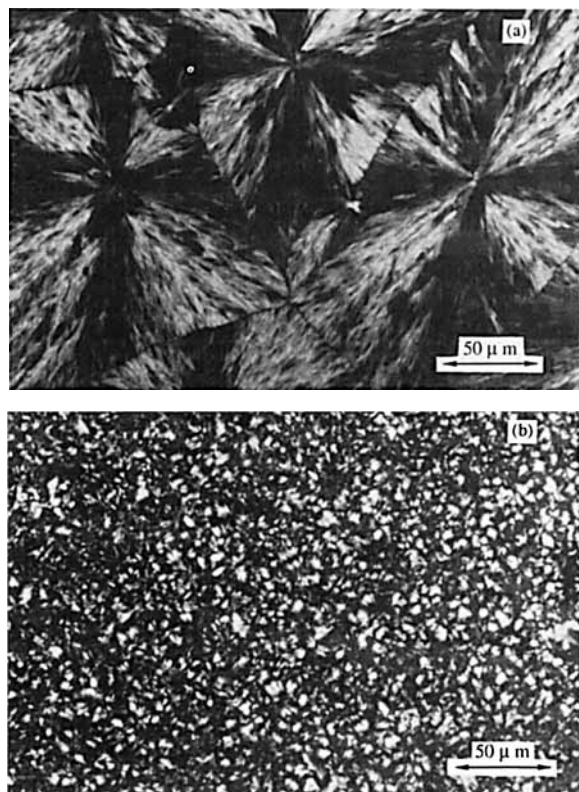
**Figure 3** DSC melting endotherms of postconsumer PP (a) before and (b) after ESP obtained by heating at 10°C/min. Both samples were first crystallized at 10°C/min.

crystallites.<sup>28-31</sup> It appears that the ESP process caused structural changes that result in the formation of different crystalline phases. X-ray scattering and DSC data for ESP processed isotactic PP films indicate that such behavior may be the result of a highly oriented melt state during ESP that leads to a *c*-texture in which the crystallites have their *c*-axes oriented preferentially parallel to the direction of extrusion.<sup>32</sup> In contrast, an *a*- or *b*-texture is common in PP processed by conventional extrusion methods. It is reported that the crystallization of this melt results in multiple crystallite types.

It is well known from melt index studies that the molecular weight of PP decreases significantly after repeated cycles in conventional extruders.<sup>33</sup> Therefore, it seems reasonable to believe that this fractionated melting is partly due to a reduction in molecular weight and increased polydispersity that result from ESP, which both influence the degree and perhaps the rate of crystallization.<sup>31</sup> However, the reported decrease in melt flow index<sup>17</sup> of the same batch of postconsumer PP after ESP seems to defy this reasoning. Also, we see an apparent, albeit slight, decrease in the overall crystallinity as quantified by 8 and 5% lower enthalpies of melting ( $\Delta H_f$ ) and crystallization ( $\Delta H_c$ ), respectively. This leads us to suspect that the multiple melting peaks may also reflect a slight change in tacticity of the PP, which is obviously not possible in the PEs, and/or introduction of chain branching or cross-linking. These irregularities in chain configuration would act as amorphous regions that should affect the crys-

tallization scheme. It has been reported that the appearance of multiple melting peaks in PP is promoted by decreases in either isotacticity or molecular weight, with stereoregularity being the dominating factor in the melting behavior of high molecular weight fractions of PP.<sup>31</sup>

The change in morphology after ESP is best illustrated by the polarized light optical micrographs of melt crystallized virgin PP thin films shown in Figure 4. In both cases, the samples were kept isothermally at 200°C for 10 min then cooled at 10°C/min prior to observation. A drastic reduction in spherulite size of approximately 100-fold can be seen in the pulverized sample, reminiscent of the effects of an externally added nucleating agent.<sup>25,34</sup> We present these results with caution, acknowledging the possibility that impurities may be present in the ESP extruder, which would increase the nucleation density. However, a qualitatively similar reduction in spherulite size was observed for the pulverized postconsumer PP, in spite of the presence of commercial nucleating agents that caused the average spherulite size to be smaller than that of their virgin counterparts. We have further reason to trust the validity of this result, because the reduced spherulite size is consistent with the overwhelming evidence of physical and chemical changes in the chain structure of PP as indicated by the ESR and DSC data. Comminution (of which ESP may be considered an example) of polymers is known to result in the destruction of crystalline structure.<sup>15,16</sup> Our DSC data of pulverized PP do not show a large reduction in



**Figure 4** Optical micrographs of melt-crystallized thin films of (a) unpulverized and (b) pulverized virgin PP under polarized light.

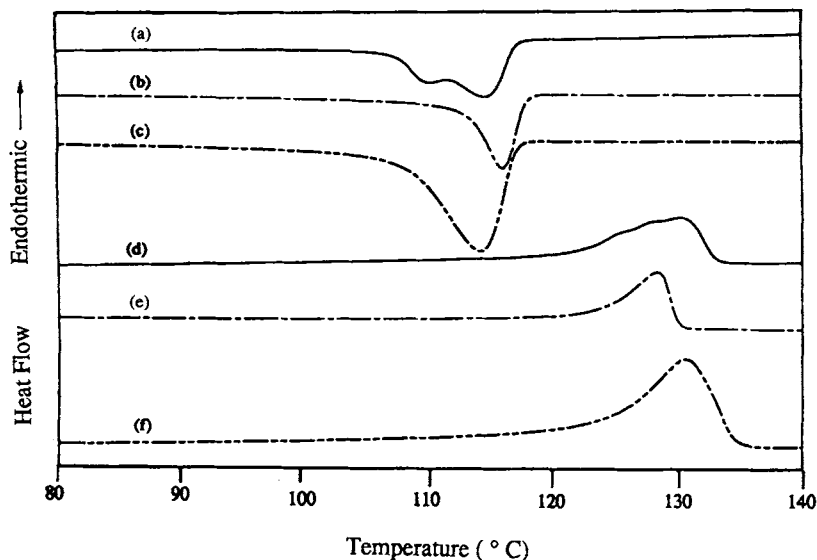
$\Delta H_c$  and  $\Delta H_f$  that would accompany destruction of overall crystallinity, but rather indicate an alteration of the crystallization scheme. It is possible that the introduction of small, dispersed amorphous regions from changes in chain structure would create a different type of heterogeneous nucleation site for crystallization.

It is well known that commercial PPs are largely isotactic. When mainchain bonds are broken, free radical termination by recombination may occur in any configuration (iso- or syndio-) resulting in a decrease in isotacticity and the development of chain branching. Conventional free radical mechanisms do not favor this type of chemistry, but the uniquely high pressures involved in ESP may increase the likelihood of recombination. Direct examination of the structure of the pulverized PP by nuclear magnetic resonance (NMR) or Fourier transform infrared (FTIR) may help to determine if configurational changes occur during ESP. Although such a change is undesirable for most applications of PP, detection of an increase in syndio-configured segments would confirm that the recombination of macroradicals does occur during ESP.

### Melting Behavior of HDPE/LDPE Blends after ESP

Polymer blends can be physically compatibilized by cocrystallization of the components. Studies of melting and crystallization behavior of crystalline polymer blends have been used to determine if such homogenization of crystalline phases has been induced by ESP. The most dramatic changes due to ESP were observed in postconsumer blends of HDPE and LDPE. The crystallization peaks of “before” and “after” postconsumer 60/40 HDPE/LDPE blends are shown in Figure 5(a–b). These data were obtained by cooling at 10°C/min subsequent to melting at 170°C for 5 min. Despite identical thermal treatment, the bimodal peak seen in (a) the unpulverized sample narrows and merges into (b) a single, sharp exotherm after ESP. This indicates that the HDPE and LDPE phases are homogenized by ESP to induce cocrystallization. In the pulverized samples, crystallization occurs over a narrower range that peaks at 1°C higher than the unpulverized sample. Figure 5(d, e) also shows the subsequent melting scans obtained with a heating rate of 10°C/min. Once again the (e) pulverized sample exhibits a narrowing of the broader, multiple peak originally present in the unpulverized mixture. As expected from the increased peak  $T_c$ , which indicates faster nucleation and less developed crystallization, we observe that  $T_m$  is decreased by 2°C in the pulverized blends.

In order to determine if this is simply due to inadequate mixing of the unpulverized mixtures, the same blends were dissolved in boiling xylene to insure intimate physical mixing of the components, then dried and subjected to the same thermal schedule as before. The crystallization and melting scans of xylene-dissolved samples of the unpulverized 60/40 HDPE/LDPE blend are presented in Figure 5(c, f). We observe approximately the same temperature ranges as in the undissolved, unpulverized samples for both melting and crystallization. However, the rough, multiple peaks have been resolved by mixing in xylene. Repetition of the same experiment with a 40/60 HDPE/LDPE blend yielded similar results. Because the broad peaks present in the original undissolved specimens were no longer present, it appears that the HDPE and LDPE blends are miscible. Therefore, we cannot claim that ESP actually induces compatibilization in HDPE/LDPE blends, but the unification of melting and crystallization peaks common to both undissolved pulverized blends and dissolved unpulverized blends indicates that ESP does lead to intimate mixing of the components that appears to be as effective as dissolution in a common

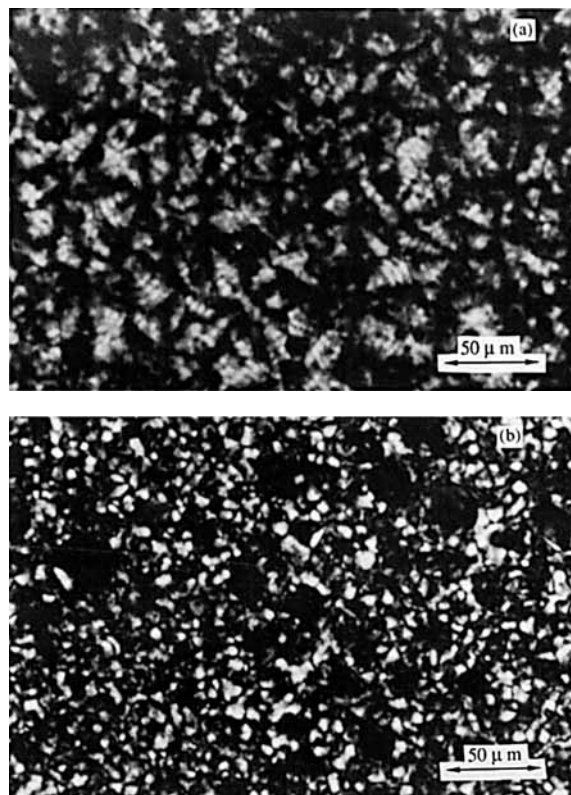


**Figure 5** DSC scans of postconsumer 60/40 HDPE/LDPE. The crystallization and melting scans for: (a) and (d) unpulverized, bulk blends; (b) and (e) copulverized bulk blends; and (c) and (f) unpulverized blends mixed in xylene prior to drying. All scans were obtained by ramping at  $10^{\circ}\text{C}/\text{min}$ .

solvent. Although we have not made an experimental comparison, it is doubtful that such a degree of mixing can be attained in a single pass through a conventional extruder.

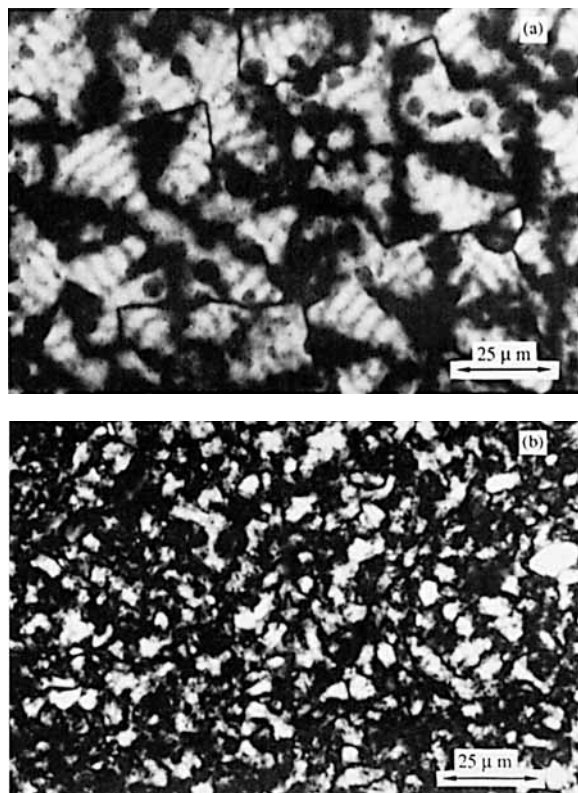
#### Spherulite and Phase Domain Size Reduction of Polymer Blends

Blends of postconsumer HDPE/LDPE, HDPE/PP, and HDPE/PS were observed under polarized light in an optical microscope. Melt crystallized thin films of all pulverized polymer blends that we studied exhibited a smaller average spherulite size than did their corresponding unpulverized films. In Figure 6, micrographs of the 70/30 HDPE/PP blend samples best illustrate this observation. The reduction in spherulite size is consistent with the results observed for the homopolymer PP, and we are convinced this is a result of changes in chain structure of the components. On a supermolecular level, compatibilization of the blend phases could also result in such an effect. This is made clearer by studying a crystalline/amorphous blend. The effect of coprocessing a 90/10 blend of HDPE/PS is seen in the polarized light micrographs in Figure 7. Spheres of PS appear to be trapped in a matrix of crystalline HDPE in the unpulverized blend, while the dispersed amorphous PS phase is not distinguishable in the pulverized blend. Observation of these samples under unpolarized light confirms that the PS spheres become much



**Figure 6** Polarized light micrographs of melt-crystallized thin films of (a) unpulverized and (b) copulverized postconsumer 70/30 HDPE/PP blends. Both samples were first cooled at  $10^{\circ}\text{C}/\text{min}$ .





**Figure 7** Polarized light micrographs of melt-crystallized thin films of (a) unpulverized and (b) copulverized postconsumer 90/10 HDPE/PS blends. Both samples were first cooled at 10°C/min.

finer after ESP. Because the PS phase is more finely dispersed by the pulverization, there must be greater interfacial surface area between the phases of the pulverized blend, which would occur if there were some type of compatibilization effect that reduces the interfacial energy. This supports previous results that indicate that ESP induces phase homogeneity in polymer blends.<sup>9,12,13</sup>

## CONCLUSIONS

The results of this study have confirmed that processing of polymers by elastic strain pulverization induces significant changes in morphology and microstructure of both homopolymers and polymer blends. We have used ESR to confirm that main-chain carbon bonds are broken to generate a significant number of free radicals in postconsumer plastics. Although the subsequent free radical reactions have not been studied yet, it is clear that further reactions can be promoted by this mechanochemical initiation step. The occurrence of multiple peaks in

the melting endotherms of PP after ESP indicate that there has been some physical transformation, which is due in part to a change in structure brought on by crosslinking, chain branching, and/or syndio-recombination of macroradicals. Chemical analysis of these materials by NMR should clarify the nature of these structural changes.

The similarity in DSC thermograms of pulverized HDPE/LDPE blends to unpulverized blends mixed in solution indicates the degree of mixing afforded by ESP. This is of considerable interest in itself. Further, we have seen supportive evidence of phase homogenization in incompatible polymer blends by the striking reduction in domain size observed by polarized light microscopy. *Although we have no unequivocal evidence that ESP creates compatibilizing copolymer molecules in situ, none of our experimental results refute this possibility.* On the contrary, the combination of ESR data with our observations of thermal and microstructural changes indicate that this type of partial compatibilization is likely to occur in an optimized process. This warrants more fundamental study in the future. Because the presence of a small amount of copolymer should rapidly propagate the formation of more copolymer molecules via a "domino effect," it is conceivable that further compatibilization could be achieved by multiple passes through the ESP extruder. To confirm the presence of mechanochemically synthesized compatibilizing copolymer molecules, more sensitive analytical techniques, such as FTIR and NMR should be used because they are able to directly probe the chemical structure of the processed blends.

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