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Cryogenic mechanical alloying as an alternative strategy for the recycling of tires

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Abstract

Cryogenic mechanical alloying (CMA) is investigated as a viable strategy by which to produce highly dispersed blends composed of thermoplastics and tire, thereby providing a potentially new route by which to recycle discarded tires. Morphological characterization of these blends by near-edge X-ray absorption fine structure (NEXAFS) microscopy demonstrates that, upon CMA, ground tire is highly dispersed within poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate) (PET) matrices at sub-micron size scales. Incorporation of polyisoprene (PI) homopolymer into the blends to improve dispersion efficacy is also examined. Neither PI nor the tire is found to interact chemically with PMMA or PET under the milling conditions employed here. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer recycling; Cryogenic mechanical alloying; Polymer blends

The environmentally responsible handling of large volumes of discarded polymeric materials, such as the elastomeric component of tires, poses a growing problem that must be faced by the polymer science community. As the options of disposal and incineration become increasingly less viable due to cost and environmental concerns, a wide variety of reclamation methods have been investigated to recycle expended tires [1–4]. Although these methodologies have enabled re-utilization of numerous waste tires, the mammoth volume of discarded material generated annually requires continual development of alternative recycling methods. This problem is exacerbated by the fact that elastomers, including natural and synthetic rubbers, are likewise utilized in a myriad of other applications and account for a significant fraction of the world-wide polymer consumption [1]. Thus, while we focus on tire recycling in the present work, elastomer recycling constitutes a general and immediate challenge. The recycling strategy examined here is cryogenic mechanical alloying (CMA), which has recently been shown [5–9] to produce novel organic blends composed of highly immiscible polymers and exhibiting nanoscale dispersion. This communication details an abbreviated study aimed at discerning the efficacy of CMA in producing blends of thermoplastic polymers and recycled tires.

Mechanical milling (one material) and mechanical alloying (two or more materials) refer to high-energy ball-milling techniques used to process materials in the solid state [10]. This processing method, initially developed for the dispersion strengthening of metallic superalloys [11], has expedited the production of various metastable inorganic materials and nanostructures (both single component and alloys) [10,12,13]. Following the pioneering efforts of Pan and Shaw (see Ref. [14] and the references therein), several studies have recently addressed the efficacy of mechanical alloying [15–17] and related solid-state blending strategies [18] as alternative routes to novel polymer blends. We have previously provided experimental evidence to demonstrate that CMA can produce substantial changes in polymeric materials by: (i) decreasing the molecular weight of poly(methyl methacrylate) (PMMA) [19] and poly(ethylene terephthalate) (PET) [20], (ii) promoting amorphization and molecular orientation in semicrystalline PET [20], and (iii) inducing chemical cross-linking in polyisoprene (PI) [19]. Combination of molecular scission and free radical formation suggests that CMA may be able to break down discarded tire and concurrently produce a chemically active surface, which could be used to produce polymer alloys with interesting and useful properties. In the present work, we

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examine the degree of dispersion achieved in CMA blends composed of PMMA or PET and tire.

Ground tire (70 mesh) was kindly provided by the Continental Tire Corporation and used as-received. The PMMA ($\bar{M}_n = 252$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 4.11$) was purchased from Aldrich and also used as-received, whereas the PET ($\bar{M}_v = 44$ kg mol^{-1}) was obtained from the Hoechst Celanese Corporation and ground into a coarse powder in a Brinkmann-Retch grinder prior to blending [20]. The PI ($\bar{M}_n = 72.1$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.05$) was custom-synthesized via living anionic polymerization and characterized by gel permeation chromatography [19]. Blends of the PI and/or tire and each of the thermoplastics were prepared by CMA. Predetermined amounts of each polymer (3 g in total) were placed in a hardened steel vial with 30 g of steel ball bearings (6.4 and 7.9 mm in diameter), and subsequently sealed in an inert Ar environment (<10 ppm O_2). The vial was placed in a custom-designed nylon sleeve that allowed peripheral circulation of liquid nitrogen around the steel vial. A thermocouple monitored the external vial temperature during milling so that the vial temperature remained constant at −180°C. The vial assembly was placed in a heavily reinforced SPEX 8000 mill and aggressively shaken for 5 h to produce a fine powder. After milling, the vial was allowed to return slowly to ambient temperature.

Blend powders were consolidated in a standard Carver press to generate solid plaques: PMMA blends were pressed at 125°C and 17 MPa, while PET blends were pressed at 125°C and 181 MPa. Specimens were maintained at temperature for 5 min before being quenched to ambient temperature. Resultant plaques were sectioned at −100°C in a Reichert-Jung Ultracut S cryoultramicrotome to produce thin films for analysis by near-edge X-ray absorption fine structure (NEXAFS) microscopy, which was performed at the National Synchrotron Light Source (Brookhaven National Laboratory). This instrument utilized a high-intensity, tuneable soft X-ray source in conjunction with a diffraction monochromater to provide a coherent X-ray source with an energy resolution of about 150 meV at the C K-edge (~290 eV) [21]. The photon energy was varied at fixed specimen position to generate NEXAFS spectra, whereas the photon energy was held constant and the specimen was raster-scanned to yield a position-dependent X-ray absorbance map [22,23]. Since NEXAFS constitutes a sensitive probe of system chemistry, it was used to differentiate between the polymers employed here, which possess similar elemental composition but differ in chemical functionality. For this reason, NEXAFS microscopy is emerging as a complementary analytical method by which to characterize the morphologies of multicomponent polymer systems [5–9,24].

To differentiate between the constituents within a polymer blend, we first identify the characteristic X-ray energies of each polymer from its NEXAFS signature. Fig. 1 shows mass-normalized NEXAFS spectra (set equal to 0.0 at 282 eV and 1.0 at 310 eV) acquired from the materials utilized in this study. The peaks in these spectra identify energies where X-rays are highly absorbed. By generating absorbance maps at these specific energies, the blend morphologies can be unambiguously determined. The primary peak in the PMMA spectrum is located at 288.4 eV and corresponds to excitation of the C=O functional group. Likewise, the peak at 285.0 eV in the PI spectrum can be attributed to C=C bond excitation. The PET, however, consists of both C=C and C=O functional groups. Due to conjugation between these groups, each moiety is responsible for the existence of two peaks: 284.7 and 285.8 eV for the C=C functionality, and 288.4 and 290.4 eV for the C=O group [25]. Thus, PET can be distinguished from PMMA and PI. As expected a priori, the NEXAFS spectrum acquired from tire closely resembles that of PI with a prominent peak positioned at 285.0 eV. Additives in the tire formulation are responsible for intensity reduction and broadening of this peak, as well as other apparent spectral differences. Comparison of the spectra in Fig. 1 therefore reveals that blend morphologies can be elucidated from images collected at 285.0 and 288.4 eV for blends with PMMA, and at 284.5 and 287.4 eV for blends with PET.

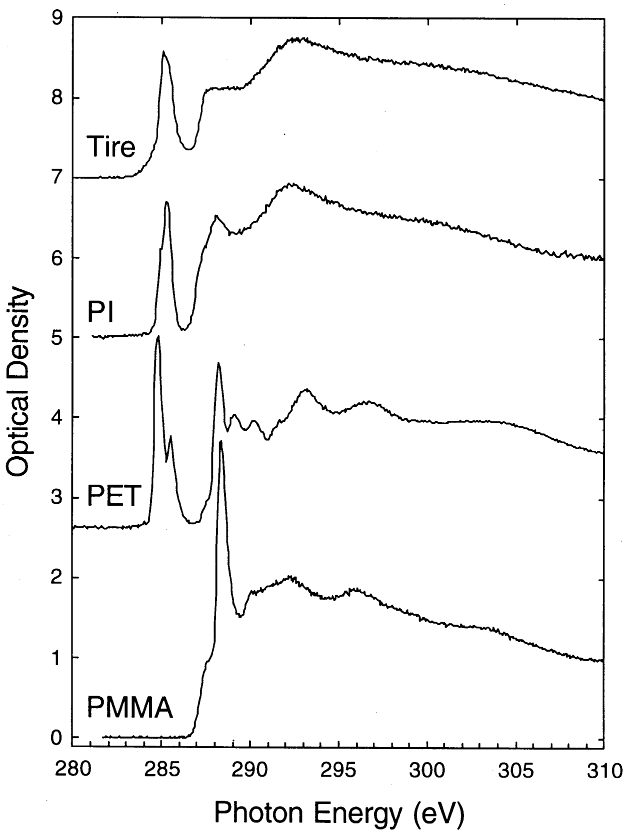

Fig. 1. NEXAFS spectra acquired from pure reference samples of PMMA, PET, PI and tire (labeled). These spectra have been mass-normalized (i.e., set equal to 0.0 at 282 eV and 1.0 at 310 eV) and offset vertically to facilitate comparison.

Images of tire/PMMA blends acquired at 285.0 eV,

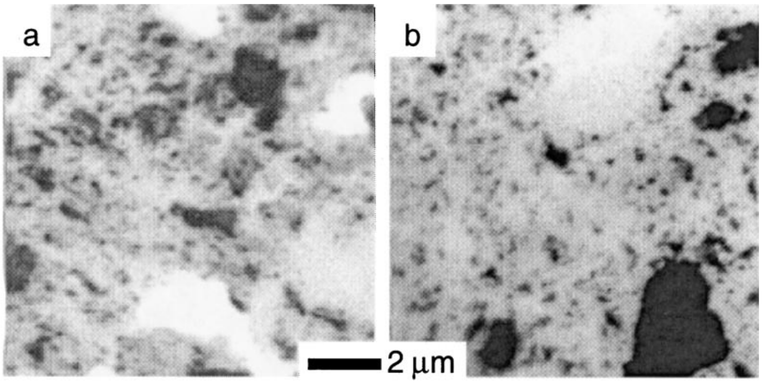

Fig. 2. NEXAFS micrographs of tire/PMMA blends with (a) 25 and (b) 10 wt% tire. The images have been collected at 285.0 eV, where the tire appears dark relative to PMMA. White areas reveal holes in the section.

where the tire selectively absorbs X-rays and appears dark relative to PMMA, are presented in Fig. 2. The blends displayed in this figure consist of 25 and 10 wt% tire (Fig. 2a and b, respectively) and demonstrate that the tire forms discrete dispersions within a continuous PMMA matrix. Tire dispersions produced as a consequence of CMA (note that the consolidation temperature is near the glass transition temperature of PMMA) and measuring as small as 200 nm and as large as 3 μm across are evident in both images. The jagged appearance of the large tire particles is consistent with the low consolidation temperature [8], as well as the cross-linked nature of the elastomer. The domains in these tire/PMMA blends are larger than PI domains in PI/PMMA blends produced by CMA [7]. This difference is not surprising since the tire is cross-linked and reinforced with additives to reduce wear, in which case it should be more resistant to mechanical attrition than virgin PI. In addition, the 10/90 w/w tire/PMMA blend could be readily cryomicrotomed, but a 10/90 PI/PMMA blend processed in identical fashion is too brittle to be sectioned. This observation implies that inclusion of tire to PMMA improves the physical properties of the blend relative to virgin PI, and warrants further investigation as a potential rubber-toughening methodology.

X-ray micrographs of tire/PET blends with 25 and 10 wt% tire are provided in Fig. 3a and b, respectively. At an X-ray energy of 287.4 eV, the tire appears dark relative to PET. As seen in these images, the morphologies of these tire/PET blends are comparable to those of the tire/PMMA blends, again illustrating that the tire is highly dispersed within the PET matrix due to CMA. Discrete particles of tire measure as small as 200 nm and are primarily extended, suggesting considerable extensional deformation during CMA. This extended domain morphology is qualitatively similar to the CMA blend morphology previously reported for poly(oxybenzoate-*r*-2,6-oxynaphthoate) (Vectra$^{®}$) in PET [5,26]. Such similarity confirms that the consolidation temperature (125°C) employed here is insufficient to permit substantial chain mobility, which is consistent with the fact that the consolidation temperature is far below the melting temperature of PET [20]. Even at low consolidation temperatures, though, the results presented here establish that CMA can produce sub-micron dispersions of tire within tire/PET blends.

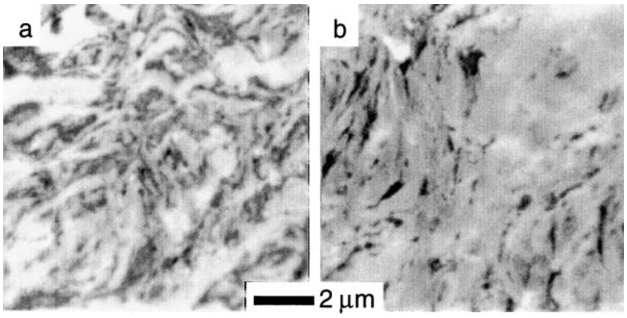

Fig. 3. NEXAFS micrographs of tire/PET blends with (a) 25 and (b) 10 wt% tire. The images have been acquired at 287.4 eV, where the tire appears dark relative to PET. White areas identify holes in the thin section.

As mentioned earlier, high-energy milling of pure PI has been found [19] to promote chemical cross-linking, eventually producing an almost completely insoluble material. In blends with PMMA, cross-linked PI maintains a high degree of dispersion or forms a continuous network upon post-processing at elevated temperatures [7,8]. This observation suggests that inclusion of PI in blends containing tire might allow cross-linking between the tire and PI and facilitate dispersion of the tire within the thermoplastic or incorporation of the tire within a network nanostructure. We have examined this possibility by preparing ternary PI/tire/PMMA blends with total rubber concentrations of either 25 or 10 wt% (to facilitate comparison with the analogous binary blends displayed in Fig. 2). The rubber content is 50/50 w/w tire/PI. Images of these blends with compositions of 12.5/12.5/75 and 5/5/90 PI/tire/PMMA are shown in Fig. 4a and b, respectively. As before, these micrographs have been acquired at 285.0 eV, where the rubber (PI/tire) appears dark relative to PMMA. These images reveal that the rubber is highly dispersed within PMMA, forming domains as small as 100 nm across. A nearly bimodal size distribution of rubber domains is also evident in Fig. 4. Comparison of

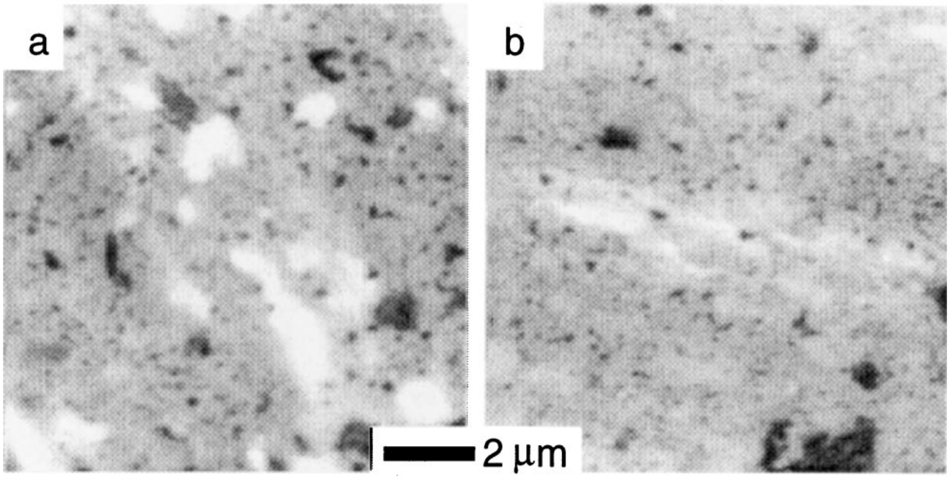

Fig. 4. NEXAFS micrographs of (a) 12.5/12.5/75 and (b) 5/5/90 PI/tire/PMMA blends. The images have been acquired at 285.0 eV, where the PI/tire appears dark relative to PMMA. The smaller domains are expected to be PI, whereas the larger domains are most likely tire. White areas correspond to holes in the thin sections.

these images with previous micrographs of PI/PMMA blends identifies the smaller domains (in the 100–200 nm range) as most likely PI, whereas the larger domains with jagged edges are probably tire. If this is the case, this result indicates that the tire and PI do not significantly interact in these blends under the CMA conditions employed here. By extending the milling time, greater molecular interaction may be induced and the dispersion efficacy improved.

In this study, we have explored the possibility of using CMA to produce polymer blends consisting of recycled tire. The aggressive mechanical action incurred during milling is expected to simultaneously reduce the size of ground tire particles and promote the formation of chemically active surfaces. X-ray micrographs of blends composed of tire and PMMA or PET reveal that CMA yields blends with sub-micron dispersions of rubber within both thermoplastics. The tire domains are found, however, to retain a jagged appearance due to a combination of low consolidation temperature and the cross-linked nature of tire. Addition of virgin PI to tire/PMMA blends in an effort to improve dispersion is also explored. While no significant chemical interaction between the PI and tire is observed in two ternary PI/tire/PMMA blends, an increase in milling time will most likely increase the probability of such interaction. These preliminary results confirm that CMA, as well as related solid-state processing strategies [18], constitute a viable technological alternative for recycling elastomeric materials such as those used in tire production.

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