Nanoscale Polymer Blends via Mechanical Milling

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Conventional melt and solution processes cannot overcome some of the technical barriers inherent in blending polymers. In fact, many polymers are immiscible with respect to each other, and the kinetic and thermodynamic limitations of compatibilizers prevent fulfillment of optimal property enhancement by blending [1]. In melt blending, excessive heating often leads to thermal degradation of polymer chains – a detrimental process that gives rise to phase separation and a broadened molecular weight distribution due to random chain scission [2]. In solution blending, the solvent is frequently difficult to remove once the blend is formed. This presents toxicity concerns and limits property enhancement. In both melt and solution routes, the potential for undesirable side reactions always exists, and nonuniform mixing and dispersion can result in poor blends [1]. Mechanical milling (MM) provides a solid state route to intimately mix polymers at the nanoscale in order to overcome thermodynamic macroscale phase separation.

The ultimate goal of this research is to compatibilize polymer pairs that are conventionally immiscible due to one or more factors. These barriers to compatible blending include large differences between blend components in terms of morphology and crystallinity, glass transition temperature (T_g), particle size and molecular weight (which influences T_g and viscosity). Other factors that inhibit immiscible polymers from compatibilization are nonuniform mixing and dispersion, little or no hydrogen bonding, and poor adhesion. The interest in compatibilization, therefore, arises because synergistic properties often result when dispersed-phase particle sizes are maintained on the order of a micron or less [1]. Finer dispersions resulting from small interfacial tension have large interfacial thicknesses and are more compatible, but as the interaction energy between the polymers grows, the blend morphology destabilizes as weaker, smaller interfaces result from large interfacial tension [3]. It is hypothesized that MM can amorphize semicrystalline polymers as well as intimately mix blend components as particle size is reduced. Adhesion between the polymers can be enhanced by MM-controlled entanglements that create broad interfaces [4].

High-energy ball milling (HEBM) has been studied thoroughly for mechanical alloying of dissimilar metals by Koch [5]. It is noted that severe plastic deformation induced by MM drives the amorphization, particularly at lower temperatures. The effects of HEBM at both ambient and cryogenic temperatures on the molecular weight, crystallinity and mechanical properties of both selected polymers and their blends have also been described in the literature by Smith et al [2]. For instance, the molecular weight (MW) degradation characteristics of PMMA and the effect on the glass transition temperature, T_g, are illustrated. Not surprisingly, MM increases the polydispersity index with milling time for both types of milling, and cryogenic milling degrades molecular weight less than ambient milling. These molecular weight decreases correspond to analogous reductions in T_g. The crystallization behavior of PET, annealed PET, PBT, PEEK, and PEI are illustrated by Font et al [6]. The more crystalline annealed PET, PBT, and PEEK amorphized to a greater degree than the more amorphous PET and PEI – more proof that MM destroys crystalline content. The rates of these MM-induced decrystallizations were not as sharp as those evidenced in melt or solution quenching, meaning that morphological changes are not as drastic.

Preliminary studies were performed to determine if MM produced a substantial amount of ultrafine particles (<100 microns). The polymer chosen for these analyses was substituted poly (p-phenylene) (PPP), a high-temperature, extremely hard thermoplastic (structure shown in Figure 1a). The SPEX millers, milling media, vials, and setup are illustrated in Figure 2. It was found that both ambimilling and cryomilling generated ultrafine particles of PPP. Cryomilling also introduced less contamination than ambimilling. HEBM in the SPEX 8000 at ambient temperatures has been shown to introduce contamination from the milling vials [7]. However, chemical analysis of cryomilled PPP revealed negligible contamination.

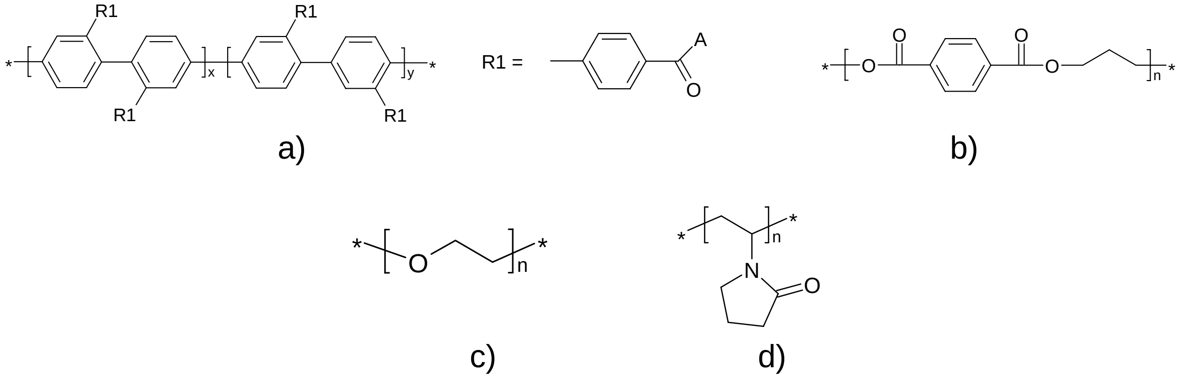

Figure 1 Molecular structures for studied polymers: a) substituted poly(p-phenylene) (PPP) and b) polyethylene terephthalate (PET), c) Polyethylene oxide (PEO) and d) polyvinylpyrrolidone (PVP). The PPP is a high-temperature amorphous thermoplastic with mechanical properties better than mild steel. PET is a semicrystalline commodity polymer. PEO and PVP are water-soluble semicrystalline polymers.

Figure 2 SPEX 8000 miller and stainless steel vials/media; SPEX 6750 cryogenic miller and polycarbonate vials with steel impactor.

Molecular weight characterization (by GPC and light scattering in series) of PEO and PVP was done to determine if MM affected their molecular weight distributions (MWDs). Figure 3 shows that both polymers do not mechanically degrade much with MM and that PEO undergoes slightly less molecular weight degradation with milling than PVP. This is consistent with their chemical structures (Figure 1), as PVP is more likely to undergo scission due to the presence of weaker C-N bonds. It can also be attributed to the fact that PVP has more amorphous content than PEO and has fewer polymer chains involved in crystalline lattices, thus leaving more chains exposed at amorphous/crystalline interphase regions for scission to occur. These results also imply that cryogenic milling can reduce particle size while maintaining molecular weight, a parameter that affects both thermal transitions (like glass transition and melting point) and mechanical properties (such as elastic modulus). These data are also in line with trends discussed in the literature.

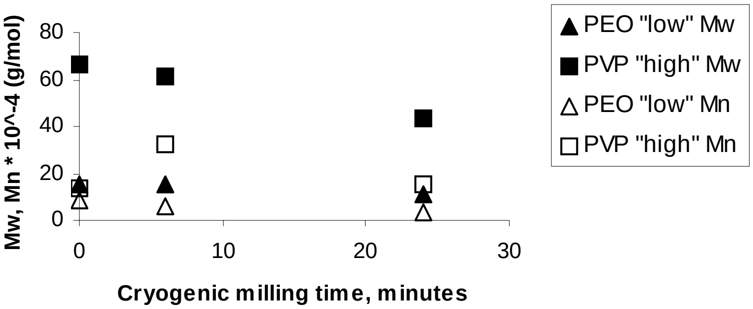

Figure 3: The effects of cryogenic milling on PEO and PVP weight- and number-average molecular weights. A low and high initial molecular weight was chosen for each polymer. Both polymers show little molecular weight distribution broadening or increase in polydispersity.

The amount of crystallinity for PEO and PVP was determined by X-ray diffraction (XRD) as well as differential scanning calorimetry (DSC). Weight percent crystallinities were obtained for XRD by methods outlined in the literature by Chung and Scott [8] as well as by numerical integration. The heat of fusion for 100% crystalline PEO is known to be close to 200 J/g [9]. Integration of melting peak areas with thermal analysis software allowed percent crystallinities to be calculated by DSC. A value for the heat of fusion for 100% crystalline PVP of around 970 J/g was determined by back-calculating it from known peak areas in DSC and percent crystallinities generated by XRD. The agreement between the two techniques was good.

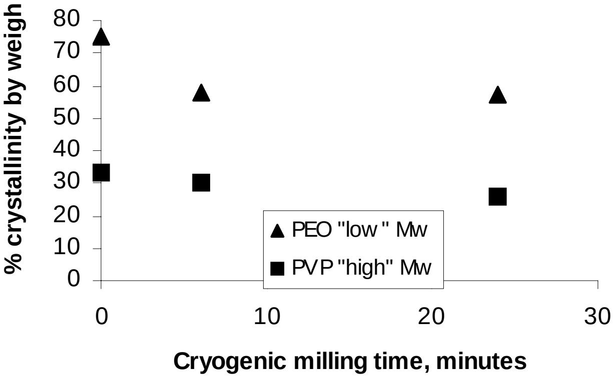

Figure 4: Weight % crystallinity versus cryogenic milling time for PEO and PVP. The more semicrystalline PEO loses more crystallinity within the first few minutes of milling because of a higher thermodynamic driving force. PVP is considerably more amorphous.

Figure 4 shows highly crystalline PEO (~75 wt %) reduced to 55 – 62 wt % by MM. PVP XRD patterns have a much larger amorphous halo, and subsequently, its crystallinity was less affected by MM (30 to 25 wt %). These findings agree with the aforementioned claims of Font et al. FWHM data allowed crystallite sizes to be calculated, and PVP had a crystallite size lower than PEO (1.5 nm vs 23 nm on average). PVP's crystallite size remained unchanged with increased MM, but PEO's crystallite size decreased with MM.

These data are not surprising, but the relationship with the molecular weight data is intriguing. The energy imparted from MM changed the two polymers in different ways. The PEO, being more crystalline in nature, showed almost no change in the shape and breadth of its MWD with MM. The impact energy was used up in amorphization or destroying the lattice structures rather than altering MW. PVP is more amorphous and has no reason to reduce its crystallinity significantly, so the impact energy went into changing its MWD more so than PEO. The structure of PVP allows it to be more amorphous and have more interphase chain scission than PEO.

XRD can also indicate phase separation in polymer blends if there is single phase crystallization or co-crystallization [10]. Crystallization studies of blends of high and low MW PEO blends have been well-characterized by Balijepalli et al. [11], and the interesting relationship between the MW of PEO, the crystallization temperature of the blend and its components, and the mechanism of PEO chain folding and morphology demands further questioning. Future factorial design experiments will determine whether molecular weight ratio, milling time, and composition are interdependent control parameters that affect amorphization, dispersion, and compatibility.

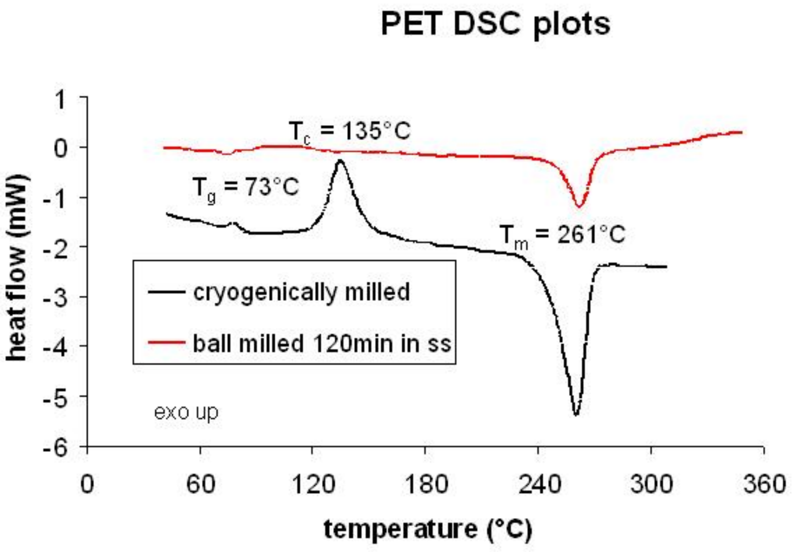

Figure 5: DSC plots for cryogenically milled PET (bottom plot) and ball milled PET (top plot) that illustrate the differences in crystallization behavior. T_g for both plots is ~ 73 °C. The cryomilled PET also has a crystallization temperature T_c at 135 °C and a melting point endotherm at T_m of 261 °C.

Polyethylene terephthalate (PET) as well as PPP were the polymers of choice for various thermal characterization techniques. DSC plots revealed the discrepancies in crystallization behavior for ambimilled and cryomilled PET: the low temperature inherent in cryomilling allowed for both the amorphous and crystalline components of PET to be present while HEBM showed little amorphous content (Figure 5). These results are consistent with XRD studies with PEO and PVP. The differences in impact energy and temperature between the two types of MM led to differences in morphology in PPP, PET, and their blends.

Fourier transform infrared spectroscopy (FTIR) analysis of these polymers and their blends was performed, and initial results showed some unique combinations of component spectra for several blends, including the globar IR spectra for PEO/PVP seen in Figure 6. Synchrotron IR was also investigated as a possible route to probe blend heterogeneity and later determining the size of the interface between blend components. Figure 7 shows how line mapping across a particle consisting of both PEO and PVP can be used to essentially probe the concentration of the components. Transmission electron microscopy (TEM) images of the blends show the affinity between the blend components and reduced domain size for semicrystalline polymer PEO (Figure 8).

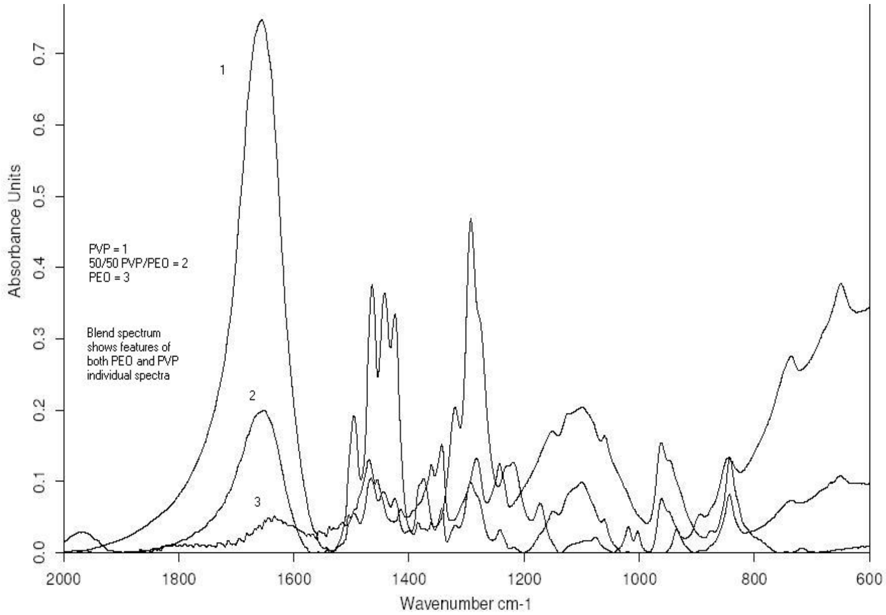

Figure 6: Globar IR spectra for PVP, PEO, and a 50/50 blend showing the contributions of each component to the spectrum of the blend.

Scanning electron microscopy (SEM) had been performed on some of the polymers and polymer blends. The results show that thermal history and milling type easily change the morphology of these compounds. However, they cannot distinguish between the components of the blends. Selective leaching of a blend component and subsequent observation by SEM is a probable technique to be utilized in the future.

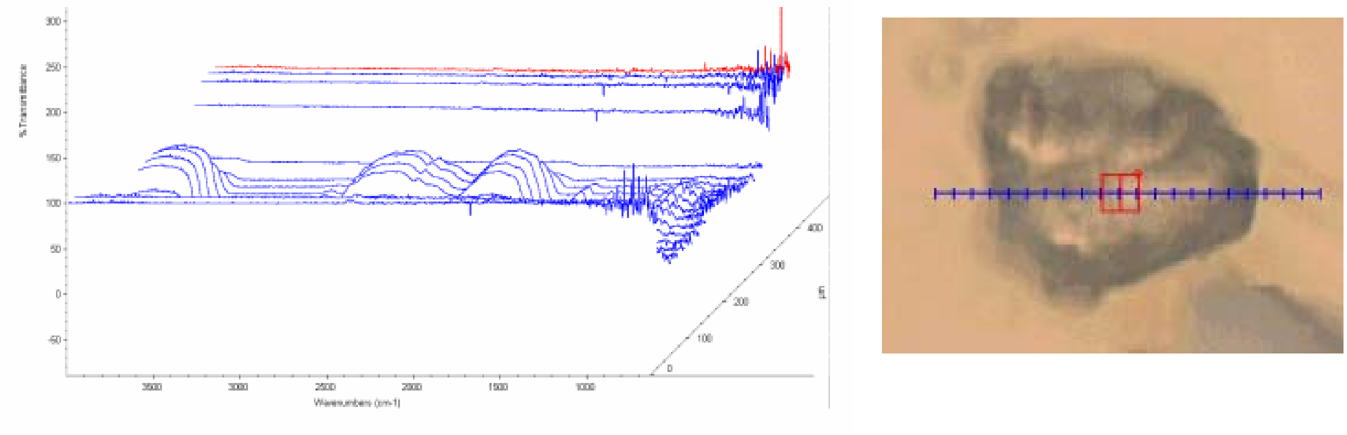

Figure 7: Synchrotron IR spectrum line-mapped profile for a particle consisting of PEO and PVP. The xy plane corresponds to a spectrum at some distance into the particle catalogued by the z-axis. The presence or absence of distinct, known peaks for certain components allows for easy characterization and estimation of domain sizes.

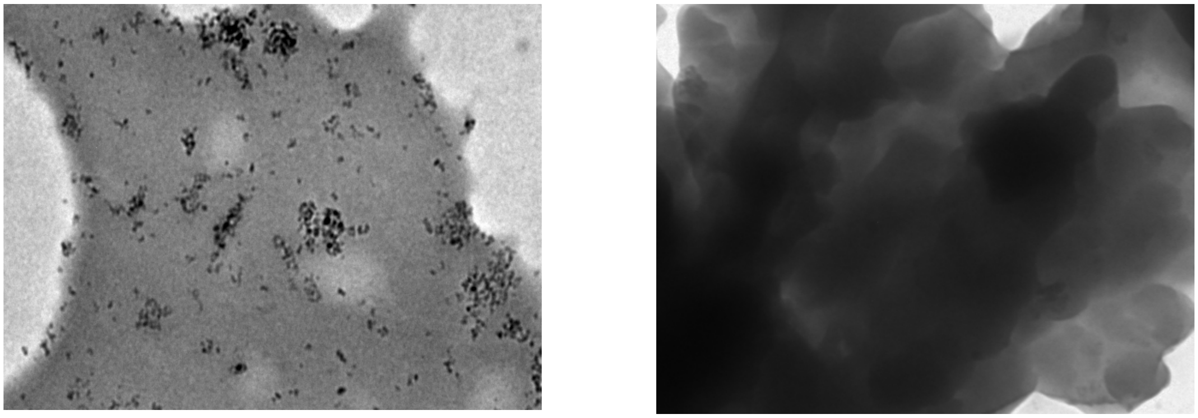

Figure 8: TEM photographs of a PVP/PEO blend (left) and a PPP/PEO blend (right). Magnifications are 6000 X for both pictures. The dark crystalline regions of PEO are visible against a bigger amorphous particle of PVP. However, against the dark flaky particles of PPP, the PEO is not visible. The compositions were confirmed by EDS.

As stated previously, the goals of this research are to learn how to create solid-state polymer blends from previously immiscible polymers. MM can provide the impact energy necessary to plastically deform, elastically fracture, and create new interfaces. The interest lies in the in-depth analysis of the interplay of intimate mixing, amorphization, particle size reduction, and cold welding. The improvement of adhesion by maximizing entanglements at the interface between polymers will lead to improved polymer blends.

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