On the similarity of macromolecular responses to high-energy processes: mechanical milling vs. irradiation

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Received 30 November 2000; received in revised form 10 January 2001; accepted 14 January 2001

Abstract

Recent efforts to blend and compatibilize intrinsically immiscible polymers in the solid state by high-energy methods have shown that macromolecules may undergo scission, crosslinking or amorphization, depending on the chemical nature of the repeat unit, the processing temperature and the initial degree of polymer crystallinity. Identical process-induced molecular and structural modifications have been previously observed in polymers exposed to large doses of electron and $\gamma$ radiation, suggesting that the responses of polymers to high-energy processes may be mechanistically similar. In this work, we explore a variety of similarities between mechanically-milled and irradiated polymers in terms of molecular characteristics, process temperature and polymer crystallinity, and we demonstrate that these similarities provide predictive guidance for the selection of polymers to be subjected to solid-state processing. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Mechanical milling; Solid-state processing; Chemical structure; Radiation damage

1. Introduction

Diversification, as well as an overall increase, in the usage of polymeric materials in numerous technological applications requires an in-depth understanding of the response of chain molecules to processes that subject the molecules to harsh environments and possible degradation. Most commercial polymer processes are designed to minimize chain stress and molecular degradation by operating within moderate levels of mechanical energy at elevated temperatures (in the melt state) [1]. In the past few years, high-energy solid-state processes — e.g. pulverization [2–4] and ball milling [5–9] — have been explored as alternative methods by which to modify polymer chains and produce novel polymer systems through complex physico-chemical means. High-energy ball milling, originally developed in the 1960s to produce oxide dispersion-strengthened alloys [10], constitutes one such processing route by which to synthesize metastable and nanostructured materials in the solid state. Mechanical milling (one component) and alloying (two or more components) of inorganic species have yielded a wide variety of materials possessing unique properties, extended stability limits and nanostructural elements [11–13]. Extension of these thriving process strategies to thermoplastic polymers in the early 1990s has not enjoyed comparable success due principally to the nontrivial degree of ensuing molecular degradation. Although independent efforts investigating solid-state polymer processing have consistently identified process-induced physical and/or chemical changes in the polymers employed, systematic evaluation of this outcome is lacking.

In several companion works, we have recently reported the effect of high-energy mechanical milling on the molecular characteristics of poly(methyl methacrylate) (PMMA), poly(ethylene-alt-propylene) (PEP) and polyisoprene (PI) [14], as well as the utility of high-energy cryogenic mechanical alloying to blend PMMA with either PEP or PI [15–17], poly(ethylene terephthalate) (PET) with poly(oxybenzoate-r-2,6-oxynaphthoate) (Vectra\textsuperscript{®}) [18], and PET with recycled tire [19]. An unexpected implication of our findings is that the molecular response...
of polymers subjected to high-energy ball milling appears mechanistically similar to that resulting from high-energy irradiation. While studies addressing high-energy solid-state polymer processing are scarce, those aimed at elucidating the effect of radiation damage on polymers are voluminous, since they reflect the importance of high-energy radiation in polymer processing and characterization [20–22]. High-energy irradiation typically promotes chain scission and/or crosslinking in organic media, thereby affecting the molecular weight and molecular weight distribution of most polymers, and likewise induces collapse of the crystalline structure in semicrystalline polymers [23,24]. The severity of these effects depends on the type of radiation energy (e.g., electron or gamma) employed, as well as on polymer structure, atmosphere and temperature. The primary objective of the present work is to identify and discuss similarities in the manner by which macromolecules respond to high-energy processes (mechanical milling and irradiation) in terms of molecular and environmental characteristics. By doing so, we identify design paradigms that can be used to judiciously select polymeric materials for solid-state mechanical processing.

2. Experimental

Three grades of PMMA differing in number- and weight-average molecular weight ($M_n$ and $M_w$, respectively), along with a single grade of polystyrene (PS), were purchased from Aldrich and used as-received. The molecular weight characteristics of these materials and their designations are listed in Table 1. Milling was conducted at ambient and cryogenic temperatures ($am$ milling and $cryo$ milling, respectively) by placing 3 g of polymer in a hardened steel vial with 30 g of steel ball bearings (6.4 and 7.9 mm in diameter) and sealing the vial in Ar. For amibimilled specimens, the vial was seated in a standard SPEX 8000 mill and agitated. In both cases, milling times ($t_m$) varied up to 10 h, after which time resultant powders were removed from the vial and stored. Molecular weight measurements were performed by GPC with a Waters 2690 injection unit and Styrage® HR4 columns. Differential pressure and light scattering measurements were simultaneously acquired at ambient temperature from polymer solutions (10 mg/ml) in THF with a Viscotek T60A dual detector and a Wyatt Technology Interferometric Refractometer, respectively. Sol-gel analysis of the PS was performed by vacuum-assisted filtration on 0.4 wt.% solutions in toluene using Fisher quantitative filter paper Q2 (particle retention <1 µm).

3. Results and discussion

3.1. Molecular characteristics

High-energy irradiation of long polymer molecules typically promotes main-chain scission and is accompanied by the formation of free radicals, crosslink sites, unsaturation and reactive endgroups [21,25]. Changes in the molecular weight and molecular weight distribution of an irradiated polymer depend sensitively on the relative probabilities associated with each of these events. Quantitative comparison of radiation-induced damage in macromolecules such as scission and crosslinking is possible through the $G$-value [21], the number of events per 100 eV of dose. These $G$-values are generally accepted as an intrinsic material property, and tabulated values of $G$ for the polymers discussed here are included in Table 1. Moreover, several empirical rules establishing the relative importance of the chemical events listed above have likewise been proposed. The first of these rules addresses the influence of substituent groups on vinyl polymers. Specifically, polymers with a tertiary

Table 1 Molecular weight characteristics for several different polymers subjected to cryomilling

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Initial $M_n$ (kg mol$^{-1}$)</th>
<th>Initial $M_w$ (kg mol$^{-1}$)</th>
<th>Final $M_n$ (kg mol$^{-1}$)</th>
<th>$t_m$ (h)</th>
<th>$M_w/M_n$</th>
<th>$\varepsilon^a$ (%)</th>
<th>$t_c$ (h)</th>
<th>$G$ (X)$^b$</th>
<th>$G(S)$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-PMMA</td>
<td>1040</td>
<td>253</td>
<td>258</td>
<td>3.5</td>
<td>4.1</td>
<td>-75.9</td>
<td>2.6</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>m-PMMA</td>
<td>121</td>
<td>67.1</td>
<td>43.2</td>
<td>3.5</td>
<td>1.8</td>
<td>-64.3</td>
<td>4.5</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>l-PMMA</td>
<td>16.6</td>
<td>14.8</td>
<td>8.55</td>
<td>3.5</td>
<td>1.12</td>
<td>-48.5</td>
<td>4.8</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>378</td>
<td>280</td>
<td>253</td>
<td>5</td>
<td>-33</td>
<td>0.02-0.05</td>
<td>0.01-0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PET$^c$</td>
<td>44.5</td>
<td>–</td>
<td>38.3</td>
<td>16</td>
<td>-14</td>
<td>106</td>
<td>&gt;0.8</td>
<td>0.08$^d$</td>
<td>0.16$^d$</td>
</tr>
</tbody>
</table>

$^a$ Molecular weight reduction, defined as $[(Final M_w - Initial M_w)/Initial M_w] \times 100\%$.

$^b$ In vacuum, $\gamma$ irradiation (from Ref. [21]).

$^c$ Data from Ref. [33] are expressed in terms of $M_c$.

$^d$ Electron irradiation (from Ref. [21]).
backbone carbon atom (–CH₂–CHR–)ₙ tend to undergo interchain crosslinking, while polymers with a quaternary carbon atom in the backbone (–CH₂–CR'R''–)ₙ most likely undergo scission upon irradiation [21]. This trend is illustrated by comparing poly(methyl acrylate) (R=COOCH₃), which is found [26] to crosslink, with PMMA (R'≡CH₃, R''≡COOCH₃), which degrades predominantly by scission (thereby making it ideally suited as a photoresist) [27,28].

A comparable dependence of chemical crosslinking/scission on polymer chemistry is observed in high-energy mechanical milling. Fig. 1 shows the solubility of ambimilled PS as a function of tₘ, as discerned from sol–gel analysis. This figure reveals that about 20% of the milled PS is insoluble after milling even for a short time. The time independence of solubility after 1 h indicates that crosslinking occurs quickly and that a steady state ensues wherein chain crosslinking and scission occur at nearly equal rates. This steady state is attributed to an increase in chain scission efficiency with increasing molecular weight [14,29,30]. High-energy mechanical milling of PMMA, however, results in a rapid and dramatic decrease in molecular weight [14]. In Fig. 2, the values of Mₙ for three different grades of cryomilled PMMA (h-PMMA, m-PMMA, l-PMMA) are presented as a function of tₘ. To estimate the propensity for scissioning to occur on a per monomer basis, we turn our attention to the data collected at short tₘ. Specifically, we have fit an exponential function to the data from 0 to 3.5 h and used the critical time (tₛ) defined as the time at which the molecular weight has dropped to 37% of the initial molecular weight, as a proxy for scissioning. The resultant values of tₛ are 2.5, 4.5 and 4.8 h for the high-, medium- and low-molecular-weight PMMA grades, respectively (see Table 1). The polydispersity indices (each index is given by $M_w / M_n$) of these PMMA grades are not the same and the high polydispersity of 4.1 for h-PMMA might account for the low tₛ observed for this polymer. It is interesting to note that the tₛ for m-PMMA and l-PMMA with polydispersity indices of 1.8 and 1.1, respectively, are almost identical. This similarity implies that the efficiency of mechanically induced scission per mass is not compromised even as $M_n$ decreases below the critical molecular weight of entanglement ($M_c = 27$ kg mol⁻¹) [25]. The relative constancy of tₛ even for molecular weight differences of almost two orders of magnitude is equivalent to a single G-value for any PMMA in the case of irradiation. On the basis of this result, we propose that tₛ in the same vein as G, can be considered an intensive material property. Correspondingly, mechanical milling seems to cause random scissioning events with a certain probability per mass.

While these milling-induced molecular weight changes in PS and PMMA — examples of one “quaternary” and one “tertiary” polymer species — are certainly not comprehensive, they strongly suggest that the molecular mechanisms by which polymers respond to mechanical milling and irradiation could be related.

Another empirical rule regarding the relationship between radiation damage and polymer chemistry applies to polymers possessing unsaturated bonds along their backbones. Irradiation of such polymers results in a greater tendency for interchain crosslinking relative to that in comparable saturated polymers. This effect is exemplified by PI, which contains a high level of unsaturation along the backbone and readily undergoes chemical crosslinking upon high-energy irradiation [21]. In a similar vein, cryogenic mechanical milling of PI has also been found [14] to promote chemical crosslinking.

Fig. 1. The solubility of ambimilled PS as a function of tₘ, revealing that about 20% of the polymer becomes insoluble due to milling-induced crosslinking. This is consistent with the expectation from irradiation studies that polymers with a tertiary carbon backbone atom are capable of crosslinking. The solid line serves as a guide for the eye.

Fig. 2. Dependence of $\bar{M}_n$ on cryomilling time (tₘ) for three PMMA grades differing in initial $M_n$ (in kg mol⁻¹): 255 (○), 67.1 (●) and 14.8 (▲). The solid lines serve as guides for the eye.
According to the same sol-gel analysis used to produce Fig. 1, cryomilled PI becomes increasingly insoluble with increasing $t_m$ so that only 20% of the material remains soluble after 10 h of milling. Analysis of these data on the basis of the Charlesby–Pinner relationship [21,31] indicates that PI crosslinks at a 50% higher rate than chain scission when subjected to mechanical milling. Although this rate of crosslinking is less than that recorded for radiation-induced PI crosslinking (in which crosslinking is $5$–$10\times$ more likely than scission [21]), the prevalence of PI crosslinking during milling is consistent with the existence of a general correlation between milling- and radiation-induced molecular degradation.

The last empirical rule between polymer chemistry and irradiation addressed here concerns the presence of conjugation, specifically aromaticity. Due to the ability of phenyl rings to absorb energy without undergoing bond rupture, aromaticity generally serves to reduce the extent of any reaction (i.e. crosslinking or scission) induced by radiation exposure [21,32]. Similar behavior is observed during mechanical milling, as evidenced by the data provided in Table 1. The values of $M_\infty$ of PMMA and PS measured by GPC are listed [14], as is the $M_\infty$ of PET from viscosity measurements [33], before and after cryomilling. The $t_c$ listed in Table 1 are conceptually inversely proportional to $G$-values, and proportional to a scissioning probability. Unfortunately, the energy absorbed by the polymers during alloying or milling is unknown and the number of scission events on an energy basis cannot be presently established for milling. Ratios or rank-orders of $G$-values and critical milling times must be used at the present time to permit meaningful comparisons.

Table 1 reveals that PMMA degrades the most rapidly of the three polymer species. In the cases of PS and PET, $M_\infty$ decreases more slowly than that of PMMA due to the stabilizing influence of aromatic substitution. Furthermore, PET is seen to experience the slowest rate of molecular weight degradation. Tabulated $G$-values for PS and PET suggest that PET should undergo scission more readily than PS. We note that recent experiments measuring the critical dose ($d_c$) for mass loss of PET and PMMA due to soft X-ray exposure yield a ratio of $d_c$PET/$d_c$PMMA > 100 [32], whereas the ratio of critical times during milling ($t_c$PET/$t_c$PMMA) is about 25. Values of $G(S)_{PMMA}/G(S)_{PET}$ range from 2 to 10 for the literature values quoted in Table 1. The radiation damage values for PMMA and PET, both of which occur predominantly by scission, thus bracket the value derived from mechanical milling. In contrast, PS seems to undergo scission much more readily during mechanical milling at cryogenic temperatures than anticipated. We hasten to point out, however, that the response of PS to milling in terms of its scission and crosslinking rates is strongly temperature-dependent, which might confound a proper comparison with prior radiation damage studies. With the reversed rank order of PS and PET notwithstanding, the mechanistic responses of these polymers to high-energy mechanical milling and irradiation appear to be remarkably similar in that aromatic groups stabilize the polymer against scissioning.

### 3.2. Process temperature

According to Dawes and Glover [21], the efficiency of radiation-induced macromolecular reactions tends to be enhanced with increasing temperature. This finding is responsible for dictating that polymer characterization by electron microscopy/spectroscopy should be performed at cryogenic temperatures on beam-sensitive materials to reduce the deleterious chemical and structural effects associated with radiation exposure [22,23,34]. Surprisingly, this trend is likewise observed in the high-energy mechanical milling of polymers, despite the intuitive expectation that a reduction in temperature would increase polymer brittleness and subsequently facilitate fracture and molecular degradation. The data presented in Fig. 3 clearly demonstrate that the dependence of $M_\infty$ on $t_m$ for PMMA is highly sensitive to milling temperature (note that Fig. 3 is presented on semi-logarithmic coordinates). The $M_\infty$ of this PMMA is initially 1040 kg mol$^{-1}$ and is reduced to 236 kg mol$^{-1}$ after 10 h of cryomilling. In marked contrast, $M_\infty$ is reduced to $<8$ kg mol$^{-1}$ after 10 h of ambimilling, indicating that molecular degradation is substantially more pronounced at ambient temperature than at cryo-

![Fig. 3](image_url) Time-dependent reduction of $M_\infty$ for PMMA ($M_\infty = 1040$ kg mol$^{-1}$) subjected to cryomilling (○) and ambimilling (●). Note that $M_\infty$ of the cryomilled sample decays more slowly than that of the ambimilled sample. The solid lines serve as guides for the eye.
genic temperatures. This counter-intuitive behavior is not restricted to PMMA, as it has also been recorded [33] for PET: cryomilling for 16 h yields a 14% loss in $M_t$, whereas ambimilling for the same $t_m$ promotes a corresponding reduction of 47%. Milling temperature can, however, affect macromolecules in ways other than molecular weight reduction. As mentioned earlier, PS undergoes chemical crosslinking when ambimilled even for relatively short $t_m$, but remains uncrosslinked during cryomilling. The crystallization and melting endotherms of PET have been discerned [33] from thermal calorimetry to shift with $t_m$ during high-energy mechanical milling, but occur more slowly for cryomilled, rather than ambimilled, samples. These examples provide evidence that lower temperatures inhibit milling-induced changes in several polymers, although the molecular mechanism responsible for these observations is not yet fully understood. Such behavior is, however, consistent with radiation-induced polymer damage. These findings imply that bulk polymer characteristics such as brittleness play only a secondary role in determining the rate and extent of degradation during both high-energy mechanical milling and irradiation.

### 3.3. Polymer crystallinity

The stability of crystalline structure is also very sensitive to irradiation and mechanical milling in polymeric, as well as in metallic, materials. Structural modifications such as amorphization and order-disorder transitions in metallic systems can be driven by either irradiation or mechanical alloying [35,36], and are sufficiently similar that they can be mathematically described in identical fashion [37,38]. In semicrystalline polymeric materials, irradiation generally induces defects into, and progressively collapses, the crystalline lattice, which is accompanied by a reduction in the melting point [21,23]. For example, PET exhibits a decrease in melting point of about 25°C after irradiation at high dose [21]. Milling-induced reductions in crystallinity have been observed repeatedly in polymeric systems. High-energy mechanical milling of polyethylene and poly(tetrafluoroethylene) results in amorphization, as evidenced [6] by reduced intensities and peak broadening in X-ray diffraction (XRD) patterns. Similarly, XRD and $^{13}$C nuclear magnetic resonance (NMR) studies of mechanically milled polyethylene [39] and polyamide [39,40] reveal a less crystalline material relative to their unmilled analogs. Moreover, milling-induced amorphization of PET has been recently reported [9,33,41]. The complementary XRD and calorimetry results of one study [33] support the formation of an oriented amorphous PET morphology during milling. Subsequent annealing of milled PET is accompanied by complete recovery of the crystalline structure, indicating that the mechanically induced changes are primarily physical in nature. In the absence of chemical changes, these examples again demonstrate that high-energy irradiation and mechanical alloying promote similar effects within polymeric materials.

### 4. Extension to mechanical alloying

Solid-state blending of two or more immiscible polymers by mechanical alloying offers tremendous potential as a means by which to create novel blends and blend morphologies that are otherwise unachievable [15,18]. Two issues that must be overcome for this technique to become a viable processing strategy are the molecular weight degradation during alloying [14] and phase coarsening that proceeds during post-processing in the melt [17]. By recognizing that polymers respond in similar fashion to both high-energy irradiation and mechanical milling, and relying upon the body of knowledge accumulated from radiation damage studies of polymers, these identified shortcomings can be addressed in an expedient manner. Since molecular weight degradation is strongly dependent on temperature and polymer chain structure, a radiation-resistant polymer can be combined with cryomilling to minimize degradation during milling. Likewise, by selecting two polymers with the ability to crosslink, the as-milled morphology could be fixed during milling and the problems of phase coarsening largely overcome. Optimization of such crosslinking would be required, however, to ensure post-processability of the blend. The promise of mechanical alloying as a viable means of blending polymers can be realized upon judicious selection of the constituent polymers, which can be greatly facilitated by knowing the response of the candidate polymers to high-energy irradiation.

### 5. Conclusions

In this work, we have compared the response of several macromolecules to two high-energy processes, one based on mechanical deformation (milling) and the other on radiation. Mechanically-milled polymers exhibit chain scission, crosslinking and crystalline degradation much in the same manner as irradiated polymers, and the factors influencing these molecular changes (e.g. polymer chemistry and temperature) appear to be process-independent. Limited data available thus far further indicate that bulk polymer properties such as brittleness are of only secondary importance in both processes. This mechanistic correlation between milling- and irradiation-induced polymer modification expedites the rational use of existing data regarding polymer radiation damage to predict the effect of solid-state mechanical processing on polymeric materials. Potential problems associated with the use of mechanical alloying to produce novel blends of
immiscible polymers can be overcome and an alternative technology for blending polymers more fully realized.

Acknowledgements

Support for A.P.S. and H.A. has been provided by the National Science Foundation through Young Investigator Award DMR-9458060. We are grateful to Professor C.C. Koch for the generous use of his mill, and we thank Dr. J.S. Shay for technical assistance.

References

[22] Smith AP, Ade H, Koch CC, Spontak RJ. Cryogenic mechanical alloying as an alternative strategy to tire recycling. Polymer, in press.
[23] Smith AP, Ade H, Koch CC, Spontak RJ. Cryogenic mechanical alloying as an alternative strategy to tire recycling. Polymer, in press.
[42] Smith AP, Ade H, Koch CC, Spontak RJ. Cryogenic mechanical alloying as an alternative strategy to tire recycling. Polymer, in press.