

HIPS/ γ -Irradiated UHMWPE/Carbon Black Blends: Structuring and Enhancement of Mechanical Properties

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ABSTRACT: CB-containing HIPS/UHMWPE and HIPS/XL-UHMWPE are unique systems, in which structuring takes place, affecting the electrical (to be described in a future article), rheological, mechanical, and dynamical-mechanical properties. The XL-UHMWPE particles have undergone structural fixation due to the crosslinking, maintaining their porosity and internal intricate structure even after high-temperature melt processing, as opposed to the UHMWPE particles. Differences in the flow mechanisms of HIPS/UHMWPE and HIPS/XL-UHMWPE blends have been attributed to polymer viscous flow in the former case vs. particle slippage in the latter. The mechanical properties of HIPS/UHMWPE are enhanced when utilizing XL-UHMWPE as a dispersed phase, especially the strength, because of changes in the inherent properties of the UHMWPE following irradiation, and in particular, the nature of the HIPS/XL-UHMWPE interface. The results for the CB-containing 70HIPS/30XL-UHMWPE blend are especially surprising and of practical importance, due to the fact that no degradation of the mechanical properties has occurred as a result of the CB incorporation. The dynamical mechanical properties reflect the differences between the UHMWPE and XL-UHMWPE-containing blends as well. The presence of either type of UHMWPE, CB content, and blend composition affect the dissipation, but have only a minor influence on the transition temperatures of the components. Of special interest is the increased damping of XL-UHMWPE-containing compositions. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1731–1744, 1999

Key words: HIPS; UHMWPE; XL-UHMWPE; mechanical properties; dynamical-mechanical properties; flow mechanisms

INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) possesses outstanding physical properties, enabling its utilization in a range of industrial applications. However, its high molecular weight constitutes a drawback, namely, an extremely high melt viscosity, limiting its processability by

conventional melt forming.^{1–4} Furthermore, its sensitivity to melt shearing, as reflected in the early appearance of melt fracture and chain scission, demands less conventional and low-shear processes, such as compaction and sintering, compression molding, or ram extrusion. An additional possibility of exploiting the valuable properties of this material is by blending it with another polymer, either by solvent blending^{5–7} or melt mixing,^{6,7} as in the present study.

The effects of high-energy radiation on polyethylene are of considerable scientific and commercial importance, and have been studied in some detail.^{8–13} Commonly used for medical purposes,

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UHMWPE is often sterilized by irradiation at low doses, which has been found to enhance some of the already unique properties of this material. The irradiation produces simultaneous crosslinking and chain scission events that occur preferentially in the amorphous phase and at the crystal fold surfaces. At high doses, chain scission may become a significant competitive process to crosslinking.¹¹ Chain scission may lead to increased crystallinity by cutting tie molecules that may then join the crystalline regions. If irradiated specimens are melted and recrystallized, the crosslinking may inhibit crystallization associated with reduced crystallinity, and therefore, modify the mechanical properties. This process is more pronounced in UHMWPE than in HDPE, mainly due to the entanglements effect.⁸

Immiscible polymer blends constitute interesting host matrices for the incorporation of conductive fillers, such as carbon black (CB). The multiphase nature of these systems provides an opportunity for the filler to distribute nonuniformly within the phases or at the interface, due to the different properties of the blend components. When the CB-containing phase forms continuous structures within the continuous matrix, double percolation may be obtained, forming honeycomb-like structures in which conductive pathways may prevail. This exceptional structuring enhances the electrical conductivity and reduces the critical CB content essential for percolation.¹³

In this research, neat and CB-containing HIPS/UHMWPE blends were studied. UHMWPE was utilized as the dispersed phase within HIPS in place of a conventional polymer, due to its exceptionally high viscosity, which inhibits CB penetration, and the possibility of crosslinking it by γ -irradiation, prohibiting its flow. The UHMWPE was incorporated in powder form, either as-received or γ -irradiated. Initially, the effect of the irradiation on the structure and thermal behavior of the UHMWPE powder was determined. Subsequently, the blends were studied in an attempt to correlate the structure with the observed mechanical, dynamical-mechanical, and rheological properties. The electrical properties of these blends will be reported in a future article.

EXPERIMENTAL

The principal polymers used in this study were high-impact polystyrene (HIPS), Galirene HT 88-5 (MFI = 5 g/min; Carmel Olefins, Israel) and an ultrahigh molecular weight polyethylene

(UHMWPE) powder, Gur 412 (Hoechst Hostalen). Some of the same UHMWPE particles were previously γ -irradiated in vacuum by a ⁶⁰Co source at a 15 MRad dose, for crosslinking (XL-UHMWPE). Carbon black (CB) Ketjenblack EC-300 (Akzo), was used in this study. All blend ratios described relate to percentage by weight.

All the blends were prepared by melt mixing the dry-blended CB and polymer components in a Brabender Plastograph equipped with a 50 cm³ cell at temperatures of 190 and 230°C for approximately 15 min. The resulting blends were subsequently compression molded to obtain 3 mm-thick plaques. An alternative method used for some selected formulations was injection molding, using an Arburg 220/150 machine combined with a standard ASTM mold. To obtain well-mixed blends, the components were initially mixed in the Brabender plastograph, and subsequently ground to pellet size and injection molded.

Rheological studies of CB-containing polymers and blends were conducted using a MCR capillary rheometer mounted on an Instron TT-D machine, equipped with a capillary of 5 cm (2") length and 0.127 cm (0.05") diameter ($L/D = 40$). Samples prepared earlier by melt mixing in the Brabender Plastograph were extruded in the capillary rheometer at a temperature of 230°C. The apparent viscosity was measured in a shear rate range of 20 to 3000 s⁻¹.

Tensile mechanical properties of extrudates prepared by the capillary rheometer at a cross-head speed of 1 cm/min were measured by using an Instron. At least 10 extrudates of each sample were measured. Some injection-molded dumbbell-shaped specimens were analyzed as well.

Differential scanning calorimetry (DSC—Perkin-Elmer Series 7), and dynamic mechanical thermal analysis (DMTA—Perkin-Elmer Series 7) were carried out at heating rates of 10 and 2°C/min, respectively, in an inert nitrogen gas atmosphere.

The morphology of freeze-fractured samples, gold sputtered prior to observation, was characterized by a JEOL 5400 scanning electron microscope (SEM). Some powder particles and microtomed surfaces were observed as well.

RESULTS AND DISCUSSION

The UHMWPE Powder

The Effect of Irradiation on the UHMWPE Powder Structure

Reference samples of UHMWPE powder, as-received and irradiated, were observed by SEM

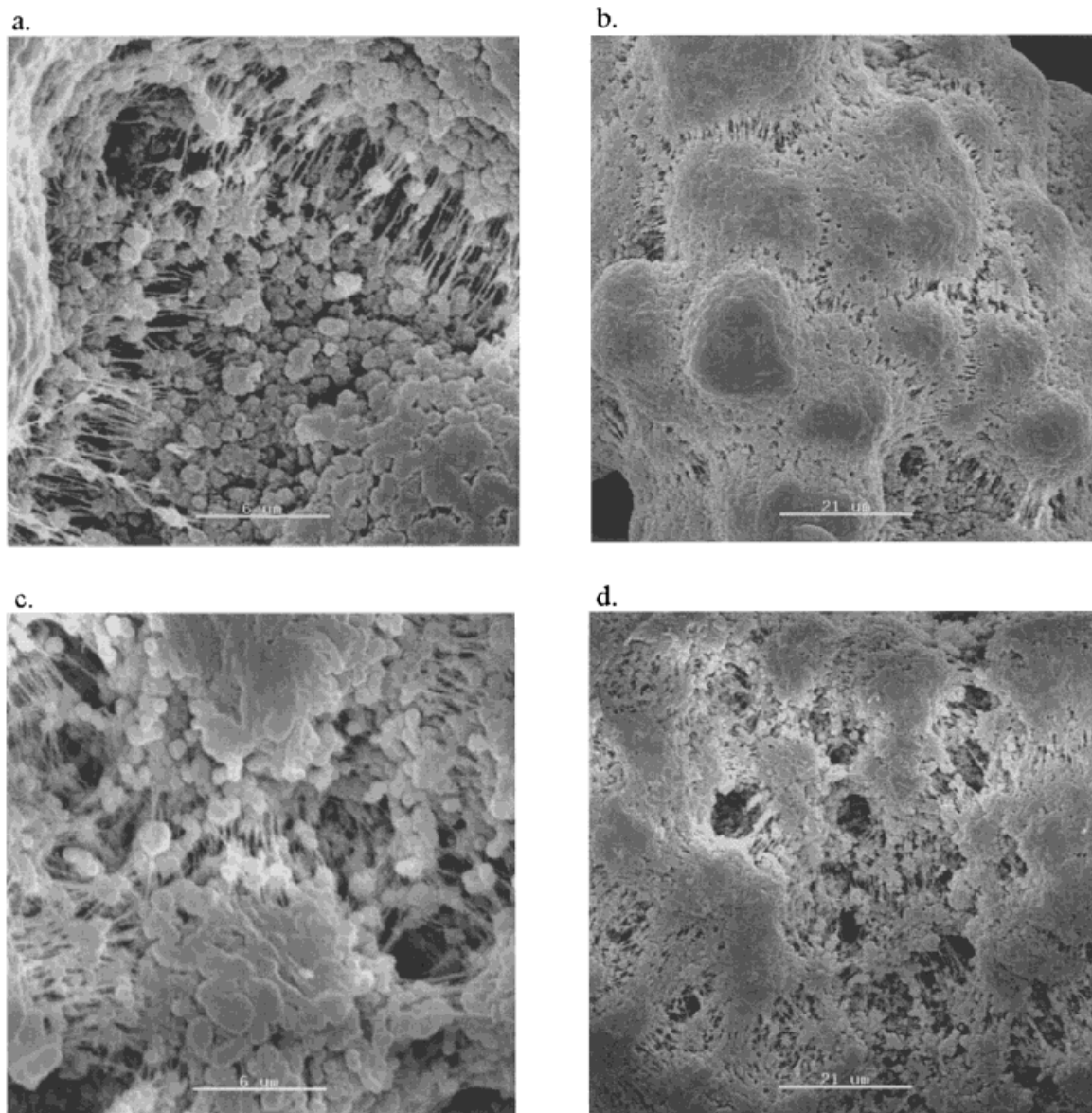


Figure 1 SEM micrographs of reference samples of UHMWPE powder: as-received, (a) at high and (b) at low magnification; irradiated, (c) at high and (d) at low magnification.

(Fig. 1) to comprehend their structure prior to compounding with HIPS and CB. As has been observed earlier,¹⁻⁴ these as-polymerized particles exhibit an interesting structural hierarchy. At low magnifications, the particles seem porous and ellipsoidal, approximately 100 μm in diameter. However, at higher magnifications a very intricate morphology is revealed. The smallest structural units observed are nodules, less than 1 μm in diameter. These nodules tend to aggregate, and form clusters of various sizes, the next unit in the structural hierarchy. Interconnecting them are very fine fibrils, highly extended, which in

certain regions form web-like networks in which an occasional nodule or aggregate is situated. It has been suggested that the unique structure of the UHMWPE powder is formed during the polymerization process, due to the hydrodynamics in the reactor. The fibrils are formed while the polymer is in the reaction medium, upon stretching the as-polymerized material. The nodules deform inhomogeneously, forming micronecks along which the fibrils are stretched. The localized deformation results in the breakdown of large nodules into small ones, linked by the fibrils. The fibrils presumably consist of highly oriented, crys-

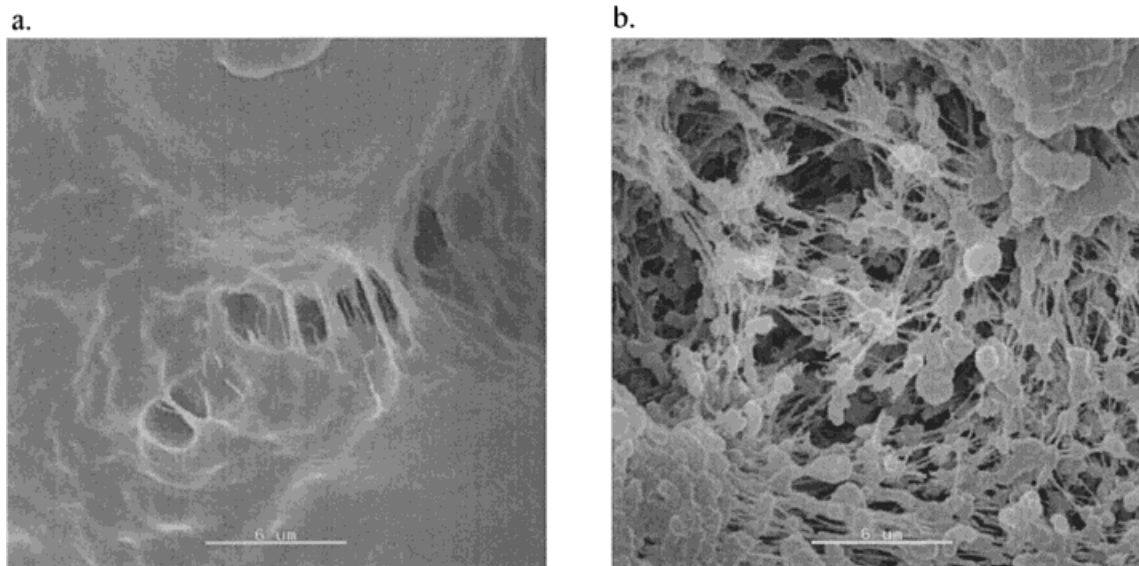


Figure 2 SEM micrographs of samples of UHMWPE powder, annealed for 5 min at 150°C: (a) as-received; (b) irradiated.

talline regions of polyethylene. It is, therefore, evident that the UHMWPE powder particles have a highly porous and complex structure, with a high surface-to-volume ratio.²

Both, as-received and irradiated particles [Fig. 1(a) and (c), respectively], reveal very similar structures, and are essentially indistinguishable. All of the distinctive characteristics described above, relating to the neat powder, are observed in the irradiated sample as well. Any changes that may have taken place due to the irradiation, are not detected at this scale of observation.

Both types of particles, after annealing at 150°C (above T_m) for 5 min are shown in Figure 2. The annealed as-received powder particle remains unchanged in size and maintains its general ellipsoidal shape; however, its inner structure is completely altered [Fig. 2(a)]. The nodules have practically disappeared and, at most, traces of the fibrillar structures are observed on the surface. An occasional extended fibril is detected in a few locations. The particle exterior porosity has changed into a relatively smooth, closed structure. Conversely, the irradiated particle [Fig. 2(b)] has maintained its highly complex morphology, and depicts the features previously described for the untreated samples, causing this sample to be indistinguishable from its counterparts in Figure 1.

These results lead to the conclusion that fixation of the original intricate particle morphology has occurred by the γ -irradiation-induced crosslinking, preventing its structure from deforming

upon annealing above the melting temperature. When the as-received powder particle is heated to 150°C, the crystalline regions undergo melting, the nodules and clusters and coalesce and the extended fibrillar structures undergo melting, giving rise to collapsed structures with external smooth textures. The irradiated sample, however, remains highly fibrillar and porous, due to the structural fixation, which hinders deformation upon heating. The amorphous regions, which undergo crosslinking, deform only slightly upon heating, and therefore act as anchor points for the adjacent crystalline regions. This enables preservation of the fibrils even during melting.

Thermal Behavior

DSC thermograms of the as-received UHMWPE and XL-UHMWPE particles are presented in Figure 3, showing two runs of melting and one of crystallization. The initial heating run is the first time both particles have ever been subjected to melting. In the first heating run, the as-received UHMWPE powder has a higher T_m than its crosslinked counterpart, but a lower melting enthalpy value. The second run yields lower T_m and melting enthalpy values for both UHMWPE and XL-UHMWPE, in relation to the first run.

These results show that significant changes in the crystalline phase take place in the UHMWPE subsequent to irradiation and recrystallization, as reflected by the first and second runs, respectively. The T_m and enthalpy of the as-received

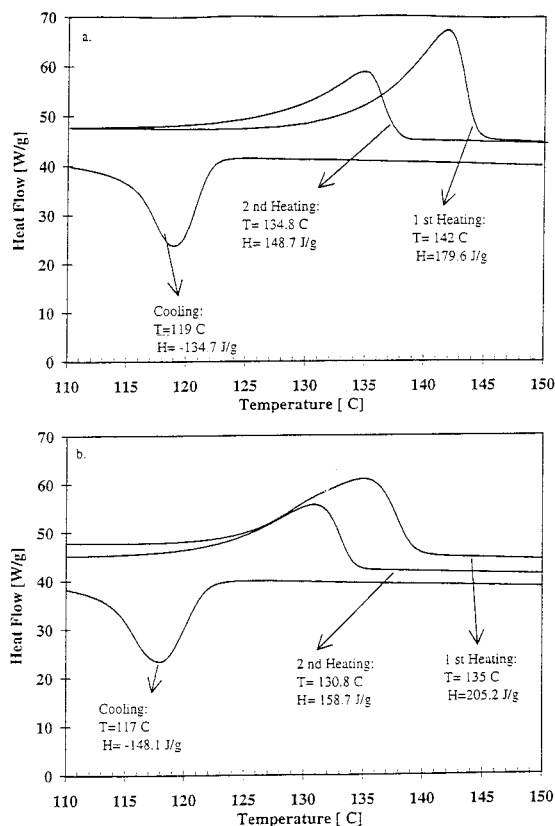


Figure 3 DSC thermogram of (a) as-received UHMWPE powder and (b) XL-UHMWPE powder.

UHMWPE (as-polymerized) undergo reduction upon crystallization from the melt (second run), representing a decrease in both crystallite size and degree of crystallinity, respectively. This may be attributed to the unique nature of UHMWPE, in which molecular entanglements of the very long chains predominate within the melt, and actually act as “physical crosslinks,” hindering the crystallization process.

The first heating run of the XL-UHMWPE shows a higher degree of crystallinity but a lower T_m than the corresponding as-received sample. Thus, the relatively large dose of γ -irradiation, 15 Mrad, has caused an increase in crystallinity.⁸ This occurs by scission of tie molecules,¹¹ followed by crystalline reorganization and transfer of chains from the amorphous to the crystalline phase. However, this results in a somewhat poorer crystalline quality, as reflected by the lower T_m value. The melting point depression has been previously suggested to stem from a reduction in concentration of segments of a length suitable for crystallization.⁹ When the XL-UHMWPE is reheated for the second time, the T_m value decreases, and the enthalpy of fusion is consider-

ably reduced, because in this case, the polymer has been crystallized from a crosslinked melt. It has been suggested that the crosslinked amorphous regions hinder the crystallization process, resulting in a lower degree of crystallinity and reduced crystallite dimensions. The melting enthalpy of the XL-UHMWPE in the second run is higher than the corresponding value for UHMWPE, again due to the irradiation-induced chain scission.

HIPS/UHMWPE Systems

Blend Morphology

The blend morphology (Fig. 4) may be directly related to the powder particle structure following melting, as described above. In the 70HIPS/30UHMWPE blend, the UHMWPE particles are observed as large ellipsoids with dimensions similar to the original particles, a few tens of microns in size. In general, the particle has lost its unique external morphology, and appears as a uniform domain, dispersed within the HIPS. Some remnants of the original particle structure are observed at the surface, as collapsed fibrils, but no porosity is detected. The adhesion between HIPS and UHMWPE is relatively weak, as reflected by the gap at their interface. It is, therefore, apparent that upon blending at high temperatures the UHMWPE particles have undergone a process similar to the heat treatment depicted in Figure 2, losing their porosity and nodular structures.

The fracture surface of the corresponding blend, HIPS/XL-UHMWPE, may be compared with the morphology of the XL-UHMWPE particles in Figure 2(b). It seems that the original small particles maintain their structural features even after the high-temperature shear processing, due to, as previously described, fixation of the morphology by crosslinking. The fibrils in the irradiated particles, however, are not detected in the blends. Although they withstood the thermal heating [Fig. 2(b)], some were probably broken during the blending process, due to high shearing at elevated temperatures. The stable porosity of the dispersed XL-UHMWPE phase enables the HIPS matrix to penetrate into its surface layer, resulting in a closely mechanically interlocked structure. The two phases appear to adhere well to each other, making it difficult to distinguish between them. The fact that the freeze fracture propagates also within the dispersed XL-UHMWPE phase rather than at the interface is a manifestation of the mechanical bond strength between the two components.

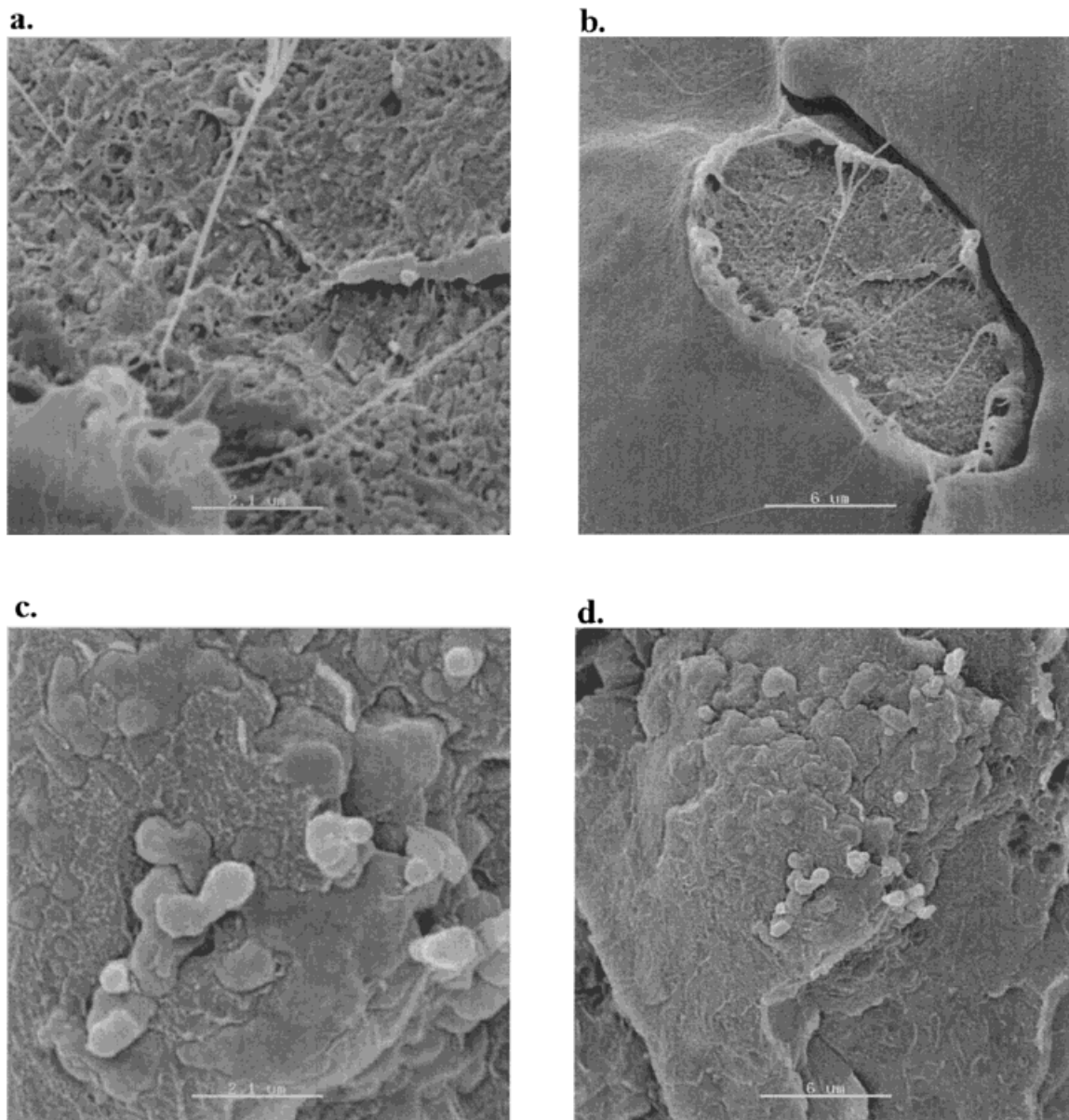


Figure 4 SEM micrographs of freeze fractured 70HIPS/30UHMWPE blends at (a) high and (b) low magnifications, and of 70HIPS/30XL-UHMWPE at (c) high and (d) low magnifications.

Incorporation of CB into blends of either the as-received or the crosslinked systems with HIPS does not significantly alter the blends' morphology (Fig. 5), as has been observed in previous systems.¹⁴ In both cases the CB is located at the interface. In the HIPS/UHMWPE blend, CB appears at the surface of the ellipsoidal dispersed UHMWPE particles. The tendency of the CB is to preferentially locate in the PE phase.¹⁴ However, the CB is unable to penetrate the UHMWPE particles due to their high viscosity; therefore, the CB particles are induced to segregate at the surface.

In the HIPS/XL-UHMWPE blend, the CB is again located in the interfacial region, mostly in the HIPS, at the vicinity of the XL-UHMWPE particles.

The phase-inverted systems, in which the UHMWPE phase constitutes the major component, have been studied as well. The 70XL-UHMWPE/30HIPS blend is similar in structure (not shown) to the 70HIPS/30XL-UHMWPE blend, just with a higher XL-UHMWPE content. The 70UHMWPE/30HIPS composition is slightly different, depicting continuity of the UHMWPE

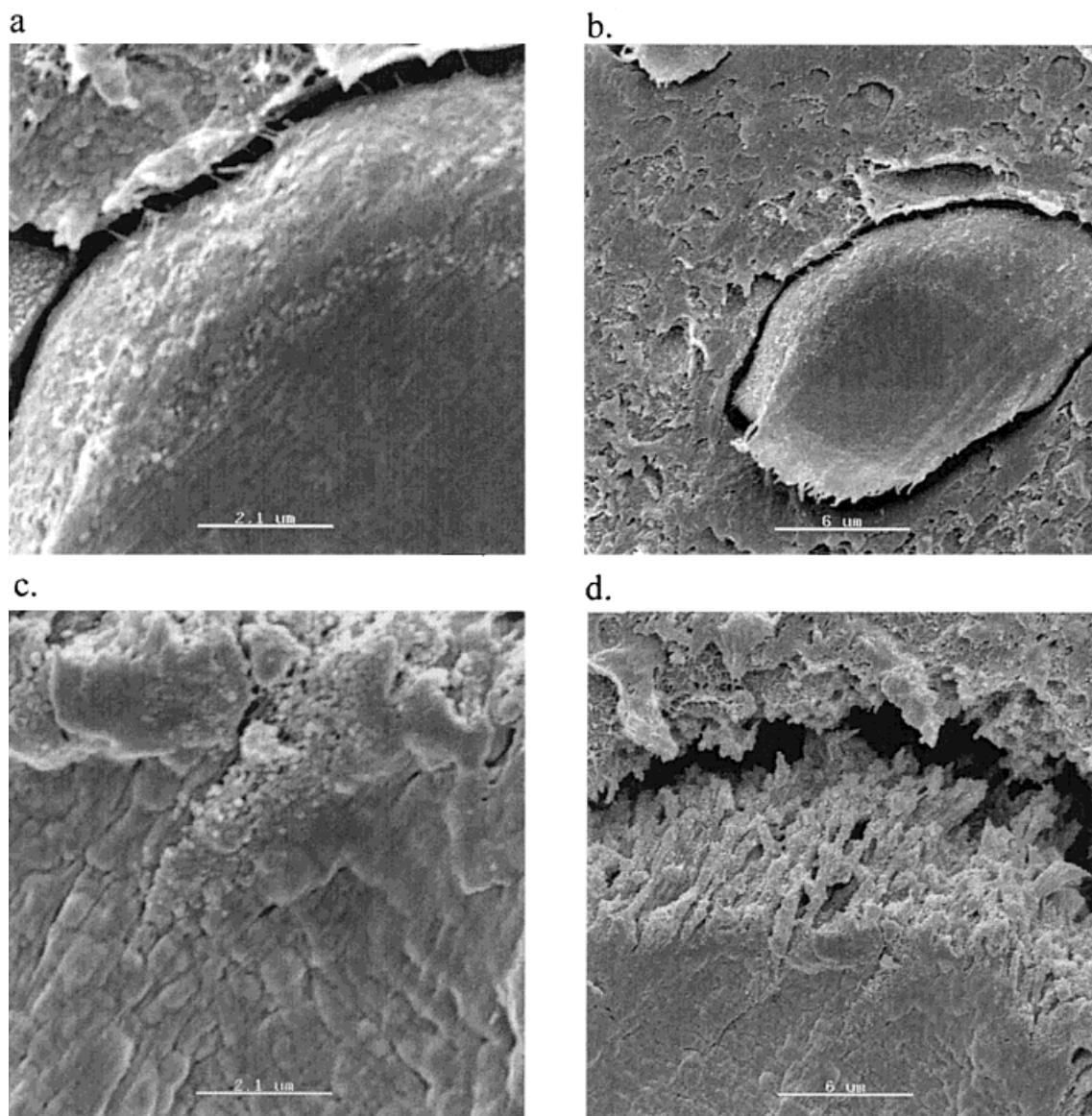


Figure 5 SEM micrographs of microtomed 4 phr CB-containing 70HIPS/30UHMWPE blends at (a) high and (b) low magnifications, and of 4 phr CB-containing 70 HIPS/30XL-UHMWPE at (c) high and (d) low magnifications.

phase, due to the particles' coalescence, which does not occur in the case of XL-UHMWPE-containing blends. This is evident when observing freeze-fractured surfaces (Fig. 6); the crack propagates through the matrix, i.e., the UHMWPE continuous phase, rather than at the particles' interface, and their inner structure (of some porosity) is revealed.

Rheological Properties

The apparent viscosity of 4 phr CB-containing blends of 70HIPS/30UHMWPE and 70HIPS/

30XL-UHMWPE is depicted in Figure 7. Both blends exhibit a typical pseudoplastic behavior, and have similar flow curves. The apparent viscosity of the blend containing XL-UHMWPE is slightly higher than the blend containing UHMWPE, possibly due to the more interlocked nature of the interface in the former case, as has been observed by SEM (Fig. 4).

The apparent viscosity of the phase-inversed 4 phr CB-containing 70UHMWPE/30HIPS and 70XL-UHMWPE/30HIPS blends is presented in Figure 8. In this case, the former blend depicts a

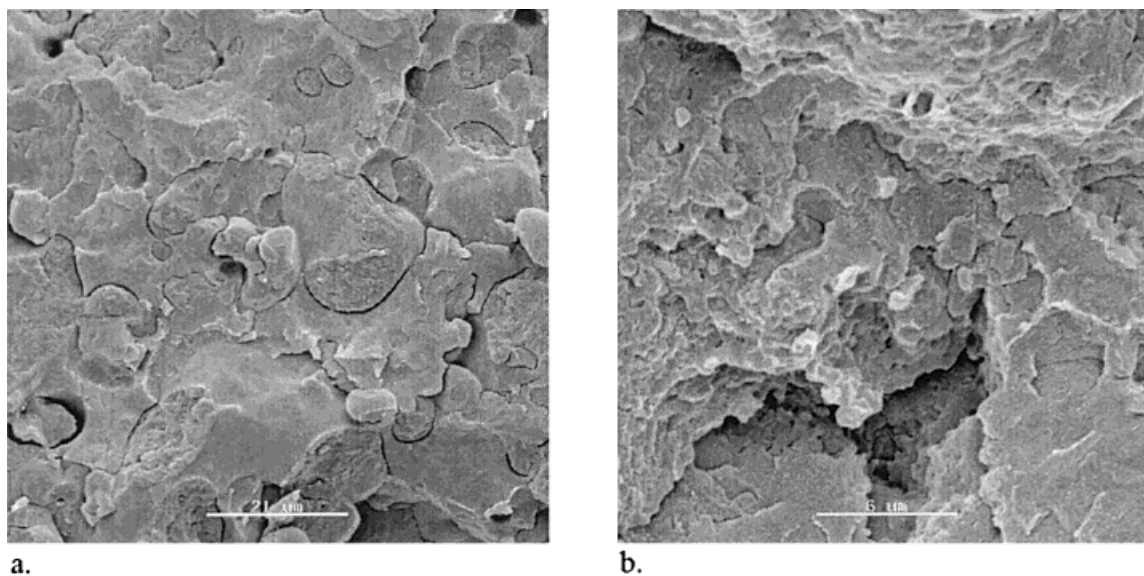


Figure 6 SEM micrographs of neat 70UHMWPE/30HIPS blends, at (a) high and (b) low magnifications.

much higher apparent viscosity than the latter. The difference is approximately one order of magnitude, in the lower shear rate range, gradually reducing as shear rates increase. The explanation for the difference in behavior between blends containing UHMWPE and XL-UHMWPE lies in their different flow mechanisms. The UHMWPE zones, of extremely high melt viscosity, deform as is typical of polymers in a shear field (molecular weight dependant). Conversely, the XL-UHMWPE

particles, have lost their polymer flow properties, and depict a behavior more typical of a soft filler particle, maintaining its shape and identity in the flow field.^{13,14} The XL-UHMWPE particles constitute supermolecular units whose flow mechanism is independent of molecular weight and governed by particle–particle friction. This mechanism involves rotation and slippage at the particle boundary, lubricated to some extent by the HIPS matrix.

The rheological behavior of the 70UHMWPE/30HIPS blend is, therefore, governed by molecular deformation. Because the UHMWPE particles underwent coalescence to form a continuous matrix, the apparent blend viscosity is increased further, in comparison to the XL-UHMWPE–containing blend. This trend is relatively indistinguishable when low contents of 30% UHMWPE are incorporated (Fig. 7). The viscosity of the 4 phr CB-containing 70XL-UHMWPE/30HIPS blend (Fig. 8) is slightly reduced in comparison to the 70HIPS/30XL-UHMWPE-composition (Fig. 7) due to the high XL-UHMWPE content: most of the rheology is governed by the soft particle flow mechanism, rather than by molecular deformation and viscous flow of the HIPS phase.

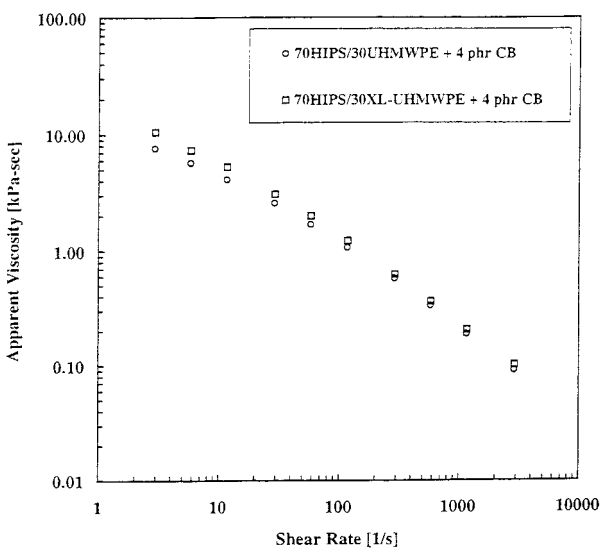


Figure 7 Apparent viscosity vs. shear rate of 4 phr CB-containing blends of 70HIPS/30UHMWPE and 70HIPS/30XL-UHMWPE.

Mechanical Properties

The stress–strain curves of 70HIPS/30UHMWPE and 70HIPS/30XL-UHMWPE capillary rheometer extrudates, both neat and containing 4 phr CB, are depicted in Figure 9. The mechanical

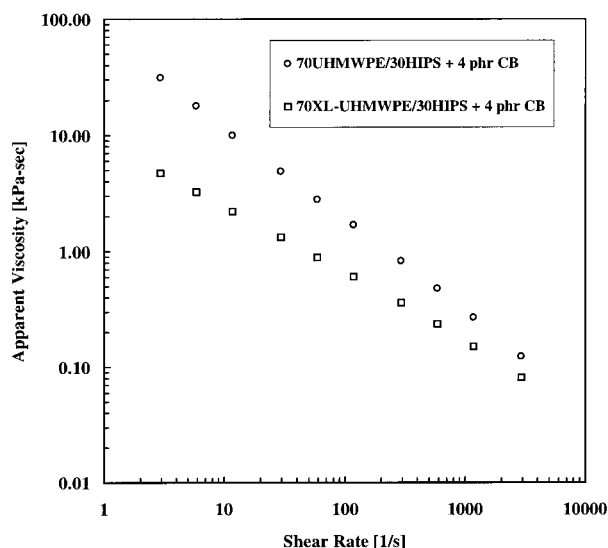


Figure 8 Apparent viscosity vs. shear rate of 4 phr CB-containing blends of 70UHMWPE/30HIPS and 70XL-UHMWPE/30HIPS.

properties of these extrudates are also summarized in Table I. The use of XL-UHMWPE within the blends in comparison to UHMWPE yields significant changes in the mechanical properties, especially the enhancement of the tensile strength. The latter doubles in the neat blends when XL-UHMWPE is used instead of UHMWPE. When CB is incorporated, the XL-UHMWPE-containing blend maintains its strength, whereas the UHMWPE blend depicts a significant decrease in strength. Interesting trends are also observed for the strain at break values (Table I). Both 70HIPS/30UHMWPE and 70HIPS/30XL-UHMWPE extrudates have similar elongations at failure when neat; however, when 4 phr CB are added, the former becomes brittle, while the latter is less sensitive. The modulus of the 70HIPS/30XL-UHMWPE blend is higher than the value for the 70HIPS/30UHMWPE blend, in both the neat and the 4 phr CB-containing blends. These results for the CB-containing 70HIPS/30XL-UHMWPE blend are especially surprising and of great practical potential.

The reason for the higher strength of the XL-UHMWPE-containing blends in comparison to the UHMWPE blends is apparent from the SEM micrographs (Fig. 4). In the 70HIPS/30UHMWPE blend, the dispersed UHMWPE particles are debonded from the matrix, due to the weak interphase adhesion. This is not the case for the 70HIPS/30XL-UHMWPE blend, where the XL-UHMWPE particles have maintained their initial highly developed structure. Their porosity is of

special importance, because it enables the HIPS to penetrate the particle and form a mechanically interlocked particle–matrix structure. When CB is incorporated into these systems, it is located at the interface, as observed by SEM (Fig. 5). In the 70HIPS/30UHMWPE + 4 phr CB system, the CB particles enhance debonding of an already weak interface, further reducing the strength of the system. In the 70HIPS/30XL-UHMWPE + 4 phr CB system the CB particles are located just close to a well-interlocked interface, and, therefore, do not cause debonding.

These considerations also apply when comparing the elongation at break of both systems. In the 70HIPS/30UHMWPE blends, due to the dewetted structure, the HIPS continuous matrix is the one undergoing deformation. In the XL-UHMWPE, a much more uniform deformation occurs because the two phases greatly interact through the described interlocking mechanism.

The increase in modulus for the XL-UHMWPE-containing blends in comparison to the UHMWPE-containing compounds may also be attributed to the bonded vs. debonded interfaces, respectively. Additionally, the modulus of the XL-UHMWPE is higher than that of the UHMWPE, due to both crosslinking and the rise in the degree of crystallinity^{8,13} to further enhance its contribution to the blend properties. Combined with a larger surface area in contact with HIPS, the modulus of the HIPS/XL-UHMWPE is increased.¹⁵

It is, therefore, apparent that the mechanical properties of HIPS/UHMWPE are enhanced when utilizing XL-UHMWPE as a dispersed phase. This is due to changes in the inherent properties of the particle through irradiation, and the unique nature of the generated HIPS/XL-UHMWPE interface. The typical payoff among strength, modulus and strain at break usually observed does not come into effect in these unique blends.

Dynamic Mechanical Properties

The dynamic mechanical properties of the HIPS, UHMWPE, and XL-UHMWPE components, as well as some of their neat and CB-containing blends have been studied. The storage moduli (not presented) depict trends similar to those observed for the static mechanical tensile measurements. The energy dissipation as a function of temperature is expressed as the loss modulus rather than $\tan \delta$. Although these data appear similar, the former is presented for its clearer transition temperatures.

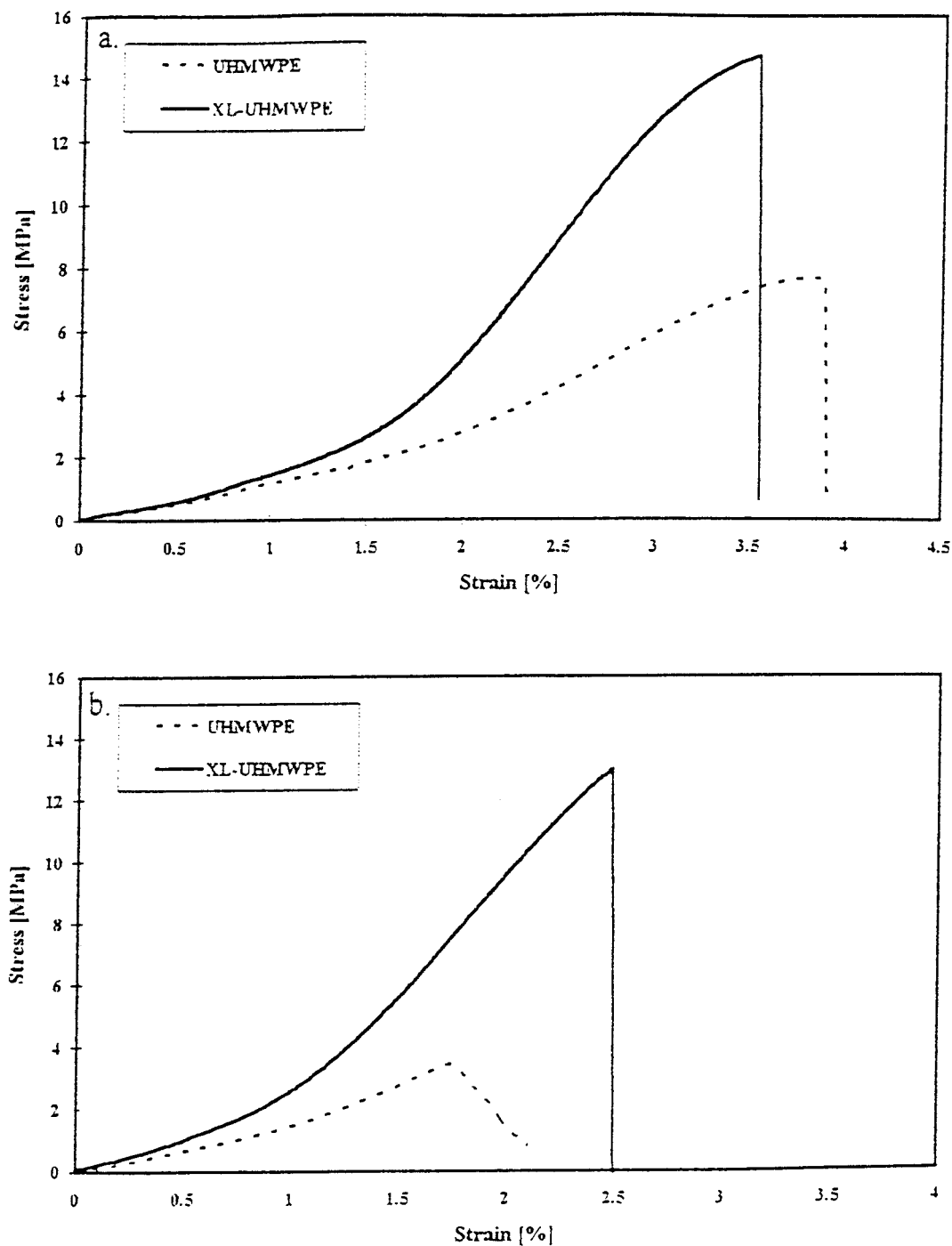


Figure 9 Stress-strain curves of capillary rheometer extrudates of 70HIPS/30UHMWPE and 70HIPS/30XL-UHMWPE (a) neat and (b) containing 4 phr CB.

Figure 10(a) depicts the loss modulus curves of both neat and CB-containing HIPS. Both samples have peaks at approximately identical temperatures: $\sim -90^{\circ}\text{C}$ — T_g of the polybutadiene component in HIPS; ~ -50 to -60°C —a broad transition, shoulder-like in shape, which has not been

observed in previous studies regarding HIPS, and may be ascribed to an additional polybutadiene species, or a less mobile region; and $\sim 100^{\circ}\text{C}$ — T_g of polystyrene, the major HIPS component. The latter is relatively hard to distinguish, because at the T_g the sample becomes distorted, and is no

Table I Mechanical Properties of 70HIPS/30UHMWPE and 70HIPS/30XL-UHMWPE Extrudates

	Neat Blends		4 phr CB-Containing Blends	
	UHMWPE	XL-UHMWPE	UHMWPE	XL-UHMWPE
Strength (MPa)	7.9 \pm 0.9	14.3 \pm 0.4	3.4 \pm 0.4	13.7 \pm 1.9
Modulus (MPa)	134 \pm 23	221 \pm 42	151 \pm 25	218 \pm 51
Strain at break (%)	3.4 \pm 0.7	3.4 \pm 0.3	2 \pm 0.5	3.1 \pm 0.6

longer capable of withstanding the stresses imposed on it by the three point bending mode. It should be noted that despite the low polybutadiene content, it has a very strong influence on the mechanical properties of HIPS, and also has a distinct peak.^{18,22} The curve of the 8 phr CB-containing HIPS shows peaks at temperatures identical to those observed for the neat matrix,²³ because temperature shifts usually occur at higher filler loadings,^{20,24–26} however, peak maxima are much lower. This reflects the reduced damping usually imposed upon a filler-containing polymer.¹⁸ It is attributed to the nonrelaxing character of the solid filler particles, which reduce the viscoelastic fraction of the material, and restrict the polymer chain mobility.^{27,28} Some broadening of the -50°C shoulder is observed upon CB addition, reflecting a variation in the polymer mobilities, possibly due to heterogeneity in the polymer structure. The segmental mobility in the composites varies continuously as the segments become more distant from a given filler particle, and this may be responsible for the observed behavior.²⁹ These data imply that the filler is located adjacent to the polybutadiene regions, and may enhance structuring, possibly explaining the relatively low percolation threshold of HIPS/CB compounds.¹⁴

The loss moduli of reference samples of compression-molded UHMWPE and XL-UHMWPE are shown in Figure 10(b). Two main peaks are observed: at $\sim -110^\circ\text{C}$, relating to the T_g of the polymer; and a very broad peak, its maximum at $\sim 70^\circ\text{C}$, possibly reflecting motions in the crystalline phase, relating to an α_c transition. UHMWPE has lower loss modulus peaks than XL-UHMWPE. Usually, crosslinking tends to decrease damping, as the motion between chemical crosslinks is restricted, and entanglements may be trapped. In this case, the opposite has occurred. This is attributed to the tendency of the as-received UHMWPE particles to fuse and form a more homogeneous material than the latter, in which the crosslinked

particles maintain most of their identity, and their developed surfaces may introduce new damping mechanisms, such as particle–particle friction.¹⁷ The peaks of the XL-UHMWPE are also broader, implying more structural heterogeneity. It is, therefore, suggested that the interface between the particles play a more significant role than the inherent properties of the particles themselves, when XL-UHMWPE was is considered.

In the 70HIPS/30UHMWPE and 70HIPS/30XL-UHMWPE blends [Fig. 11(a)], and (b)], the various phases preserve their peaks, as is typical of immiscible blends;³⁰ however, the peak magnitudes are reduced, corresponding to the phase content within the blend. The T_g peaks of UHMWPE and polybutadiene remain unshifted at -110 and -70°C , respectively, and decrease significantly in magnitude upon the addition of 4 phr CB, again due to damping imposed by the filler. The CB, located at the interface in both HIPS/UHMWPE and HIPS/XL-UHMWPE in highly segregated structures, is in contact with all phases, and therefore, affects all peaks. The 70HIPS/30XL-UHMWPE blend depicts higher peaks, perhaps due to the developed interface between the two components, which encourages interphase and interparticle friction,²⁰ increasing the magnitude of the loss peaks.

It is, therefore, apparent that there are significant differences between the UHMWPE and XL-UHMWPE-containing samples, both neat and CB incorporated. These are perceived in the morphological features, the rheological behavior, the mechanical tensile properties of blend extrudates, and the dynamical mechanical behavior.

CONCLUSIONS

The morphology and thermal properties of as-received and γ -irradiated UHMWPE powder particles have been studied. The γ -irradiation has

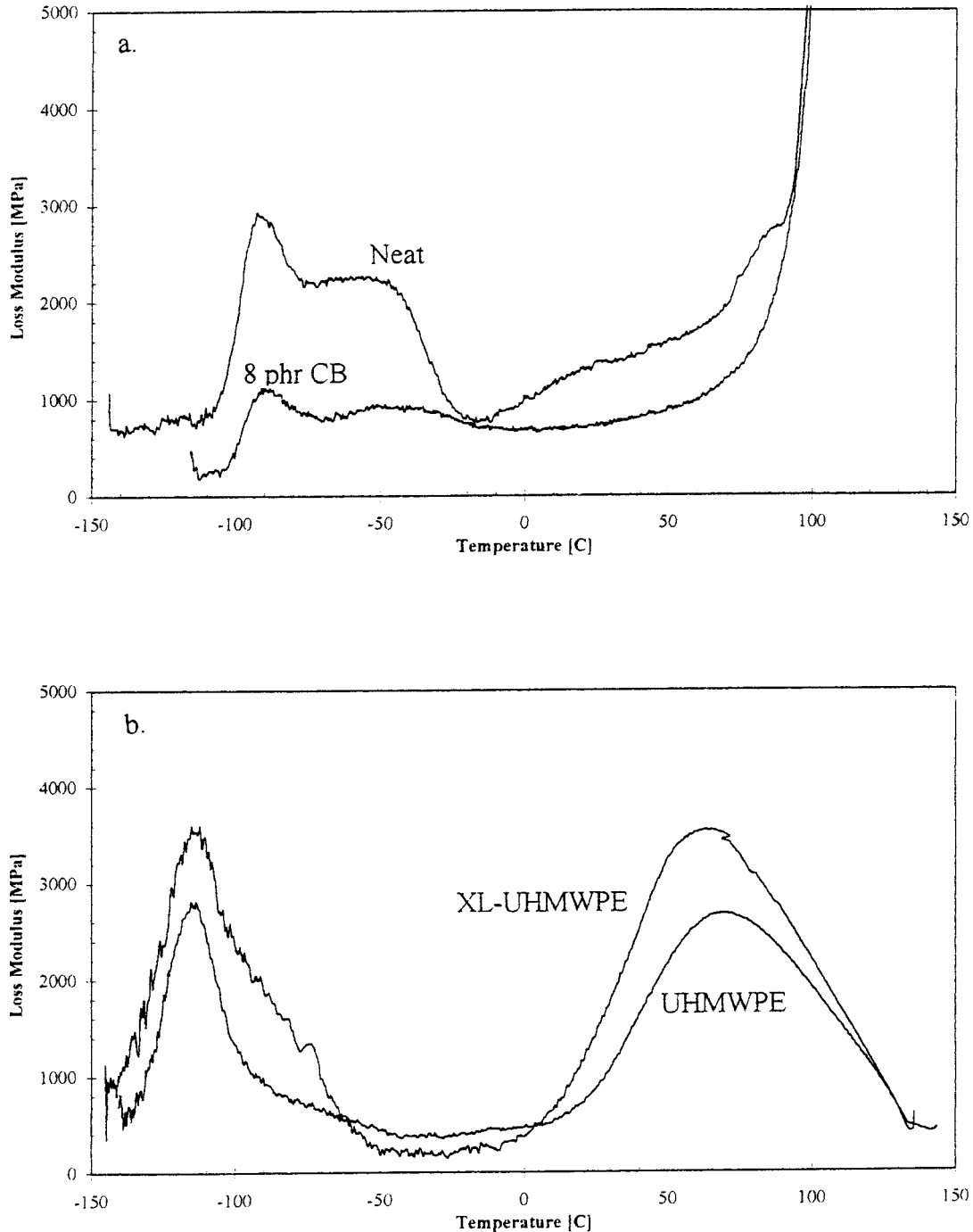


Figure 10 The loss moduli of compression molded: (a) neat and 8 phr CB containing HIPS and (b) UHMWPE and XL-UHMWPE.

been found to induce fixation of the particles, enabling them to maintain their intricate structure of pores, nodules, and fibrils even subsequent to annealing. This has been attributed to crosslinking of the amorphous regions; however, chain scission occurs as well, generating some changes also in the crystalline regions.

Blends of HIPS/UHMWPE and HIPS/XL-UHMWPE, both neat and containing CB, were studied and the following conclusions have been generated.

1. The UHMWPE is dispersed as large ellipsoid particles in HIPS, with a weak, de-

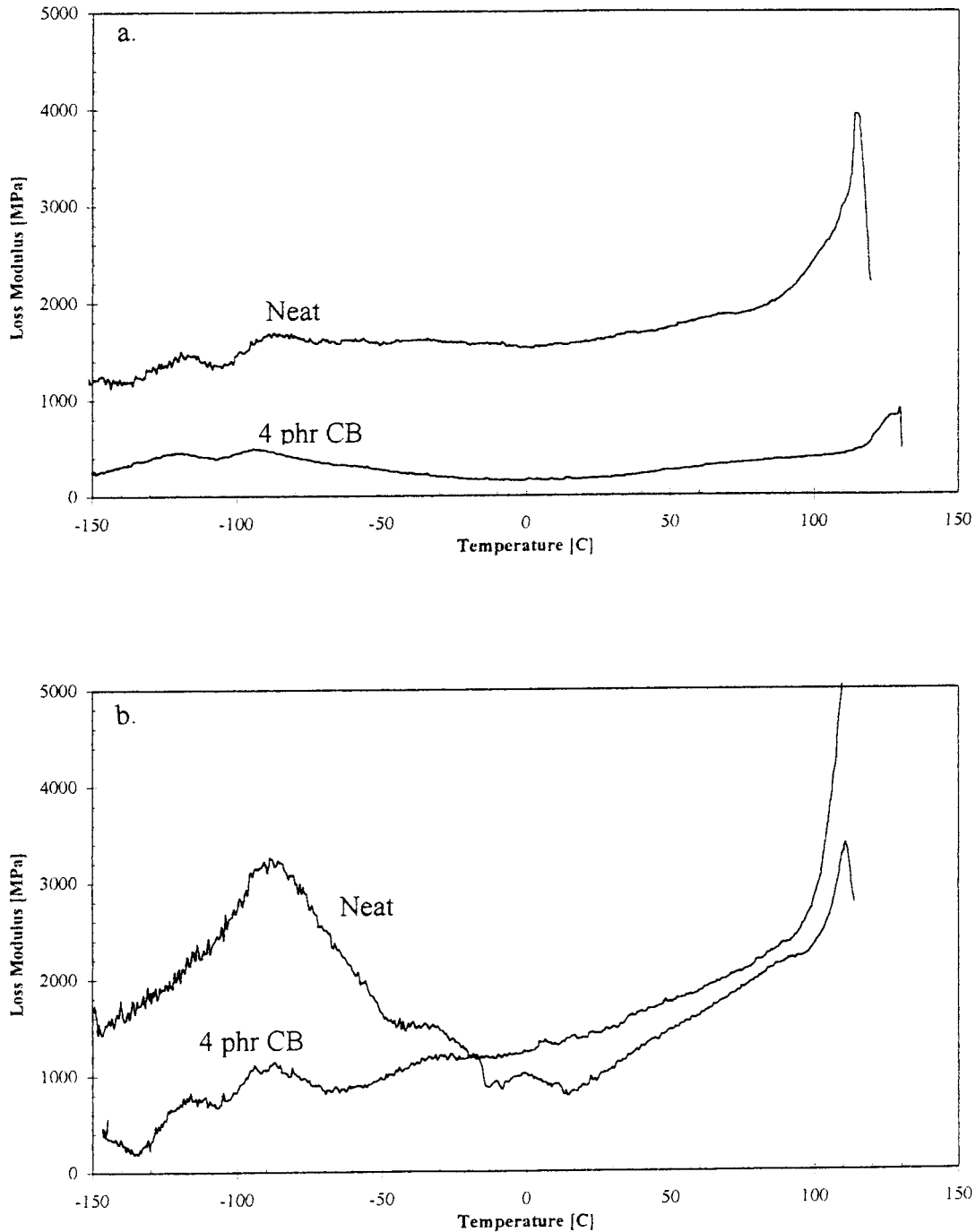


Figure 11 The loss moduli of neat and 4 phr CB containing: (a) 70HIPS/30UHMWPE and (b) 70HIPS/30XL-UHMWPE.

tached interface. The HIPS/XL-UHMWPE reveal a closely interlocked interface, due to the porous structure of the XL-UHMWPE particles, resistant to heat. Upon CB incorporation, it is located at the interface in both cases; however, the interfacial regions and their structure are significantly different.

2. The flow properties of the CB-containing compounds differ for the HIPS/UHMWPE and HIPS/XL-UHMWPE blends, especially when high UHMWPE contents are employed. The UHMWPE zones undergo viscous flow, while the XL-UHMWPE particles depict a flow behavior more typical of a soft filler, maintaining its shape and identity.

3. All the mechanical properties of HIPS/UHMWPE are enhanced when utilizing XL-UHMWPE as a dispersed phase, especially the strength, due to changes in the inherent properties of the filler, and the nature of the HIPS/UHMWPE interface.
4. The addition of CB to the 70HIPS/30XL-UHMWPE blend surprisingly does not cause degradation of the mechanical properties.
5. The dynamical mechanical properties reflect the differences between the UHMWPE and XL-UHMWPE-containing blends. The major feature is increased loss moduli peaks for the HIPS/XL-UHMWPE/CB system as opposed to the former, probably due to dissipation mechanisms evolving from the developed interface.

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