

# Preparation and Characterization of Ultrahigh Molecular Weight Polyethylene and Polyisoprene Solvent-Cast Blend Films

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**ABSTRACT:** This study covers the preparation of noncrosslinked and crosslinked solvent-cast blend films of ultrahigh molecular weight polyethylene (UHMWPE) and polyisoprene rubber (PIR) and their mechanical, thermal, IR spectroscopic, and morphological characterizations. Solvent-cast films of polymer blends with 0, 10, 20, 35, 50, and 65% PIR composition were prepared by vigorous stirring from a hot decalin solution. The films were crosslinked chemically by using acetophenone as a crosslinking agent under UV radiation. The mechanical properties, measured as ultimate properties and tensile modulus, were found to decrease with PIR content but crosslinking was found to enhance the ultimate strength and tensile modulus. DSC results revealed that melting point of UHMWPE remains almost constant in blends. However, upon crosslinking, the melting point of UHMWPE is depressed almost 5°C. We observed a similar trend in the enthalpy change of the melting of UHMWPE and the variation of percent crystallinity in UHMWPE. Scanning electron microscopy (SEM) studies on the fractured surfaces of the blends showed that the fibrillar texture is present in both crosslinked and noncrosslinked blends. The crosslinking appeared to be through oxygen linkages, which are preferentially conjugated to double bonds, in addition to the possible carbon-carbon crosslinks. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1619–1630, 1998

**Key words:** ultrahigh molecular weight PE-polyisoprene blend; crosslinking; characterization

## INTRODUCTION

Polymer blends of various polymers have been studied extensively. One of the main goals is to improve the processibility in addition to achieving better final mechanical and transport properties. Some beneficial properties may be gained in the blend compositions like surface, adhesion, and hydrophilicity and hydrophobicity. Yet, it is a common practice that the expected properties are usually found to be intermediate of the parent polymers.

Ultrahigh molecular weight polyethylene

(UHMWPE) has been defined by ASTM as those “linear polyethylenes which have a relative viscosity of 2.3 or greater at a solution concentration of 0.05% at 135°C in decahydronaphthalene.” The extreme high molecular weight (ranging from 2 to 6 million) causes limitations on the fabrication of this polymer. On the other hand, UHMWPE, due to its high molecular weight, has a unique property of forming extended chain crystallization described as a “shish-kebab” structure by processing in a suitable solvent above the melting temperature of the polymer.<sup>1–8</sup> The details of the formation and properties of this crystal structure from a gel solution of UHMWPE have been discussed and reviewed in many articles.<sup>1–3</sup>

Thermal, mechanical, rheological, and miscibility studies have been carried out for UHMWPE and conventional PE blends, like HDPE,<sup>9–11</sup>

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MDPE,<sup>12</sup> LLDPE,<sup>11,13</sup> and low molecular weight PE,<sup>14</sup> prepared by melt or solvent gelation blending. Addition of PE did not improve the flow behavior of UHMWPE.<sup>12</sup> Cococrystallization was proposed in the blends of UHMWPE/LLDPE and UHMWPE/HDPE; however, separate crystals were observed in UHMWPE/LDPE blends.<sup>11</sup> In addition to these works, gamma ( $\gamma$ )-irradiation at a low dose was investigated on the UHMWPE/HDPE blends.<sup>15</sup> The enthalpy changes of melting of PEs were found to increase while those of their blends decreased upon irradiation. These properties were found to depend mainly on the processing method because the film-forming operations usually produced morphological changes, causing different thermal and mechanical properties. The general conclusion in these works is that the properties of the blends were intermediate between that of the polymers.

Polypropylene–UHMWPE blends produced by gelation/crystallization have also been studied, particularly in terms of the variation of draw ratios where the drawability was affected by composition.<sup>16,17</sup> Surface-modified UHMWPE powders and fibers by reactive gases (fluorine and oxygen) were compounded into a thermoset polyurethane matrix.<sup>18</sup> Stress transfer was improved in fibers more than in powders in the blends.

Among the polymer blends, natural rubber (NR) and polyisoprene (PIR)–polyolefin blend studies are rather few. It was found that the mechanical properties became poor and the crystallite size of LDPE was slightly reduced compared to pure LDPE by the addition of NR.<sup>19</sup> The weakness of the interfacial interaction between NR and LDPE was improved to a certain extent by using a PE-*block*-PIR compatibilizer.<sup>19</sup> Sakuri et al. described a similar method to prepare a UHMWPE/ethylene–propylene–dieneterpolymer (EPT) blend in a decalin solution in their recent article.<sup>20</sup> The blend was precipitated by the addition of methanol from decalin, and sulfur vulcanization was carried out afterward. The tensile strength of the unvulcanized blends was found to decrease with EPT concentration, and upon sulfur vulcanization, the tensile strength improved. The melting temperature and heat of fusion of UHMWPE in the blend decreased linearly because of the presence of amorphous EPT which inhibited the formation of crystal lamellae.

Crosslinking is also attractive in UHMWPE and other polymers because crosslinking enhances the stress and elastic moduli while decreasing strain. The radiation and chemical crosslinking of UHMWPE fibers showed a difference

in the fracture failure.<sup>21,22</sup> A particular improvement in the mechanical properties of chemically crosslinked UHMWPE fibers was seen.<sup>21</sup> The variation in the fracture behavior, from fibrous to ductile and then to brittle (and also its influence on the mechanical properties), was also studied in the cold drawing of HDPE with respect to the crosslink density.<sup>23</sup>

Our objective in this study was to investigate the properties of solution-cast blends of UHMWPE–PIR at various compositions. It is well known that PE and PIR are incompatible and the blends are expected to have poor mechanical properties with respect to pure polymers. However, the possible physical crosslinking, that is, entanglements, might be expected as a result of vigorous mixing in the solution blending due to the high molecular weight of the component polymer. On the other hand, a possible phase separation appears to be inevitable during the casting process. The solvent-cast film samples were successfully obtained in the smooth semitransparent forms of varying thickness. We used UV radiation in the presence of acetophenone to induce crosslinking. Both crosslinked and uncrosslinked blends were characterized by mechanical and thermal tests, and the structural changes and the morphology were followed by FTIR and scanning electron microscopy, respectively. In this study, a type II gel with a shish-kebab structure of UHMWPE was intended to be produced in the blends as described by Keller and Willmouth<sup>2</sup> and Matthews and Hoffman.<sup>3</sup> We also kept in mind that the mechanical properties of the blends determined in this study might show time-dependent changes. The possible changes in the crystallinity and a further phase-separation phenomenon over long periods were not investigated in this work.

## EXPERIMENTAL

UHMWPE, Hostalen GUR 412 and GUR 415, were supplied by Hoechst in Ankara. They were powder and contained anticorrosive agents. The relevant properties are given in Table I. Commercially available PIR (polyisoprene rubber) with the average molecular weights of  $M_w = 745,000$  and  $M_n = 208,000$  were obtained from the tire industry.

Decalin (decahydronaphthalene, Merck Co.) was used as a solvent for dissolving UHMWPE and the preparation of the blends. A stock solution of 50–50% composition, Cyanox LDTP (a secondary stabilizer) and Cyanox 1735 (a mixture of hindered phenols and organic phosphite, both prod-

**Table I Properties UHMWPE Samples (Taken from the Producer Company)**

UHMWPE	Density (g/cm <sup>3</sup> )	Average $M_w$	Ultimate Tensile Stress (MPa)	Yield Stress (MPa)	Elongation at Break (%)
GUR 412	0.94	$4 \times 10^6$	41	22	450
GUR 415	0.93	$6 \times 10^6$	44	21	450

ucts of the Cyanamid Co.), prepared in decalin was used in the solution blending with a 0.5% final antioxidant concentration.

The weighted UHMWPE powders were placed in 50 mL decalin at 50°C for 24 h. Preswollen UHMWPE powders were transferred into an Erlenmeyer flask, as shown in Figure 1. The blending were carried out in these flasks with heating and vigorous stirring at 300 rpm. The heating was stopped at about 145°C and this temperature was kept constant until blending was completed. The dissolution temperatures of GUR 412 and 415 were determined as 137 and 138°C, respectively. The blend compositions were studied for 0, 10, 20, 35, 50, and 65% PIR by weight.

Clear and highly viscous solutions after 10 min mixing were poured into copper boxes (5 × 6 × 7 cm) which had a polytetrafluoroethylene (PTFE) plate on the base and a tap at the edge of the bottom. These boxes were immediately placed in a desiccator which was already kept in a 100°C oven. After 1 h 100°C quenching, the samples were quenched to ambient temperature while most of solvent flowed from the tap of the boxes. Another PTFE plate was put on the top of the gel and then extra pressure was applied by putting increasing weights onto the PTFE plate, from 20 to 200 g for 4–7 days. At the end of this period, the thickness of the gel was reduced approximately to 3 mm. The removal of the solvent and the casting process of the homopolymers and their blends were then continued in a vacuum oven at 25°C for 24 h until the thickness was decreased to 1 mm in the copper boxes. One-millimeter-thick samples were taken from the boxes and finally the last trace of solvent was removed from a 50°C vacuum oven after 7 days. The final thickness of the samples was measured to be 150–350 μm. Solvent-cast films of pure polymers, UHMWPE and PIR, were also prepared for the property characterizations.

The presence of any residual decalin in the solvent-cast films was determined for different blends by gas chromatography (GC). The blend films, 0.1 g, were extracted by cyclohexane for 6 h and the extract cyclohexane was analyzed for the

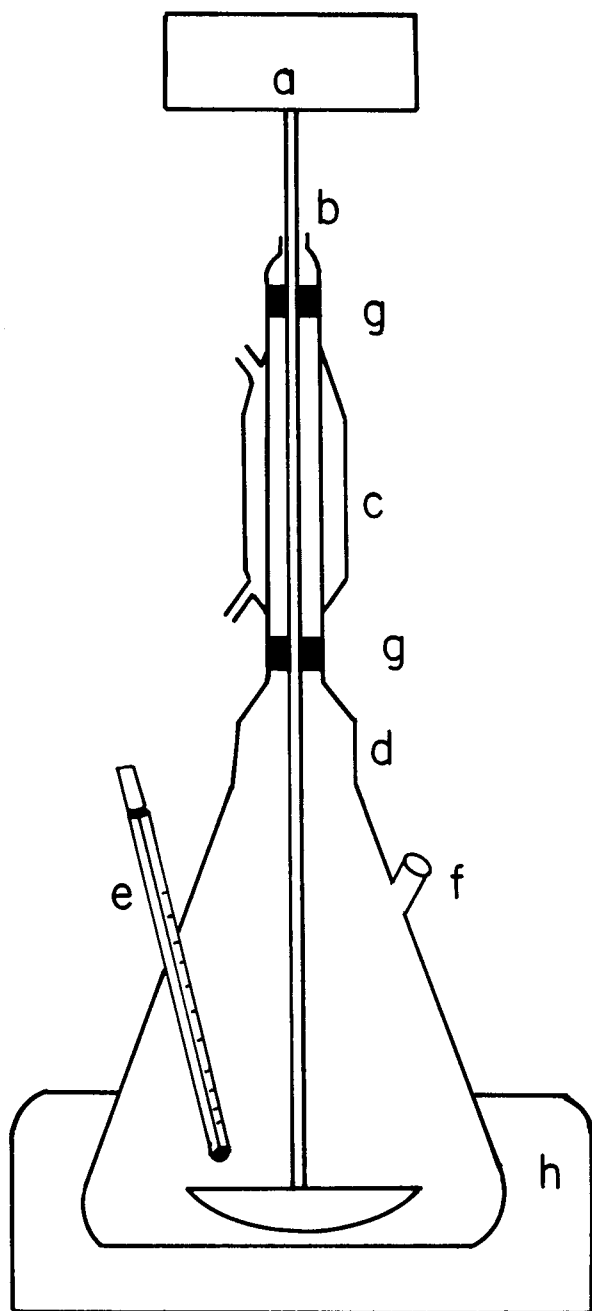
presence of decalin by GC. In all cases, no detectable decalin was observed in the blend films.

Homopolymers and blends films were cut into dumbbell shapes for the mechanical tests. Some of these samples were crosslinked in excess acetophenone in sealed polyethylene bags under UV irradiation for 10 and 24 h. Before the crosslinking process, these samples were immersed in acetophenone for 24 h to obtain homogeneous swelling. Then, the crosslinking of the swollen samples was carried out under two UV lamps (Model B100X, UV Products Inc., CA) which were placed at a distance of 20 cm away from both sides of the samples. The dose rate of UV irradiation was about 50 μW cm<sup>-2</sup>. At the end of irradiation, samples were dried and annealed at 75°C for 5 h. Further details of crosslinking were already described elsewhere.<sup>23</sup>

Mechanical tests (by Instron Testing Machine Model TM-1102) were performed for noncrosslinked and crosslinked samples at crosshead speeds of 5.0 and 0.31 cm/min for the ultimate properties and elastic modulus, respectively. The gage length in both measurements was 3.2 cm.

The thermal properties of the polymer blends of crosslinked and noncrosslinked samples (5.0 ± 0.1 mg) were determined in Perkin–Elmer Model-4 DSC with a scan rate of 10°C/min for heating and cooling cycles. The melting point peak temperature ( $T_{mp}$ ), the change in the enthalpy of melting, and the degree of crystallinity were calculated from the heating and cooling curves. For the estimation and calculation of the percent crystallinity of PE in the blends, the ratio of the calculated enthalpy change of perfectly crystalline PE (291.6 J/g) was used as described.<sup>9</sup>

A Nicolet FTIR DX-5 was used for the spectroscopic measurements of the samples. The regions of interest to follow the chemical changes during sample preparation and crosslinking are 1690–1785 cm<sup>-1</sup> for carbonyl groups, 830–1000 cm<sup>-1</sup> for unsaturation, and 1240–1300 cm<sup>-1</sup> for ether linkages. The morphology of the fractured surfaces after the tensile testing were studied with a scanning electron microscope (SEM), Cambridge S-4, at different magnifications.



**Figure 1** Experimental setup for preparation of UHMWPE-PIR blends: (a) motor; (b) PTFE stirrer; (c) condenser with a 55/44 quick fit; (d) 500 mL Erlenmeyer; (e) thermometer; (f) 19/20 quick fit opening for addition polymers and solvents; (g) stirrer supports; (h) heating jacket.

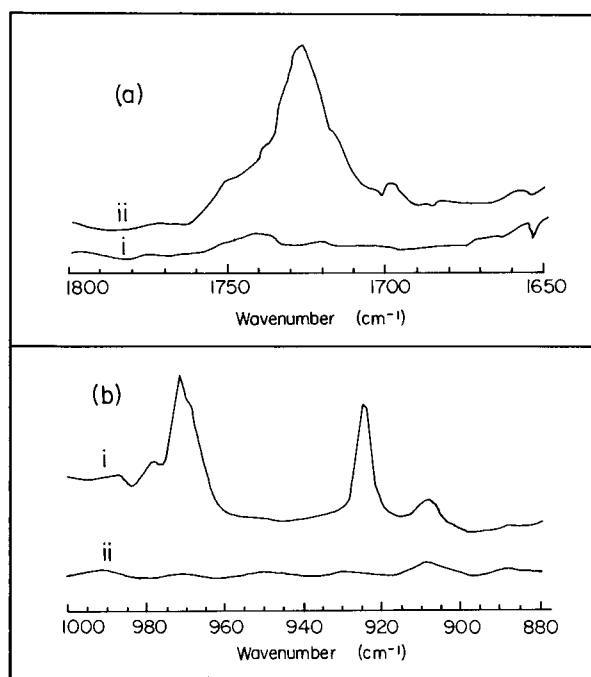
## RESULTS AND DISCUSSION

### Structural Changes and FTIR Study

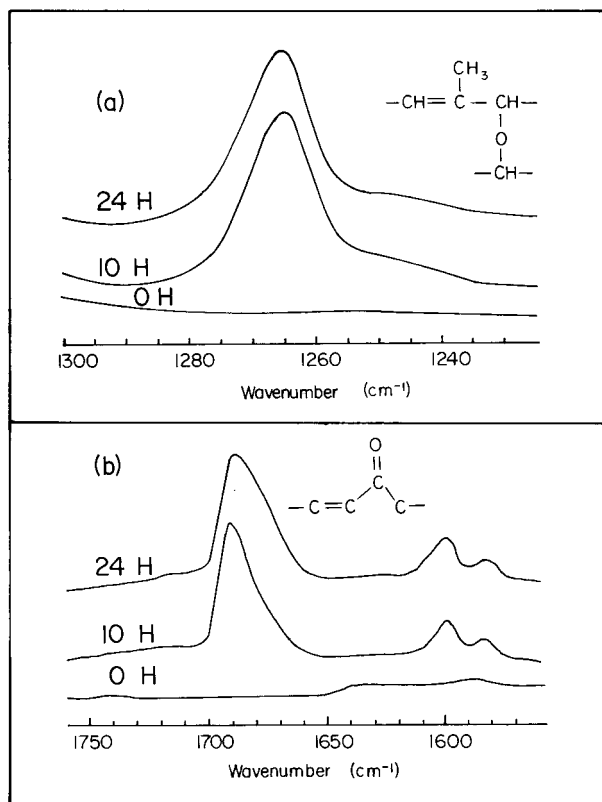
An FTIR study was carried out to follow the chemical changes on the polymers, particularly on the

UHMWPE of GUR 412 and GUR 415, that occurred during the preparation of the blends and the difference between the crosslinked and uncrosslinked blends. The results of the FTIR study, therefore, could be discussed in two parts: (i) a comparison of the solvent-cast UHMWPE and melt-mold UHMWPE films, and (ii) the difference between the crosslinked and uncrosslinked blends.

In our previous work, it was shown that UHMWPE was very vulnerable to oxidative degradation.<sup>10</sup> The molten UHMWPE in the absence of any stress was opened to an oxygen attack. The extensive oxidation of UHMWPE in the presence of atmospheric oxygen could be measured from the development of carbonyl groups by FTIR. However, as shown in Figure 2(a), the carbonyl peak (at about  $1725\text{ cm}^{-1}$ ) did not appear in the solvent-cast films of UHMWPE. It should be noted that it appears to be highly impossible to prepare the blends containing PIR at high temperatures ( $200^\circ\text{C}$  or more) by a melt-blending technique because PIR is much weaker than is UHMWPE toward thermal oxidation. No carbonyl peak was observed in any of the blends prepared in solution. This can be explained simply as the result of the protection of polymers against oxygen in the pres-



**Figure 2** Comparison of FTIR spectra of (i) solvent-cast and (ii) compression-molded films of UHMWPE: (a) development of oxidative degradation of carbonyl groups at  $1725\text{ cm}^{-1}$ ; (b) development of unsaturation at the region between  $1000$  and  $880\text{ cm}^{-1}$ .



**Figure 3** FTIR spectra of uncrosslinked (0H) and crosslinked blends (for 10 and 24 h of UV irradiation, 10H and 24H, respectively): (a) allylic ether linkages between UHMWPE (for both kinds) and PIR at  $1268\text{ cm}^{-1}$ ; (b)  $\alpha$ - and  $\beta$ -unsaturated carbonyl absorption peaks for the blends at  $1695\text{ cm}^{-1}$ .

ence of solvent during blending. The antioxidants used during blending also caused further stabilization.

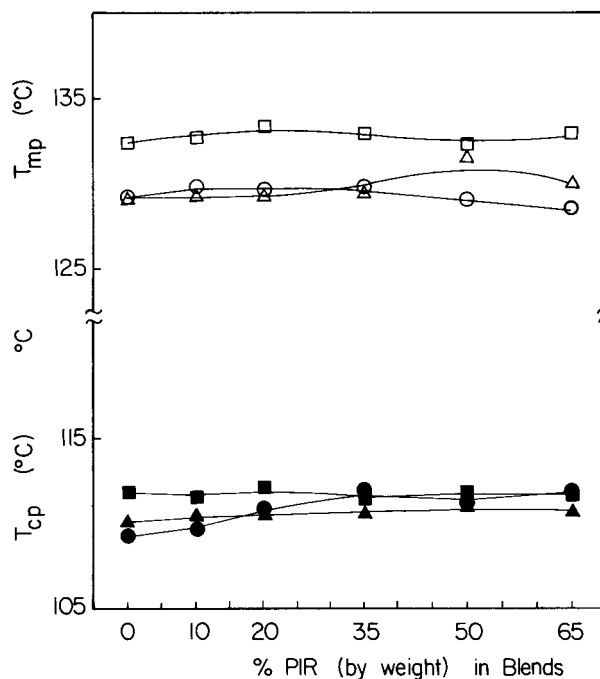
Furthermore, another structural change arose from the method of preparation in the development of unsaturation in the solvent-cast films of UHMWPE, whereas this was not observed in the mold UHMWPE, as given in Figure 2(b), followed by FTIR in the region of  $1000\text{--}880\text{ cm}^{-1}$ . A high rate of mixing seems to result in chain scission with yielding end-group unsaturation in the polymer. Consequently, although the oxidative degradation is prevented in solution stirring, it is obvious that the high shear rate of mixing causes chain breakage and the formation of unsaturated groups in UHMWPE.

Second, when the FTIR spectra of the uncrosslinked and crosslinked solvent-cast blend films were compared, they showed that the crosslinking predominantly went through allylic ether linkages in between PIR and UHMWPE; as shown in Figure 3(a), the absorption peak was at  $1265$

$\text{cm}^{-1}$ . It is more evident that these kind of linkages not only come from the unsaturation present inherently in PIR but also from the unsaturation developed during the preparation of the blend in UHMWPE. Both possible chemical structures were given also in Figure 3(a). Another observation is the peak at  $1695\text{ cm}^{-1}$  corresponding to the presence of  $\alpha$ - and  $\beta$ -unsaturated carbonyl groups in the crosslinked blends [Fig. 3(b)]. The absorbance of these peaks increased relatively with the crosslinking process under UV radiation in the presence of acetophenone. As seen in Figure 3(b), the carbonyl development with UV irradiation becomes inevitable because of the presence of environmental oxygen and also the crosslinking agent. The other peaks appeared at  $1605$  and  $1585\text{ cm}^{-1}$  also arose from the same type of bonding.

### Thermal Properties

The maximum melting point peak temperatures ( $T_{\text{mp}}$ ) corresponding to UHMWPE in the blends were found to be fairly invariant with respect to the composition of the uncrosslinked blend and also the type of UHMWPE as shown in Figure 4 for the GUR 412 and PIR blends. Indeed, this

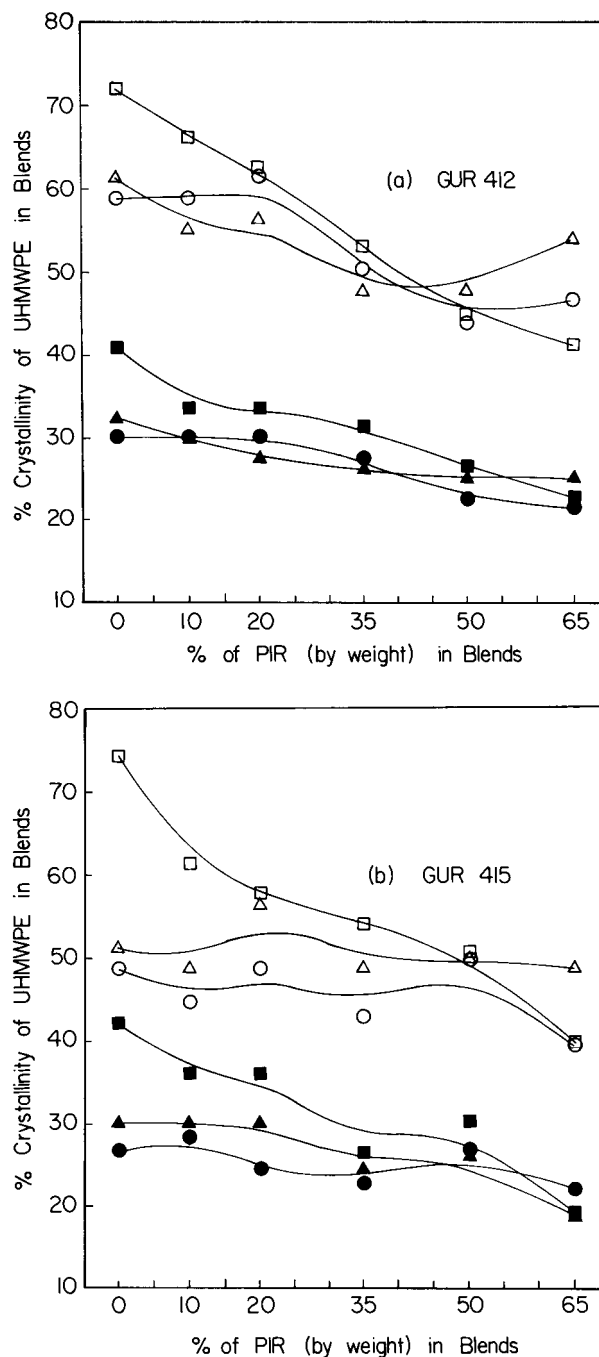


**Figure 4** Variation melting point peak temperatures (open symbols for heating cycle of DSC) and crystallization point peak (filled symbols for cooling cycle of DSC) of the blends with respect to PIR concentration for GUR 412-PIR blends. ( $\square$ ,  $\blacksquare$ ) 0H, uncrosslinked samples; ( $\triangle$ ,  $\blacktriangle$ ) 10H and ( $\circ$ ,  $\bullet$ ) 24H crosslinked samples.

invariance was present in the crystallization peak temperatures ( $T_{cp}$ ) of the blends when the cooling cycle was experimented in DSC as given again in the same figure (Fig. 4). Upon crosslinking 10 and 24 h under UV radiation in the presence of acetophenone, the  $T_{mp}$ 's of UHMWPE were depressed approximately by 2 or 3°C for GUR 412 and by 4 or 5°C for GUR 415 in the blends compared to the uncrosslinked blends for all compositions. These depressions upon the crosslinking process in both blends may be attributed to the enhanced segmental mobility of the chains next to the imperfect crystallite sites involved in the crosslinking during UV radiation in the presence of acetophenone on certain crystalline sites, particularly at the boundary regions. Yet, the  $T_{mp}$ 's of the crosslinked blends remained almost unchanged throughout the composition. The  $T_{cp}$  of the crosslinked blends showed no sharp difference compared to the uncrosslinked blends.

The variation of enthalpy change (i.e., heat of fusion and heat of crystallization) can be used for a measure of crystallinity, in case no significant change of perfection occurs in the crystals with the composition. The constancy of the  $T_{mp}$  values as mentioned above for uncrosslinked and crosslinked blends of both kinds of UHMWPE make it possible to calculate and compare the variation of the crystallinity of the PEs in the blend. In addition, slight changes in the  $T_{mp}$  of the crosslinked samples with high contents of PIR may introduce some uncertainty in the calculation of the crystallinity of the PEs in the blends. Note that in the recent publication of Sakuri et al.<sup>20</sup> the steady decrease in the  $T_{mp}$  and the heat of fusion of UHMWPE in the blends may be due to the change in the thermal history of the precipitated blends during 10 min mastication at 140°C and vulcanization at 110°C.

Figure 5(a,b) shows the variation of the percent crystallinity of UHMWPEs with regard to the percent PIR in the blends. In both cases, the crystallinity of the PEs decreases with increasing PIR in the blend. This variation of crystallinity of the UHMWPEs was calculated according to the UHMWPE content in each blend composition. The highest degree of crystallinity was observed in the solvent-cast pure UHMWPEs, more than 70%, which is well above any UHMWPE prepared in the melt compression, and with the addition of PIR, the crystallinity of the UHMWPE decreased drastically to the values around 45%. The crosslinking, where the possible effect of acetophenone and UV radiation may be encountered in this case, resulted in a further decrease in the percent crys-



**Figure 5** Variation of percent crystallinity of (a) GUR 412 and (b) GUR 415 in blends with respect to weight percentage of PIR. Symbols are the same as in Figure 4. Open symbols are for the percent crystallinity calculated from the melting enthalpy changes of the solvent-cast blends. Filled symbols are for the enthalpy changes of corresponding samples measured after the cooling cycle followed by remelting.

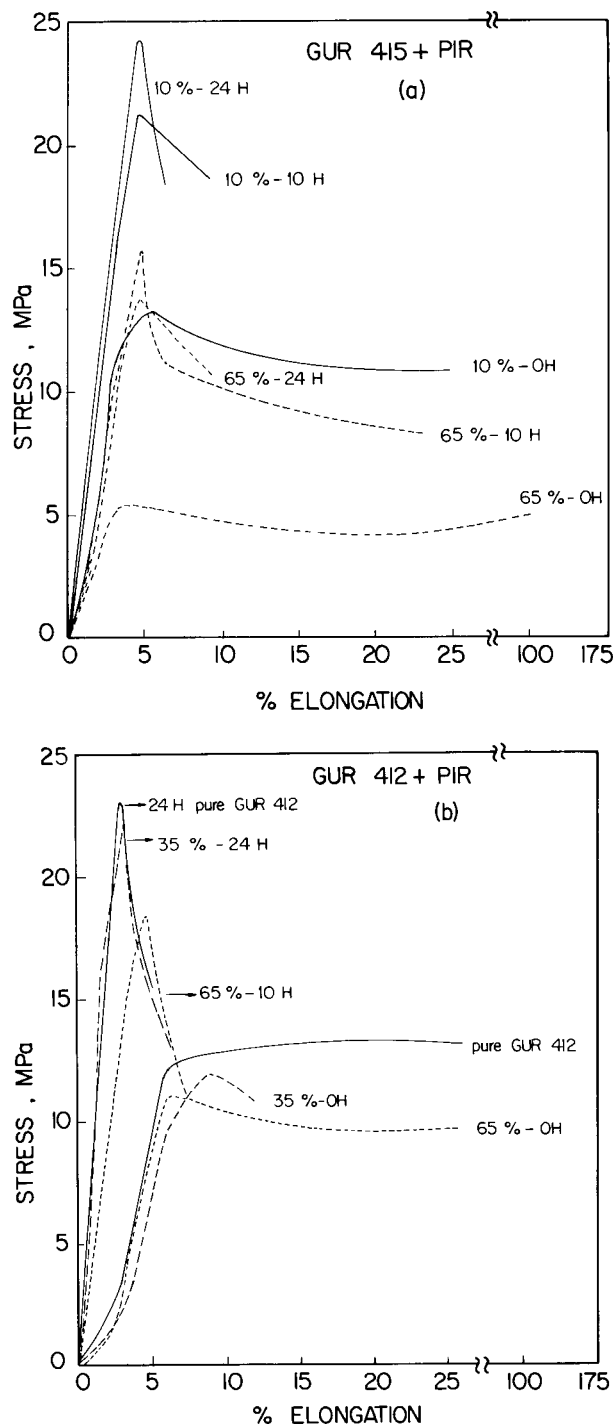
tallinity of the UHMWPEs in the blends. This decrease in the crosslinked samples is higher in GUR 415 blends compared to GUR 412 blends at

the low PIR content compositions (lower than 35% PIR). Furthermore, this fast decrease in crystallinity in the uncrosslinked samples with a PIR content was not observed in the crosslinked samples. The change in the crystallinity of UHMWPE with a PIR content in the crosslinked GUR 412-PIR blends does not show a big difference up to 20% PIR and then this also decreases to a lower value but remains almost constant for the rest of the compositions. Particularly in the GUR 415-PIR blends, within the experimental error limits, the crystallinity appears to vary little with composition after crosslinking, while in the 24 h crosslinked samples, a slight decrease in crystallinity is seen.

In the same figure [Fig. 5(a,b)], the filled symbols showed the percent crystallinity calculations upon the cooling cycle during crystallization followed by the fusion process. The sudden decrease in the crystalline percentage in the UHMWPEs can be attributed directly to the thermal process (melting-cooling-remelting) involved in the DSC experiments. When pure UHMWPEs are considered, solvent-cast UHMWPEs have a higher crystallinity than that of the melt UHMWPEs which are melted in the DSC process and recrystallized by cooling. This behavior is, therefore, directly due to the difference between the solvent-cast and melt crystallization of the UHMWPEs, whereas in the former one, the UHMWPE polymer chains find enough mobility and time to orient themselves into the crystal lattice. The melting process apparently reduces the difference between the uncrosslinked and crosslinked samples but uncrosslinked samples still show higher crystallinity. These results, the higher crystallinity in the solution-prepared UHMWPE and the depression of  $T_m$  upon crosslinking, agree well with the discussion of the melting behavior of UHMWPE of Wang and Salovey<sup>24</sup> and the work of the crosslinking of UHMWPE by de Boer and Pennings.<sup>25</sup>

### Mechanical Properties

Stress-strain curves of three different blend ratios of GUR 412- and GUR 415-PIR blends of uncrosslinked and crosslinked samples are given in Figure 6(a,b). (To avoid overcrowding, only some selected stress-strain curves are given.) The mechanical strength of the solvent-cast pure UHMWPEs is occasionally found to be less than that of compression molded ones at high temperatures. The solvent-casting process inevitably results in more free volume and a less compact structure as a whole material, but as mentioned



**Figure 6** Stress-strain curves for GUR 412-PIR and GUR 415-PIR and blends: (a) 10 and 65% GUR 415-PIR blends for crosslinked samples as indicated in (a) and (b); (b) uncrosslinked samples of pure GUR 412 and its blend with 35 and 65% PIR.

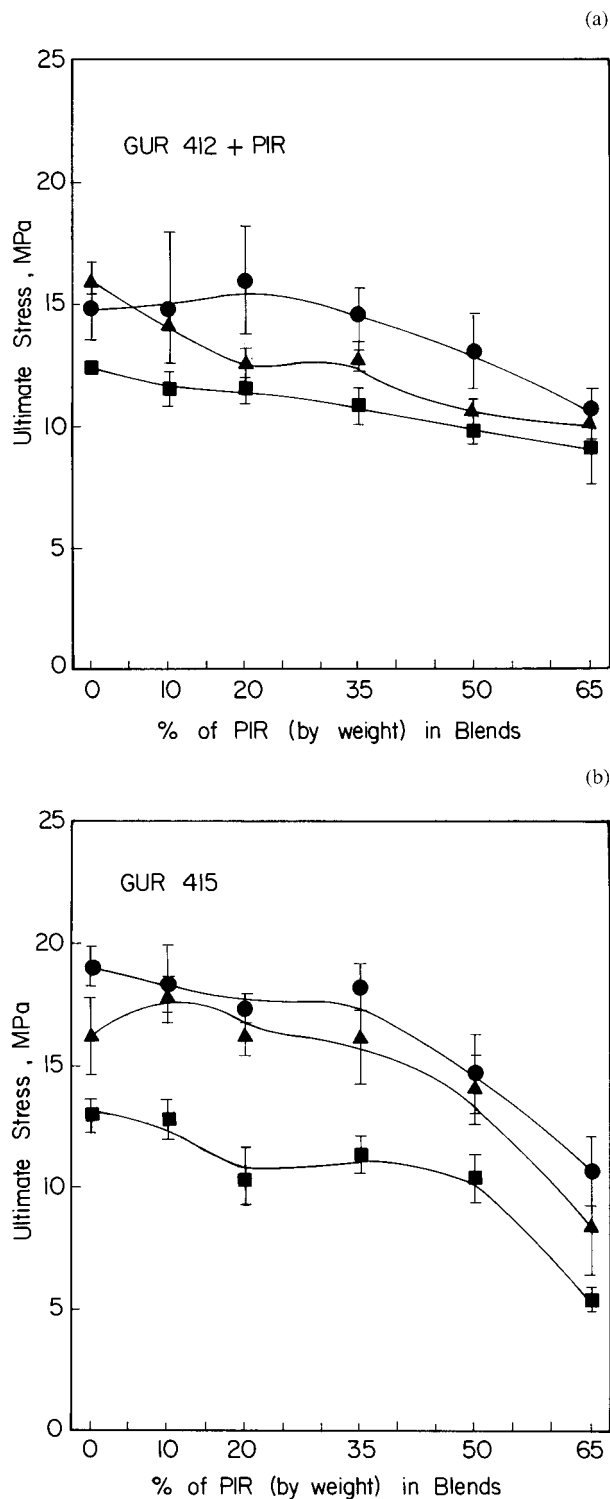
in the previous section, the solvent-cast UHMWPE and their blends had higher crystallinity than that of any melt-compression UHMWPE. On the other hand, as expected, the addition of rub-

bery material into a plastic decreases the mechanical properties such as tensile strength, tensile modulus, and yield stress, while a slight increase in the elongation at break may be observed. This can be followed from these stress-strain figures. Upon the crosslinking process, these former properties increase and the latter property, elongation at break, decreases substantially.

Figures 7–11 correspond, respectively, to the variation of ultimate stress, ultimate elongation, elastic modulus, yield stress, and yield elongation with respect to the change of PIR content in the uncrosslinked and crosslinked blends. Crosslinking improves the stress at break, tensile modulus, and yield stress to a certain extent when they are compared with the corresponding uncrosslinked ones. The increase in tensile strength is particularly more obvious in the GUR 415–PIR blends than in the GUR 412–PIR blends [Fig. 7(a,b)], while the tensile strength of pure PIR prepared by solvent casting varies from 0.4 to 1.0 MPa for the uncrosslinked and crosslinked samples, respectively. In Figure 8, the results of the percent elongation of GUR 415–PIR blends are given together with the uncrosslinked GUR 412–PIR blends. The crosslinking decreases the percent elongation, indicating the effectiveness of the process. The elongation at break values of the crosslinked blends are found to be almost equal to each other and GUR 412–PIR, therefore, is not shown in this figure. When uncrosslinked elongation results of GUR 412 and 415 blends are compared, it is seen that the elongations of the GUR 415–PIR blends are lower and crosslinking in these blends causes only a small decrease in the elongation at break, while the ultimate elongation of the crosslinked GUR 412 blends is sharply reduced and close to that of the values of the GUR 415–PIR blends. On the other hand, pure PIR shows a very high ultimate elongation (700% for uncrosslinked PIR) and it decreases to nearly 100% at 24 h crosslinking.

About a 50% increase is observed in the elastic modulus after crosslinking (Fig. 9). Since a slight difference is seen between the GUR 412 and 415 blends in the crosslinked and uncrosslinked samples, the results of the GUR 415–PIR blends are given in Figure 9. The addition of PIR sharply decreases the elastic modulus of the blends from 1 GPa (pure UHMWPE) to 0.25 GPa (65% PIR–UHMWPE blends); as can be anticipated, the crosslinking improves the elastic modulus from 1.5 to 0.75 GPa, respectively.

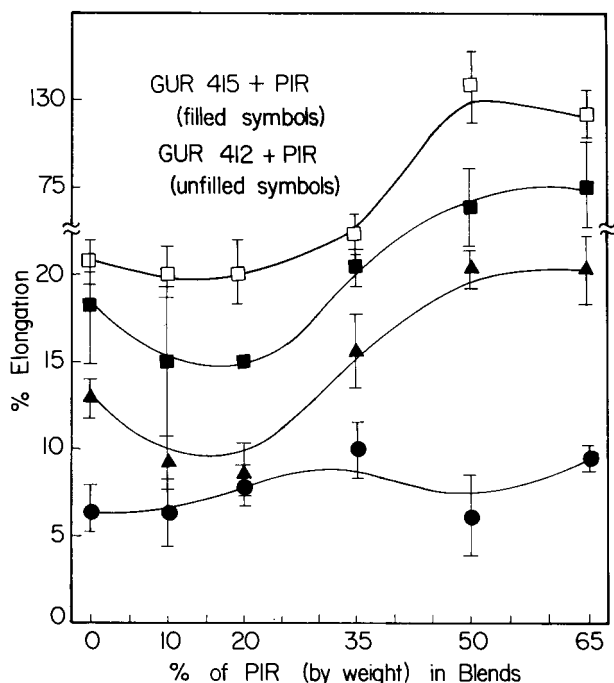
Yield stress and yield elongation are measures of the limit of elastic deformation of the material.



**Figure 7** Variation of ultimate stress for (a) GUR 412–PIR and (b) GUR 415–PIR blends with respect to composition: (■) uncrosslinked; (▲) 10H crosslinked; (●) 24H crosslinked blends.

The results of the yield stress and yield elongation of the blends are plotted in Figures 10 and 11. Both blends gave almost the same yield stress





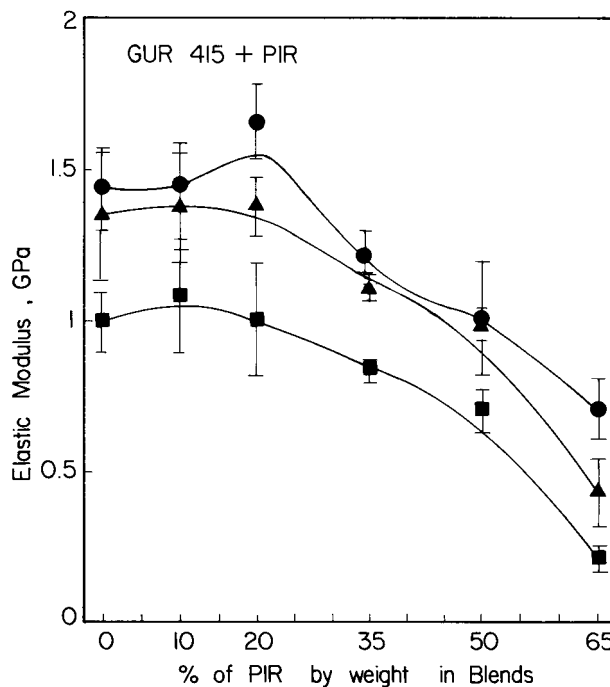
**Figure 8** Variation of percent elongation for GUR 415-PIR and GUR 412-PIR blends with respect to composition: ( $\square$ ) uncrosslinked GUR 412-PIR blends. See Figure 7 legend for other symbols.

values in uncrosslinked and crosslinked samples and only the GUR 412-PIR results are given in Figure 10. Crosslinking causes an increase in the yield stress compared to uncrosslinked samples and the difference in yield stresses between 10 and 24 h of crosslinking seen at a low concentration of PIR vanishes for more than 35% PIR-UHMWPE blends. However, the yield elongation measurements show an observable difference between the GUR 412-PIR and GUR 415-PIR blends as shown in Figure 11(a,b). The yield elongation remains almost constant with the blend concentration and the extent of crosslinking time in the GUR 415-PIR blends. Yet, the yield elongations of the uncrosslinked GUR 412-PIR blends have higher values and do not show any appreciable variation with composition. Crosslinking reduces the yield elongation of the GUR 412-PIR blends to the values close to those of the GUR 415-PIR blends. A similar behavior is observed in the ultimate elongation of the blends (see Fig. 8). This decrease in the yield elongation can be ascribed to the increased crosslinking within the amorphous region of the polymers (hence, increased yield stress), resulting in the destruction of the elastic property of the blend. However, the same conclusion cannot be used for the GUR 415-PIR blends, although the increase

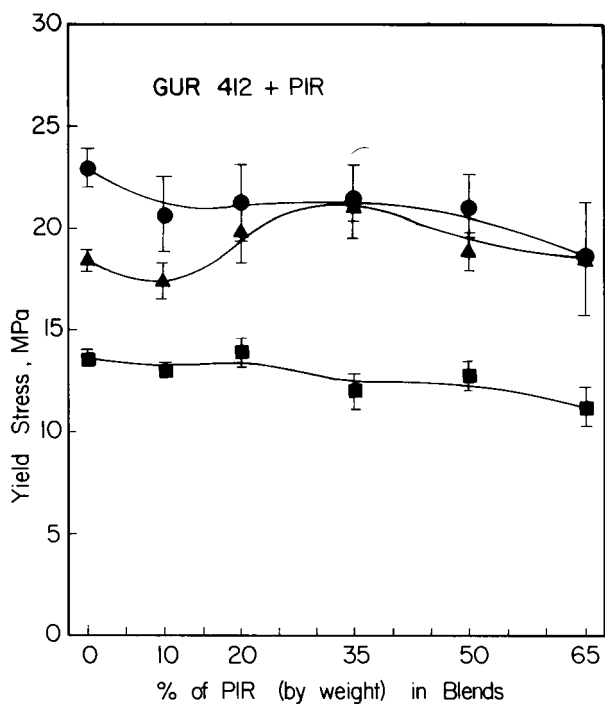
in yield stress indicates the importance of crosslinking, but yield elongation is not affected. We believe that those samples, GUR 415, already contain enough physical entanglements which maintain the same yield elongation after crosslinking. On the other hand, the higher ultimate elongation and yield elongation in the uncrosslinked GUR 412-PIR blends imply that the physical entanglements in the uncrosslinked GUR 412 blends seem to be less effective but they reduce to the lower elongation after crosslinking, close to those of crosslinked GUR 415-PIR elongation results.

### SEM Studies

Four SEM photographs are shown for the GUR 412-PIR blends having a 20% PIR composition in Figures 12-15. The surface morphology of this blend is shown in Figure 12. The smooth surface of the blend remains after crosslinking. The SEM pictures of the fractured areas of uncrosslinked and crosslinked blends are given in Figures 13-15, respectively. In all cases, the fibers originated from UHMWPE are seen clearly. The fracture behavior of the uncrosslinked sample (Fig. 13) is significantly different in comparison to that of crosslinked ones. The fracture appears to be more ductile and the sample shows less fibrillation as



**Figure 9** Variation of elastic modulus for GUR 415-PIR blends with respect to composition. See Figure 7 legend for symbols.

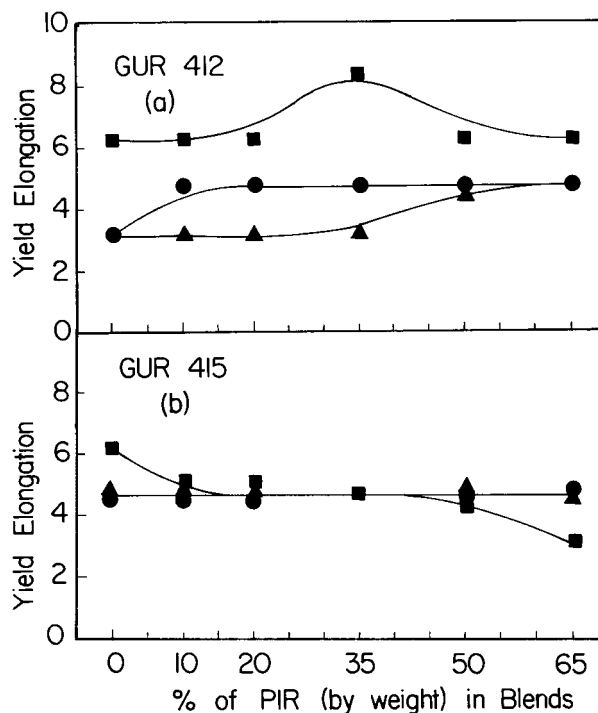


**Figure 10** Variation of yield stress for GUR 412–PIR blends with respect to composition. See Figure 7 legend for symbols.

in all uncrosslinked samples. It becomes thinner after necking and it breaks down with fibrillation after a certain extension, but it seems that most of the fibers remained embedded inside the rubbery part. Yet, with crosslinking, just after the yield point and necking, these samples break at higher stresses with an observable higher number of short fibers present at the fracture cross-section area as shown in Figures 14 and 15. Crosslinking results, therefore, in a considerable restriction of the flow (or slippage) of polymer chains over each other during the uniaxial draw, and when the sample breaks, the elastomeric part, PIR, retracts while the plastic part remains naked at the fracture surface.

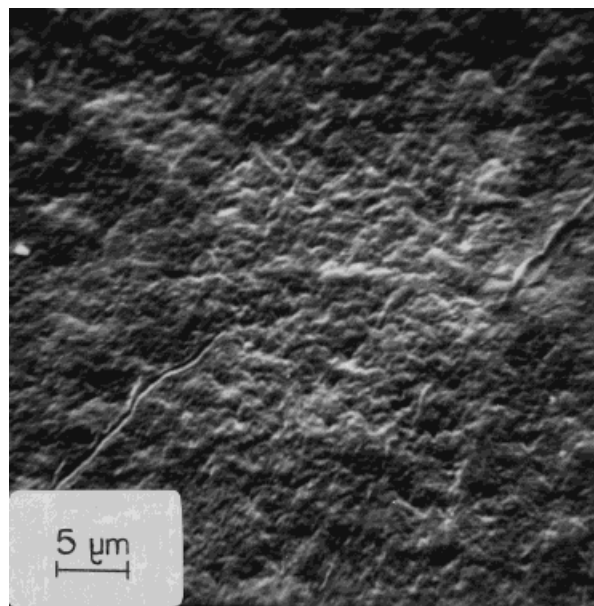
## CONCLUSIONS

The results of this experimental work can be assessed in two parts: Concerning the structural changes, the vigorous stirring during blending to achieve the formation of the required crystal structure and better blending between UHMWPE and PIR inevitably results in unsaturation due to the chain scission in UHMWPE while oxidative degradation is absent. The crosslinking between the polymers and also the same polymers appears



**Figure 11** Variation of yield elongation for (a) GUR 412–PIR and (b) GUR 415–PIR blends with PIR concentration. See Figure 7 legend for symbols.

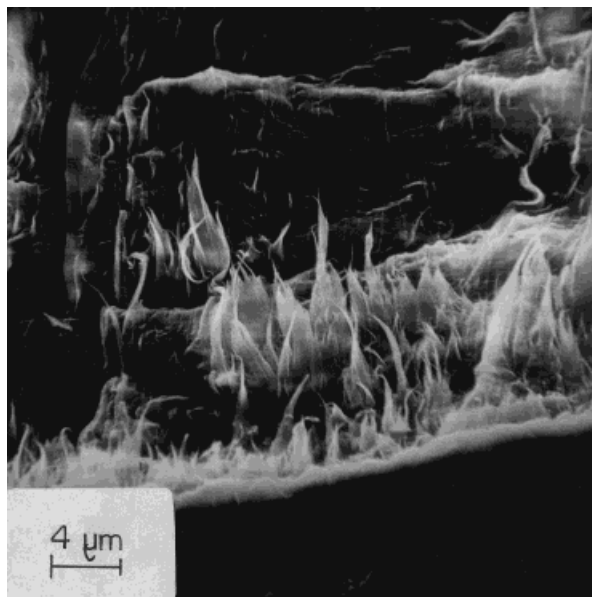
to exist through oxygen linkages in addition to that of H-abstraction crosslinking under UV irradiation in the presence of acetophenone. The crystallinity of UHMWPE is depressed by the addition



**Figure 12** Surface morphology of the GUR 412–PIR blend where PIR content is 20% by weight. For the rest of the SEM photographs, the same composition is given.



**Figure 13** Fractured area of the uncrosslinked GUR 412-PIR blend.



**Figure 15** Fractured area of 24 h crosslinked GUR 412-PIR blend.

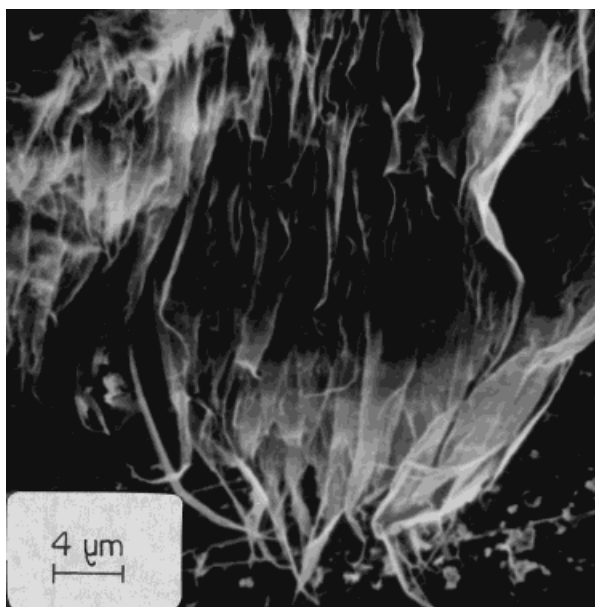
of PIR and the crosslinking process causes further decreases in the crystallinity. The mechanical properties of the blends decrease with the concentration of PIR with respect to those of pure UHMWPE. This variation is not solely due to the incorporation of PIR but also due to the method of preparation, that is, the solvent casting which results in loose interaction, giving greater free volume in

the final films, but these properties are virtually better than are those of pure PIR. The crosslinking process improves the mechanical properties with the exception of a decrease in elongation at break which is influenced basically by the presence of PIR. Regarding the formation of entanglements in the blends between polymers, it appears that the higher molecular weight UHMWPE, GUR 415, shows a higher probability than does the other UHMWPE when, particularly, the yield properties of the uncrosslinked and crosslinked blends are compared. Finally, it can be concluded that without causing any oxidative degradation and its possible consequences which may be reflected in the properties to be studied this method ensures that optimum mechanical values may be augmented with the crosslinking of the blends, but a loss in the crystallinity of the UHMWPEs seems inevitable during crosslinking.

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**Figure 14** Fractured area of 10 h crosslinked GUR 412-PIR blend.

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