

# Glass-Transition-Temperature Depression in Chemically Crosslinked Low-Density Polyethylene and High-Density Polyethylene and Their Blends with Ethylene Vinyl Acetate Copolymer

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**ABSTRACT:** A reduction in the glass-transition temperature ( $T_g$ ) was found for polyolefins chemically crosslinked by peroxide. This tendency, which was observed for low-density and high-density polyethylenes, was also validated for their blends with Ethylene Vinyl Acetate copolymer. It is proposed that the constrained crystallization process, as a result of a restriction imposed on the chain packing by the chemical crosslinks, results in an increasing net free

volume in the amorphous phase and hence reduces  $T_g$ . The  $T_g$  depression becomes greater with increasing crosslink density, whereas at the same time, the degree of crystallinity and consequently the density of the system decreases with an increase in the peroxide content. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1654–1660, 2007

**Key words:** crosslinking; glass transition; polyethylene (PE)

## INTRODUCTION

Increased utilization of polyethylene with an enhancement of its properties is normally achieved via crosslinking either by exposure to ionizing radiation such as an accelerated electron beam or by chemical means usually involving silanes or peroxides.<sup>1–5</sup> One of the most demanding applications involving the crosslinking process is the production of heat-shrinkable materials widely used in electrical industries.<sup>6–9</sup> Crosslinking by either chemicals or radiation is normally aimed at improving the thermal, chemical, barrier, impact, wear, and other properties of polyethylene.<sup>10–17</sup> Besides these changes in the properties as a result of crosslinking, one aspect is the glass-transition temperature ( $T_g$ ). Dynamic mechanical analysis (DMA) is the most widely used tool for the study of  $T_g$  of polymers.<sup>18</sup> According to the literature, DMA of linear or branched polyethylene exhibits three peaks, which labeled  $\alpha$ ,  $\beta$ , and  $\gamma$  transitions in order of decreasing temperature.<sup>18,19</sup> All these peak transitions correspond to different motions in polyethylene chains. The mechanisms of these relaxation processes have been discussed in terms

of the crystalline and amorphous phases and the third interfacial phase, which is of intermediate character and may have some structural order.<sup>18–21</sup> The  $\gamma$  transition for polyethylene occurs in the range of  $-150$  to  $-100^\circ\text{C}$ . It has been shown that the maximum in the loss modulus peak is the  $\gamma$  transition or  $T_g$ , and the influence of physicochemical parameters on the  $\gamma$  transition can be explained in terms of  $T_g$ .<sup>18,21,22</sup> The assignment of the  $\gamma$  transition to  $T_g$  is highly controversial in view of some publications,<sup>23,24</sup> in which the  $\gamma$  transition is believed to be a very local subglass transition. The measurement of the glass transitions and other structurally related transitions in polymers can often be used to characterize the miscibility or compatibility of blends, degree of miscibility, and so on.  $T_g$  of a polymer will depend on the constraints imposed upon the amorphous phase. These will include crosslinking, crystallinity, and other factors that influence the local mobility, free volume, and molecular packing, such as deformation, the presence of plasticizers, and physical aging. These final factors are incompatible with our experiments, and consequently, a description based on crosslinking and crystallinity is, qualitatively, very reasonable here.

An increase in  $T_g$  was observed by radiation crosslinking, as reported by Vaughan and Stevens.<sup>25</sup> They studied the influence of electron irradiation on  $T_g$  of poly(ether ether ketone) by differential scanning calo-

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rimetry (DSC) up to a dose of 100 MGy. They observed that  $T_g$  increases linearly with the absorbed dose at a rate of  $0.18^\circ\text{C}/\text{MGy}$ . Sethi et al.<sup>26</sup> studied  $\alpha$  and  $\beta$  transitions of electron-beam-irradiated polyethylene and poly(ethylene vinyl acetate) (EVA) blends by DMA. They showed that the transition temperatures on exposure to radiation increased.

It is also well known that by the introduction of chemical crosslinks and formation of network structures,  $T_g$  increases.<sup>18,19</sup> Moreover, generally  $T_g$  of a polymer increases somewhat as the crystalline content of the polymer increases.<sup>27</sup> It would be interesting to determine what the combined effect would be of crosslinking on an increase in  $T_g$  and at the same time its effect on the reduction of the crystallinity and finally the resultant effects on  $T_g$  in a semicrystalline polymer and its blends. In this article, we discuss our findings on  $T_g$  depression for chemically crosslinked semicrystalline polymers, namely, low-density polyethylene (LDPE) and high-density polyethylene (HDPE) and their blends with EVA.

## EXPERIMENTAL

### Materials

LDPE (grade LD 00BW), with a melt flow index (MFI) of 2 g/10 min and a density of  $923\text{ kg/m}^3$ , and EVA (grade UL 00218), with a vinyl acetate content of 18%, an MFI of 1.7 g/10 min, and a density of  $938\text{ kg/m}^3$ , were kindly supplied by ExxonMobil Chemicals (Köln, Germany). HDPE (grade MG7547A), with an MFI of 4 g/10 min and a density of  $954\text{ kg/m}^3$ , was obtained from the Borealis Group (Kongens-Lyngby, Denmark). *tert*-Butyl cumyl peroxide (BCUP), with a purity of 96% and a density of  $0.96\text{ g/cm}^3$ , was obtained from Peroxide-Chemie GmbH (München, Germany).

### Sample preparation

First, crosslinked LDPE and HDPE samples with different peroxide concentrations of 0.5–3 wt % were made via compounding in an internal mixer (model PL 2000 plasticorder, Brabender). A screw speed of 50 rpm, a temperature of  $145^\circ\text{C}$ , and a mixing time of 3 min were used. In this state, BCUP mixed with the polymers. The crosslinking of the sheet samples was carried out by compression molding in a Fontune (Holland) 400 KN laboratory hot press at a temperature of  $190^\circ\text{C}$  for 5 min under 10 MPa of pressure, and then the sheet samples were cooled at a rate of 15 K/min. Similarly, LDPE/EVA and HDPE/EVA blends, containing 0–40 wt % EVA, were melt-mixed under the same conditions but with an increased mixing time of 10 min. Later, the peroxide (BCUP) was added to the blends (0.5–3 wt %) and further mixed for another 3 min. The

crosslinking of the blends were carried out in the same way as previously.

### DMA

The thermomechanical properties of the samples were investigated by DMA with a DMA 983 (TA Instrument, Inc., United States) to determine the viscoelastic properties in the bending mode. Rectangular bar specimens with dimensions of  $50 \times 10 \times 2\text{ mm}^3$  were used for this study. The samples were heated from  $-150$  to  $100^\circ\text{C}$  at a heating rate of 3 K/min and at a frequency of 1 Hz.

### Density measurements

The densities of the crosslinked samples were determined with a Sartorius YDK 01 0D specific gravity determination kit (Sartorius AG, Goettingen, Germany).

In this measuring device, the Archimedean principle was applied for determining the specific gravity of the samples. A polymer sample immersed in a liquid (water) was exposed to the force of buoyancy. The value of this force was the same as that of the weight of the water displaced by the volume of the polymer sample. With a hydrostatic balance enabling us to weigh the polymer sample in air and in water, it was possible to determine the specific gravity of the polymer sample. For each sample, 10 measurements were performed, and the average values are reported here.

### Thermal analysis

The DSC tests were performed on a PerkinElmer (Manasquan, NJ) DSC-7 with dry nitrogen as a purge gas between  $-60$  and  $180^\circ\text{C}$  at a heating rate of 10 K/min. The degree of crystallinity ( $X_c$ ) was calculated via the total enthalpy method:  $X_c = \Delta H_m / \Delta H_m^+$ , where  $\Delta H_m$  is the specific enthalpy of melting and  $\Delta H_m^+$  is the specific enthalpy of melting for 100% crystalline polyethylene. We used a  $\Delta H_m^+$  value of  $288\text{ kJ/kg}$ .<sup>28,29</sup>

### Hot-set test

The hot-set test was carried out in a hot-set oven (UT 6050 HS, Heraeus, Germany) according to DIN 57472 Part 602 VDE 0472. The samples in the form of dumbbells were placed in the hot-set oven under a definite static load at  $200^\circ\text{C}$ , and the elongation between the two marks was measured after 15 min as the percentage ratio of the final length of the polymer to its initial length.

### Wide-angle X-ray scattering (WAXS) analysis

The overall crystallinity percentage was also determined by wide-angle X-ray diffraction. X-ray measure-

**TABLE I**  
Peak Temperature ( $T_g$ ) Corresponding to the Maximum in the Loss Modulus for Crosslinked HDPEs and LDPEs with Different Peroxide Concentrations

Peroxide (%)	$T_g$ (°C)	
	Crosslinked HDPE	Crosslinked LDPE
0	-102.4	-118.1
0.5	-104.4	-119.7
1	-106.2	-121.5
2	-108.4	-122.6
3	-108.9	-123.2

ments were carried out on a Siemens four-circle diffractometer with a Hi-Star area detector with Cu K $\alpha$  radiation at a wavelength of 1.542 Å. The samples were mounted on the goniometer in such a way that the surface of the polymer was positioned normal to the X-ray beam. The deconvolution of the X-ray images and the calculation of the crystallinity content were conducted with Diffrac Plus software developed by Siemens. The crystallinity ( $\alpha_X$ ) was estimated from the wide-angle data recorded on the area detector as the ratio of the scattering from the crystalline regions ( $I_{cr}$ ) to the total sample scattering ( $I_{cr} + I_{am}$ ; with a simple peak area method in an angular range of  $2\theta = 10\text{--}45^\circ$  and integration of the two-dimensional primary data over an azimuthal range of  $2\phi = \pm 22.5^\circ$ ) as follows:

$$\alpha_X = I_{cr}/(I_{cr} + I_{am}) \quad (1)$$

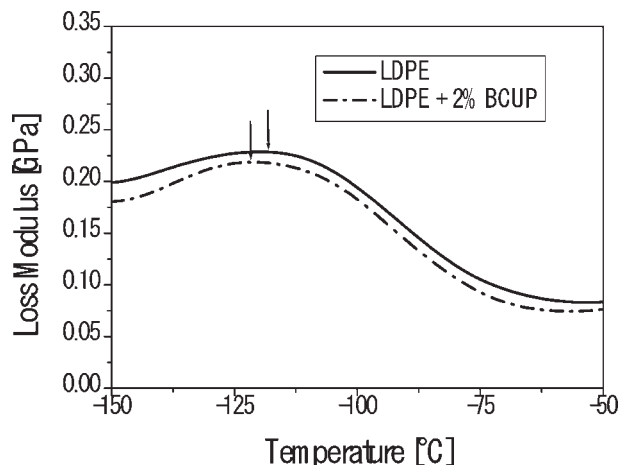
The  $2\theta$  range contained the strongest ( $hkl$ ) reflections, (110) and (200), which served as indicators for the determination of the crystallite size equivalent ( $D_{hkl}$ ), which was conducted by the application of the Scherrer equation, with  $\text{FWHM}_{hkl}$  as the full width at half-maximum of the ( $hkl$ ) reflection:

$$D_{hkl} = \lambda/(\text{FWHM}_{hkl} \cos \theta_{hkl}) \quad (2)$$

In this simple kind of manner, the influence of any crystal distortion on the full width at half-maximum was neglected. Therefore, the derived  $D_{hkl}$  data were minimum sizes.

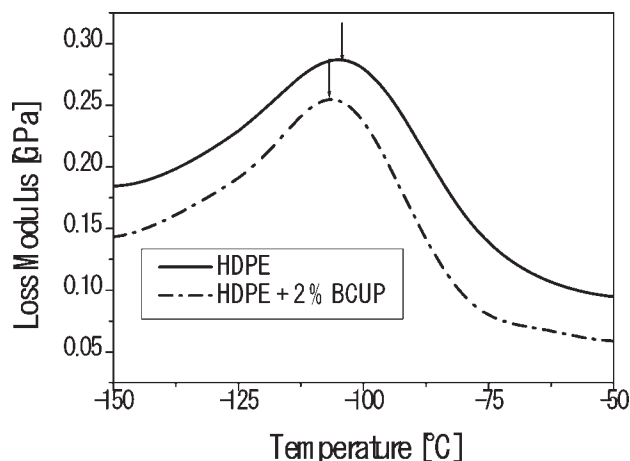
## RESULTS AND DISCUSSION

The  $\gamma$ -transition peak temperature ( $T_g$ ), that is, the temperature at which the maximum in the loss modulus occurs, for uncrosslinked and crosslinked polyethylenes at different peroxide contents (BCUP) is summarized in Table I. A clear comparison of the dynamic mechanical behavior of the uncrosslinked and crosslinked polyethylenes is given in Figures 1 and 2. An unexpected decrease in  $T_g$  has been observed as a result of crosslinking for both LDPE and HDPE.



**Figure 1** Variation of the loss modulus versus the temperature for uncrosslinked and crosslinked LDPEs containing 2% BCUP.

The usual expectation from crosslinking is an increase in  $T_g$  due to the restriction imposed by the newly formed chemical bonds (crosslinks) on the segmental mobility of the polymer chains. On the other hand, these newly formed bonds can impede the chain packing because of an increase in the chain length or formation of new bulky side chains, and hence it reduces the density. Moreover, for the semicrystalline systems crosslinked in the melt state (being totally in the amorphous state), the formation of these chemical bonds (increased chain length or bulky side chains) would interfere with crystal formation; therefore, the crystallinity of such polymers decreases with crosslinking. The crosslinks play the role of defect centers, which impede the folding of macromolecular chains and thus can also reduce the sizes of the lamellar crystals. This decrease in the density and crystallinity is consistent with an increase in the net free volume leading to a



**Figure 2** Variation of the loss modulus versus the temperature for uncrosslinked and crosslinked HDPEs containing 2% BCUP.

**TABLE II**  
Densities (g/cm<sup>3</sup>) of LDPE and HDPE Samples with Different BCUP Concentrations

Sample	Granule	Sheet	0.5% BCUP	1% BCUP	2% BCUP	3% BCUP
LDPE	0.923	0.938	0.933	0.927	0.923	0.920
HDPE	0.954	0.971	0.965	0.960	0.952	0.946

decrease in  $T_g$ . Therefore, the overall effect of chemical crosslinking of semicrystalline polymers is a combined effect of these two opposing competitive factors.

To check if the crosslinks (new chemical bonds) were formed in the polymer chain as a result of a reaction with peroxide, gel-content measurements were performed in detail and are reported elsewhere.<sup>30,31</sup> The uncrosslinked polyethylenes, which were completely soluble in boiling xylene, showed a significant increase in the gel content up to about 90 wt % with the incorporation of 3 wt % peroxide. This indicated the development of substantial crosslinks between the polymeric chains that took place randomly at elevated temperatures in the molten state in which the polymer was in an amorphous state. Then, to determine if these crosslinks had any effect on the density and crystalline structure development, the density and crystallinity measurements were performed on the crosslinked polyethylene, and the results were compared with those of uncrosslinked samples. The results could confirm the reduced effect of crosslinking on the density for the LDPE and HDPE systems. The data from the density measurements are reported in Table II. The densities of the neat LDPE and HDPE granules increased by the process of compression molding because of the rearrangement and extra packing of the polymer chains as a result of the imposed pressure, whereas the crosslinked samples showed the expected decrease in the density. Table II shows the effect of the chemical crosslinking on the density of the polyethylenes, and we observed that the density of the samples showed a trend of slightly decreasing with increasing peroxide content. The density of the LDPE samples with different BCUP contents decreased from 0.938 to 0.920 g/cm<sup>3</sup>, and for HDPE, it varied from 0.971 to 0.946 g/cm<sup>3</sup>.

These results can be explained in the context of the free-volume model, as predicted by eq. (3). The results of the free-volume calculations presented in Table III confirm these slight changes in the free volume.

The free volume of a crosslinked polymer ( $V_f$ ) can be quantitatively correlated with the crosslink density ( $\nu$ ) by the following equation:<sup>32,33</sup>

$$(V_{f0} - V_f)/V = \alpha T_{g0}(1.2M_0\nu)/(\rho - M_0\nu) \quad (3)$$

where  $T_{g0}$  is the glass-transition temperature of the uncrosslinked polymer;  $V_{f0}$  is the free volume at  $T_{g0}$ ;  $M_0$  is the molecular weight of the monomer unit (for ethylene, it is 28);  $\alpha$  is the free-volume expansion of the polymer;  $\rho$  is the density of the polymer; and  $V$  is the total volume, which consists of the volume occupied by polymer molecules ( $V_0$ ) and  $V_f$ , such that  $V = V_0 + V_f$ . For polyethylene,  $\alpha$  is  $5.4 \times 10^{-4} \text{ K}^{-1}$ .

$\nu$  of the polymer can be predicted from the theory of rubber elasticity, which is expressed by the following relation:

$$G = \nu RT \quad (4)$$

where  $R$  is the gas constant and  $T$  is the temperature. The shear modulus ( $G$ ) is approximately one-third of the creep tensile modulus ( $E$ ).  $E$  in the hot-set test can be calculated with the following relation:

$$E = \frac{\sigma}{\varepsilon} \quad (5)$$

where  $\sigma$  is the tensile stress and  $\varepsilon$  is the tensile creep strain obtained in 15 min. In the hot-set test,  $\sigma$  is constant ( $\sigma = 20 \text{ MPa}$ ):

$$\varepsilon = \frac{20}{3\nu RT} \quad (6)$$

Thus, the measurements from the hot-set test (i.e.,  $\varepsilon$ ) can be used to calculate  $\nu$ , and then the free-volume change,  $(V_{f0} - V_f)/V$ , can be calculated from eq. (3). The hot-set data and calculated free-volume changes are presented in Table III. The free volume of the crosslinked samples increased with an increase in  $\nu$ . Moreover, the crosslinked LDPE and HDPE samples

**TABLE III**  
 $\nu$  Values, Hot-Set Data, and Free-Volume Changes of Chemically Crosslinked LDPEs and HDPEs with Different Peroxide (BCUP) Concentrations

Peroxide (%)	$\varepsilon$ (%)		$M_c$ (g/mol)		$\nu$ (mol/L)		Creep modulus (MPa)		Free-volume change (%) <sup>a</sup>	
	LDPE	HDPE	LDPE	HDPE	LDPE	HDPE	LDPE	HDPE	LDPE	HDPE
0.5	— <sup>b</sup>	— <sup>b</sup>	—	—	—	—	—	—	—	—
1.5	157	163	857	919	1.0798	1.04	12.74	12.27	0.37004	0.34406
2.5	89.3	118	485	661	1.899	1.44	22.4	16.95	0.67098	0.48593

<sup>a</sup>  $(V_{f0} - V_f)/V$ .

<sup>b</sup> Failed after 10–12 min.

TABLE IV  
 $T_m$ ,  $\Delta H_m$ ,  $X_c$ , and  $T_c$  Values of Uncrosslinked and Crosslinked LDPE and HDPE Samples with Different Peroxide (BCUP) Concentrations

Peroxide (wt %)	LDPE				HDPE			
	$\Delta H_m$ (J/g)	$X_c$ (%)	$T_m$ (°C)	$T_c$ (°C)	$\Delta H_m$ (J/g)	$X_c$ (%)	$T_m$ (°C)	$T_c$ (°C)
0.0	141.4	49.1	108.8	96.0	220.5	76.5	131.4	119.7
0.5	135.9	47.2	107.0	95.2	195.5	67.8	129.9	117.3
1.0	130.5	45.3	106.1	93.3	192.8	66.9	128.5	116.7
2.0	126.8	44.0	103.1	91.0	178.9	62.1	125.9	114.7
3.0	124.8	43.3	99.5	88.8	158.3	54.9	121.0	111.2

showed a decrease in the creep strain and an increase in the creep modulus with increasing peroxide content. This implies that the high concentration of crosslinks (v) in the polymers led to a longer resistance time and hence a lower elongation in the hot-set creep conditions before failure. The molecular weight between crosslink joints ( $M_c$ ) decreased with increasing peroxide content.

Next, we could also confirm the reduced effect of crosslinking on the crystallinity development (size and content of crystals) of the LDPE and HDPE systems by DSC. The results of DSC measurements are shown in Table IV. A decrease in the melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ), heat of fusion ( $\Delta H_f$ ), and crystallinity ( $X_c$ ) was observed with an increase in the peroxide content. The decrease in  $T_m$  is related to the crystal size, whereas the decrease in  $\Delta H_f$  is an indication of a reduced crystallinity of the system and the decrease in  $T_c$  is related to the crystallization rate and growth of crystals. This constrained crystallization behavior of the LDPE and HDPE systems with crosslinking could also be confirmed by the WAXS results, which are shown in Table V. The crystallinity and crystal size decreased with increasing peroxide content. These decreases were pronounced for HDPE versus LDPE, and this was likewise related to differences in the crosslinking, which disrupted crystallization. The  $D_{hkl}$  values are also included in Table V for the two

TABLE V  
 $\alpha_X$  and  $D_{hkl}$  Values Calculated from the Scattering Curves for the Polyethylene Samples

	Peroxide (wt %)	$\alpha_X$ (%) <sup>a</sup>	$D_{hkl}$ in the (110) direction <sup>b</sup>	$D_{hkl}$ in the (200) direction <sup>b</sup>
LDPE	0.0	38	14.4	11.3
	0.5	35	14.1	11.1
	1.0	32	13.9	10.8
	2.0	28	13.7	10.5
HDPE	0.0	64	17.1	15.1
	0.5	56	17.0	14.8
	1.0	51	16.7	14.6
	2.0	45	16.1	14.4

<sup>a</sup>  $\Delta\alpha_X \approx \pm 2.0$ .

<sup>b</sup>  $\Delta D \approx \pm 0.2$  nm.

possible crystallographic directions [perpendicular to the (110) and (200) net planes] and show a similar decreasing tendency with increasing peroxide content.

Hence, we have crosslinks in the system that prevent the mobility and at the same time reduce the crystallinity and density of the system. This may lead to an enhanced free volume. The restricted mobility leads to an increase in  $T_g$ , whereas the enhancement of the free volume favors a decrease in  $T_g$ . The observed decrease in  $T_g$  for the crosslinked polyethylenes obtained by DMA was also confirmed further by a peak broadening and increase in the value of the  $\tan \delta$  peak as well as the reduction in the storage modulus (see Fig. 3). This observed reduction of  $T_g$  indicates a more dominant role of crosslinks in the reduced crystallinity and consequent enhancement of the free volume in comparison with its direct effect on the restriction of the segmental mobility of the chains in the amorphous phase. A comparison of the reduced role of crosslinks in the crystalline phase (as revealed by the reduced  $T_m$ ,  $T_c$ , and  $X_c$  values) and the reduced role of crosslinks in  $T_g$  in the amorphous phase shows that the reduction of  $T_m$  and  $T_c$  is much more pronounced than the reduction of  $T_g$ . This is because for  $T_g$ , the overall effect is a combination of two opposing factors, one being the restricted mobility of the chains (which favors an increase in  $T_g$ ) in the

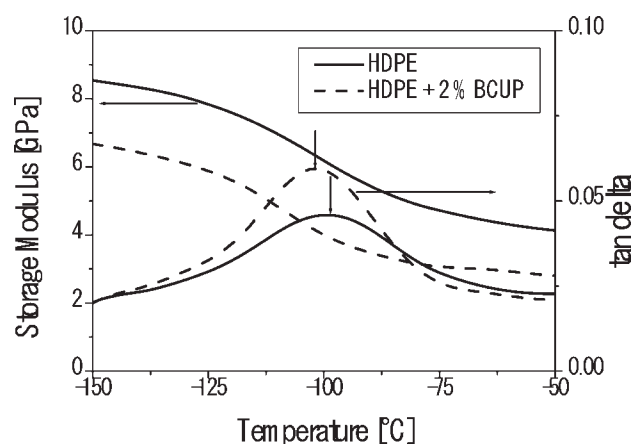
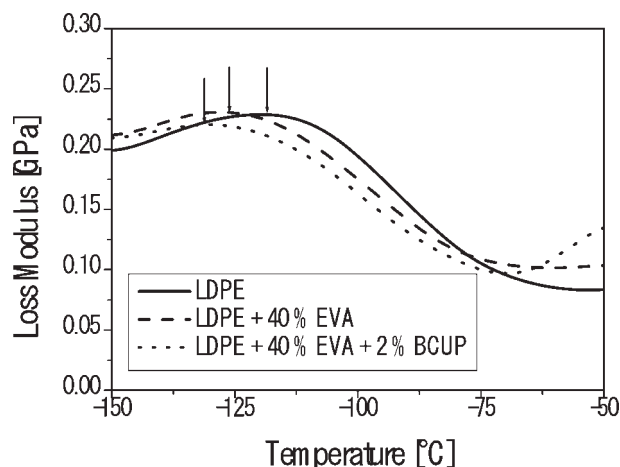


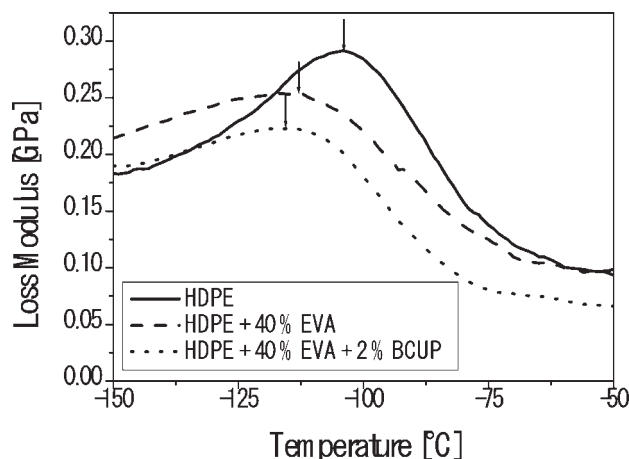
Figure 3 Variations of the storage modulus and  $\tan \delta$  versus the temperature for uncrosslinked and crosslinked HDPEs containing 2% BCUP.



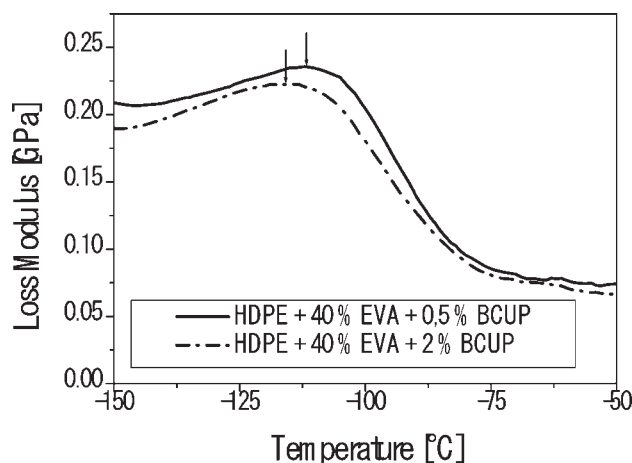
**Figure 4** Variation of the loss modulus versus the temperature for LDPE, an LDPE/EVA blend, and crosslinked LDPE containing 40% EVA with 2% BCUP.

amorphous region and the second being the reduced crystallinity and enhancement of the free volume (which favors a decrease in  $T_g$ ). However, for  $T_m$ ,  $T_c$ , and  $X_c$ , only one factor is involved, and that is the direct effect of crosslinking on the reduction of the size and content of crystals.

To check and generalize this observation of  $T_g$  depression for the blends, blends of HDPE and LDPE containing various amounts of EVA were chemically crosslinked under the same conditions used for neat HDPE and LDPE. The effect of chemical crosslinking on  $T_g$  of the blends was investigated with DMA. As typical examples for the comparison of the neat polymers, the blends containing 40 wt % EVA, and the chemically crosslinked blends containing 2 wt % peroxide with the same EVA content, the variation of the loss modulus versus the temperature is shown in Figures 4 and 5. For the blends, we have a similar unexpected  $T_g$



**Figure 5** Variation of the loss modulus versus the temperature for HDPE, an HDPE/EVA blend, and crosslinked HDPE containing 40% EVA with 2% BCUP.



**Figure 6** Variation of the loss modulus versus the temperature for crosslinked HDPEs containing 40% EVA with 0.5 or 2% BCUP.

depression as a result of the crosslinking process. It is well known that addition of a rubberlike material, such as EVA, to a semicrystalline polymer, such as polyethylene, can reduce the  $T_g$  as well as the crystallinity of the blend.<sup>34–38</sup> This decrease in  $T_g$  is mainly due to the plasticizing role of the rubbery region of the amorphous phase of the EVA random copolymer. However, after the addition of 2 wt % peroxide to these blends, a further decrease in  $T_g$  was observed that could be attributed to the crosslinking process. The chemical crosslinking of the blends could further reduce the crystallinity and enhance the net free volume; hence, the crosslinked blends had the lowest  $T_g$  values in comparison with the neat polymers and the uncrosslinked blends. Moreover, with an increasing crosslinking level (peroxide content) in the blends, the  $T_g$  depression became more significant. This can be clearly seen in Figure 6, which shows the variation of the loss modulus versus the temperature for crosslinked blends containing 0.5 and 2 wt % with a fixed EVA content of 40 wt %. The chemical crosslinking effect on  $T_g$  depression in the blends was less pronounced than that of the neat polymers. This was due to the fact that the addition of EVA to the polyethylene had already reduced the crystallinity significantly; hence, the further decrease in the crystallinity as a result of chemical crosslinking by peroxide was less sensible than the decrease in the crystallinity in the neat polymers. Therefore, the effect of the peroxide content on the  $T_g$  depression for the blends was less pronounced in comparison with the neat polymers.

## CONCLUSIONS

LDPE and HDPE and their blends with EVA were chemically crosslinked with BCUP. The effect of crosslinking on  $T_g$  was studied with DMA. It was found that this chemical crosslinking process resulted in a reduction

of  $T_g$  for both LDPE and HDPE and their blends with EVA. This reduction in  $T_g$  could be explained by the observed reduction in the crystallinity, as determined by DSC and WAXS, and the consequent decrease in the density and enhancement of the net free volume. It has been proposed that the constrained crystallization process, as a result of the restriction imposed on the chain packing by the formation of the chemical crosslinks, results in an increasing net free volume in the amorphous phase and hence decreases  $T_g$ . The  $T_g$  depression becomes greater with increasing  $v$ , whereas at the same time,  $X_c$  and consequently the density of the system decrease with an increase in the peroxide content.

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