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An investigation of chemical crosslinking effect on properties of high-density polyethylene

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Abstract

High-density polyethylene (HDPE) was chemically crosslinked with various amounts of di-*tert* butyl cumyl peroxide (BCUP). Crosslink density determined by rubber elasticity theory using hot set test showed an increase with increasing BCUP. Glass transition temperature (T_g), thermal stability, crystallization, melting behavior and tensile properties were studied. The results showed a new finding about decrease in T_g as a consequence of the 'chemical crosslinking' of HDPE. This was explained by observed reduction in crystallinity and expected increase in free volume as a result of restriction in chain packing. However, chemical crosslinking had no significant effect on the thermal stability. The stress at break, Young's modulus yield strength and elongation at break generally decreased with increase in BCUP. By increasing the temperature for slightly crosslinked HDPE, the elongation at break was increased but by increasing the crosslinking level an opposite effect was observed. Crosslinked HDPE showed an decrease in creep strain and an increase in creep modulus with increasing BCUP.

Keywords: High-density polyethylene; Crosslinking; Thermal–mechanical properties

1. Introduction

Polyethylene (PE) is one of the most important thermoplastics but its use is restricted in certain applications due to its low melting point, solubility or swelling in hydrocarbons and tendency to crack when stressed. In an effort to tackle these disadvantages there has been considerable work based on the crosslinking of PE. Crosslinking adds a very important feature to the polymer, it will not melt and flow when heated. On the other hand, by crosslinking, the semi-crystalline polymer exhibits the mechanical properties of a thermoplastic below its melting temperature (T_m), and exhibits the mechanical properties of a rubber above T_m [1–4]. Crosslinked PE is used in hot water piping installation, wire and cable industry, heat-shrinkable products, etc. [5–7].

Several methods have been used to crosslink PE such as irradiation, peroxides and silanes crosslinking. The most usual method of crosslinking is the chemical method especially by peroxides. Peroxides are incorporated into the polymer by extrusion below the activation temperature of the peroxide [8–10]. The extruded crosslinked PE will be later formed by one of the processing methods and cured under pressure and temperature. A suitable peroxide has to be selected to give fast crosslinking without pre-curing in the extruder, and dicumyl peroxide is widely used for this purpose. For compounding in-line during the extrusion process, there are advantages in using a liquid instead of a powder. Di-*tert* butyl cumyl peroxide (BCUP) is liquid and has some distinct advantages over dicumyl peroxide, among them easier feeding into the polymer melt stream in the extruder and safer margin of temperature for preventing scorch or premature crosslinking inside the extruder. Therefore, the know-how about the effect of BCUP on properties of PE would be advantageous before carrying out the crosslinking process in an extrusion.

The effect of the crosslinking on the properties of various types of PE has been extensively studied [11–18]. Most of these studies were on the crosslinking of PE by radiation. There is an agreement concerning some of the basic

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properties change on crosslinking of PE. The crosslinking leads to an increase in the viscosity of the polymer melt, increased tensile strength, improvement of creep properties and an increase in the resistance to environmental stress cracking [19–20]. The most studies on the PE were on the low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE). Lyons has studied the effect of radiation on the solubility and other properties of high and LLDPE [21]. Wong et al. have studied the role of molecular structure on the silane crosslinking of three types of PE [22]. They investigated the silane grafting efficiency for various PE types and also the moisture diffusion rate into the polymer for crosslinking process.

In this article we investigate the effect of crosslinking content on thermal and mechanical properties of HDPE. Physical and chemical properties were determined, the molecular weights between crosslinks and crosslink density were also predicted by a new approach and their relation concerning the peroxide content was investigated. Moreover, the thermal properties of chemically crosslinked HDPE were studied by dynamic mechanical analysis (DMA), differential scanning calorimetery (DSC) and thermal gravimetery analysis (TGA). Finally, the tensile properties of crosslinked HDPE were also reported at different temperatures.

2. Experimental

2.1. Materials

High-density polyethylene (HDPE) grade MG7547A, with MFI of 4 g/10 min and density of 0.954 g/cm^3, was supplied by Borealis group, Denmark. Irganox 1010 antioxidant with density of 1.15 g/cm^3 was purchased from Ciba Co., Switzerland. Masterbatch with a content of 10% carbon black was obtained from Colorplast Döbeln GmbH, Germany. BCUP with purity of 96% and density of 0.96 g/cm^3 was provided by Peroxide-Chemie GmbH, Germany. The mixing formulations are shown in Table 1.

2.2. Sample preparation

The HDPE and other additives, in different ratios as shown in Table 1, were melt mixed in an internal mixer (Plasti-Corder, Model PL 2000, BRABENDER, Germany) with a speed of 50 rpm at 145 °C for 5 min, and then BCUP was added and mixed for 3 min. At this state the BCUP mixes with HDPE and other additives without going through chemical reactions because the mixing temperature is not sufficient to activate the peroxide initiation reactions. The chemical crosslinking took place during compression molding of sheet samples using a Fontune 400 KN laboratory (Holland) hot press at elevated temperature of 190 °C and pressure of 10 MPa for 5 min. Then the sheet samples were cooled to ambient temperature with a cooling rate of 15 °C/min.

Table 1
Mixing formulations

Sample no.	HDPE (wt%)	Masterbatch (wt%)	Irgannox 1010 (wt%)	BCUP (wt%)
1	97.4	2.0	0.1	0.5
2	96.9	2.0	0.1	1.0
3	96.4	2.0	0.1	1.5
4	95.9	2.0	0.1	2.0
5	95.4	2.0	0.1	2.5
6	94.9	2.0	0.1	3.0

2.3. Gel measurement

The gel content of the crosslinked HDPE was determined gravimetrically, according to ASTM D 2765 using a 16 h Soxhlet extraction cycle with *p*-xylene as the solvent at 140 °C. Irganox 1010 was added at 0.5 wt% to inhibit polymer degradation during the extraction. Approximately 0.3 g of the crosslinked polymer sample was cut into small pieces and placed in a preweighted stainless steel fine wire mesh. After the extraction cycle, the sample was washed with acetone and vacuum dried to a constant weight. The gel fraction was calculated as the percentage ratio of the final weight of the polymer to its initial weight.

2.4. Density measurement

The density of the crosslinked samples were determined by a Sartorius YDK 01 0D Specific Gravity Determination Kit (Sartorius AG, Goettingen, Germany). In this measuring device the Archimedean principle is applied for determining the specific gravity of samples. A polymer sample immersed in a liquid (water) is exposed to the force of buoyancy. The value of this force is the same as that of the weight of the water displaced by the volume of the polymer sample. With a hydrostatic balance, which enables one to weight the polymer sample in air as well as in water, it is possible to determine the specific gravity of the polymer sample if the density of the water is known using the following relationship:

$$\rho = [W(\mathrm{a})/(W(\mathrm{a}) - W(\mathrm{fl}))]\rho(\mathrm{fl}) \tag{1}$$

where ρ is the specific gravity of the polymer sample, $\rho(\mathrm{fl})$ is the density of the liquid, $W(\mathrm{a})$ is the weight of the polymer in air, $W(\mathrm{fl})$ is the weight of the polymer in liquid.

For each sample ten measurements were performed and average values are reported here.

2.5. Melt flow index

The melt flow index (MFI) of the crosslinked HDPE samples was measured according to ASTM D-1238 using a Zwick 4100 apparatus (Germany). The MFI measurements were carried out at temperature of 190 °C under 2.16 and 21.6 kg weight and the values are expressed in g/10 min.

2.6. Thermal analysis

The DSC tests were performed on a DSC-7 Perkin–Elmer (Germany) with samples of about 5 mg sealed in aluminium pans under nitrogen atmosphere in a temperature range between −60 and 180 °C at a heating rate of 10 K/min. The melting and crystallization temperatures as well as melting enthalpy of the samples were determined. The TGA of the samples was carried out using a TGA-6 of Perkin–Elmer in the temperature range of 50–600 °C at a heating rate of 10 K/min in nitrogen atmosphere. The dynamic mechanical properties of the samples were determined by DMA. DMA was carried out using a DMA 983 (TA Instrument, Inc., USA) to determine the viscoelastic properties in bending mode. Rectangular bar specimens of dimension $50 \times 10 \times 3\ \text{mm}^3$ were used for this study. Samples were heated from −150 to 0 °C at a heating rate of 3 K/min at a frequency of 1 Hz.

2.7. Mechanical properties

The mechanical properties of uncrosslinked and crosslinked HDPE were determined according to ISO 527-2: 1996 on an UPM 1456 Zwick ULM; Germany. The test was carried out with crosshead speed of 100 mm/min at three temperatures namely, at the ambient, at 90 °C (below the maximum crystallization temperature) and also at 140 °C (above the melting point) temperatures.

2.8. 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 °C and the elongation between two marks was measured after 15 min.

3. Results and discussion

3.1. Chemical properties

In this section the phenomenon of the HDPE crosslinking through chemical reactions with the peroxide used as a crosslinking agent is discussed. The mechanism of crosslinking is proposed and the extent of crosslinking was determined by gel fraction test. Finally an attempt has been made to determine the crosslink density by use of the rubber elasticity theory.

3.1.1. Reaction mechanism

The crosslinking of PE with BCUP is based on free radical mechanism. The free radicals generated on thermal decomposition of peroxides can attack to the molten PE free chains and crosslinking of the polymer chains may occur. A general scheme for the crosslinking reaction of PE initiated by free radicals is quite simple, consisting of the formation of macroradicals and their subsequent recombination.

Thermal decomposition of peroxide

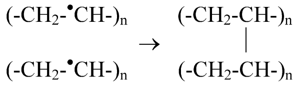
$$\mathrm{RO{-}OR'} \xrightarrow{\triangle} \mathrm{RO^{\cdot}} + {}^{\cdot}\mathrm{OR'}$$

Initiation

$$(-\mathrm{CH_2}-\mathrm{CH_2}-)_n + {}^{\cdot}\mathrm{OR} \rightarrow (-\mathrm{CH_2}-{}^{\cdot}\mathrm{CH}-)_n + \mathrm{ROH}$$

$$(-\mathrm{CH_2}-\mathrm{CH_2}-)_n + {}^{\cdot}\mathrm{OR'} \rightarrow (-\mathrm{CH_2}-{}^{\cdot}\mathrm{CH}-)_n + \mathrm{R'OH}$$

Crosslinking



$$\begin{matrix}(\text{-CH}_2\text{-}^{\bullet}\text{CH-})_n \\ (\text{-CH}_2\text{-}^{\bullet}\text{CH-})_n\end{matrix} \rightarrow \begin{matrix}(\text{-CH}_2\text{-CH-})_n \\ | \\ (\text{-CH}_2\text{-CH-})_n\end{matrix}$$

where R and R′ are $\mathrm{C(CH_3)_3}$ and $\mathrm{C(CH_3)_2C_6H_5}$, respectively. Some side reactions are possible for example disproportionation, leading to molecular scission and the formation of molecular branches. The disproportionation reaction is known to have a higher activation energy; thus it is favored by high temperature at the expense of crosslinking.

The similar mechanism of crosslinking for PE with dicumyl peroxide was proposed by Campus [23] and Lazar [16]. In fact for the dicumyl peroxide R and R′ would be the same. It is known that an increase in temperature results in a higher rate of the chemical reaction. It was, however, found in the laboratory and under actual industrial conditions, that an increase in temperature will not necessarily improve the final PE crosslinking degree achieved [23].

3.1.2. Gel fraction

HDPE is a thermoplastic consisting of a continuous amorphous phase in which the crystalline domains are distributed. Peroxide crosslinking takes place randomly at elevated temperatures in the molten state where the polymer

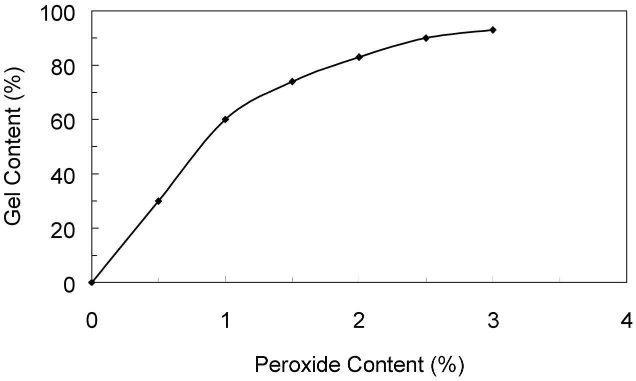


Fig. 1. Effect of peroxide (BCUP) content on the gel content of crosslinked high-density polyethylene.

has only amorphous structure. Fig. 1 shows the gel content (wt%) against BCUP content (wt%). As the curve indicates, there is a continuous increase in the gel content with peroxide content up to about 2.5 wt% after which the curve gradually levels off.

3.1.3. Use of rubber elasticity theory for determination of crosslink density (ν)

The number of crosslinks in a unit volume is called crosslink density and is correlated with the molecular weight of the chain between two crosslinks point (M_c) by $\nu = \rho/M_c$, where ρ is the density of polymer. The values of ν for crosslinked HDPE calculated by use of rubber elasticity theory and creep data are reported in the subsequent section. Thus the molecular weight of the chain between two crosslinks point (M_c) can be calculated by value of crosslink density and density of polymer. The M_c for crosslinked HDPE samples with different content of BCUP can be calculated according to the above relationship knowing the value of ν. The data for M_c are reported in Table 2. As it is expected with increase in crosslink density (ν) content, the M_c decreases. The similar result was reported by Klein et al. on irradiated PE in which the apparent molecular weight between network junctions was decreased with increase in irradiation dose [24].

The crosslink density (ν) of the polymer can be predicted from the theory of elasticity, which is expressed by the following relation: [25,26]

$$G = \nu RT \qquad (2)$$

where G is the shear modulus of the polymer, R is the gas constant and T is temperature (K). The above relationship shows that the G increases with an increase in ν. The shear modulus may be written as:

$$G = \frac{E}{2(1+V)} \qquad (3)$$

Poisson's ratio, V, for rubber is approximately 0.5 (incompressibility assumption), therefore it gives $G = E/3$. Replacing the value of G in the Eq. (2) results in the following equation:

$$E = 3\nu RT \qquad (4)$$

The creep tensile modulus in the hot set test can be calculated from the following relation:

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

where σ is the tensile stress and ε is the tensile creep strain in 15 min. In the hot set test the tensile stress is constant ($\sigma = 20$ MPa). Hence,

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

Thus the measurement from the hot set test (i.e. ε) can be used to calculate the crosslink density (ν).

The crosslink density (ν) for crosslinked HDPE samples with different content of peroxide is calculated according to the above relationships and data are reported in Table 2. As it can be seen the crosslink density increases with increase in BCUP content. The uncrosslinked HDPE crept rapidly under a constant load of 20 MPa and it failed immediately. On crosslinking, at a low BCUP content, the sample still failed but the failure occurred at longer time intervals as compared to the uncrosslinked HDPE. At 1.5% of BCUP content, an optimum creep elongation of 163% was obtained without any sign of failure. However, at higher crosslinking level (2.5% BCUP) the extent of elongation of crosslinked HDPE decreased dramatically (118%) which is not so favorable for heat shrinkable products. Considering the high gel content of the latter sample (Fig. 1), the reduction in creep elongation can be attributed to the high degree of crosslink density formed at the high BCUP content. This implies that the high concentration of crosslinks (crosslink density) in the polymer leads to a longer resistance time and a lower elongation in the hot set creep conditions before failure. Comparison of the gel contents with the hot set values suggests that the optimum percentage of elongation in the hot set test could be achieved at a gel content of about 60–80%.

The hot set test can be used in industries as a rapid quality control test for heat shrinkable products. Since the determination of the gel content is quite time consuming process it is not a preferable method of measurement. The crosslink density of the products can be determined by the hot set data in a relatively much short time, once the master calibration curve is made using the gel content versus the hot set data for various level of crosslinking.

Table 2
Crosslink density and hot set data for HDPE with different BCUP content

Peroxide content (%)	Tensile creep strain ε (%)	Creep modulus, (σ/ε) (MPa)	Molecular weight between crosslinks M_c (g/mol)	Crosslink density, ν (mol/l)
0.5	[a]	–	–	–
1.5	163	12.27	919.35	1.04
2.5	118	16.95	660.76	1.44

[a] Failed after 10–12 min.

3.2. Physical properties

3.2.1. Density

The results of density measurements for the crosslinked HDPE samples are reported in Table 3. The density of the neat HDPE without crosslinking is also given as a reference point in comparison with crosslinked samples containing various amount of peroxide with and without carbon black masterbatch. As it is seen from Table 3, the density of HDPE granules increases by process of the compression molding due to rearrangement and extra packing of the polymer chains as a result of the imposed pressure. But, with increase in crosslinking, the density of HDPE decreases systematically for both types of the samples with and without carbon black masterbatch. This can be explained by the reduced crystallinity of the system and hence the increase in the free volume as a result of crosslinking process. The higher density of the masterbatch and more packing of carbon black in the matrix gives a higher density for the crosslinked samples containing carbon black masterbatch.

3.2.2. Melt flow index

Under the MFI test conditions (at 190 °C with load of 2.16 and also 21.6 kg), the crosslinked HDPE samples containing different amounts of peroxide did not show any flow and therefore the MFI could not be determined. In fact the samples showed a rubber like behavior with no flow. This indicates that the level of peroxide content used for crosslinking was quite sufficient to crosslink the PE chains and to converts its plastic nature to a more rubber like material.

3.3. Thermal properties

The effect of crosslinking on the thermal properties of HDPE are discussed here. For this purpose the effect of crosslinking on both the amorphous and crystalline region of HDPE were considered. For the amorphous region, the glass transition temperature being as the main feature of the amorphous phase determined by DMA is discussed. Whereas, for the crystalline region, the crystalline melting temperature, crystallization temperature and the corresponding enthalpies measured by DSC are considered. Finally the results concerning the effect of crosslinking on thermal stability of the samples determined by TGA are discussed here.

3.3.1. Dynamic glass-transition temperature (T_g)

According to the literature, DMA of PE prior to melting reveals three peaks termed as α, β and γ transitions. All these peak transitions correspond to different motions in PE chains. The γ transition occurs in the range of -150 to -100 °C [27]. Initially it was suggested that the γ transition is due to motion of the polymer chains in the amorphous regions [28,29]. This suggestion was subsequently refined to the motion in the amorphous regions of segments of the chains comprising of three or four CH_2 units [30]. It has also been shown that γ transition is the glass transition, and influence of physicochemical parameters on the γ transition can be explained in terms of T_g. The γ transition peak temperature (T_g), i.e. the temperature at which maxima in loss modulus occurs, for the noncrosslinked and crosslinked PE with 2 wt% of BCUP are shown in Fig. 2. A decrease in γ transition temperature with increase in crosslinking content is observed for HDPE. These decreases in γ transition temperature is attributed to reduction in crystallinities with increase in BCUP content, which enhances the molecular motions of the amorphous phase, leading to an increase in free volume and hence lower downs the T_g. The free volume also increases as a result of restriction of the chain packing due to crosslinking of the polymer chains. Fig. 3 shows the storage modulus and tan δ versus temperature for the uncrosslinked and crosslinked PE with 2 wt% of BCUP. The temperature, at which the maximum in the tan δ and a sharp drop of storage moduli (E') occurs, decreases on increase in BCUP content. There is a decrease in log E' values with increase in BCUP content, which is attributed to reduction in crystallinity (Table 4) and enhancement of free volume on increase in BCUP content. The value of tanδ, being ratio of E''/E', increases with increase in BCUP content which is attributed to the increase in value of loss moduli E'' and the decrease in value of the storage moduli E'.

It is to be noted that for the crosslinked PE obtained by radiation method, unlike our observed decrease in T_g on crosslinking by chemical method, an increase in T_g is reported by increase in crosslinking level [21,31]. This could be due to the fact that in the radiation method as the exposure is done in the solid state, therefore the crystalline phase does not undergo any changes rather the crosslinking takes place only in the amorphous phase. This restricts molecular mobility of the polymer chains and hence increases the T_g. In the chemical method as it is mentioned earlier, the T_g of the system decreases because of the reduction of the crystallinity, increase in free volume and

Table 3
Density of two types of HDPE with different BCUP content

Name of samples	Granules	Sheet	0.5% BCUP	1% BCUP	2% BCUP	3% BCUP
HDPE4	0.954	0.96992	0.96452	0.95968	0.95394	0.94438
HDPE4 + 5% MB	–	0.97186	0.96774	0.96287	0.95698	0.94826

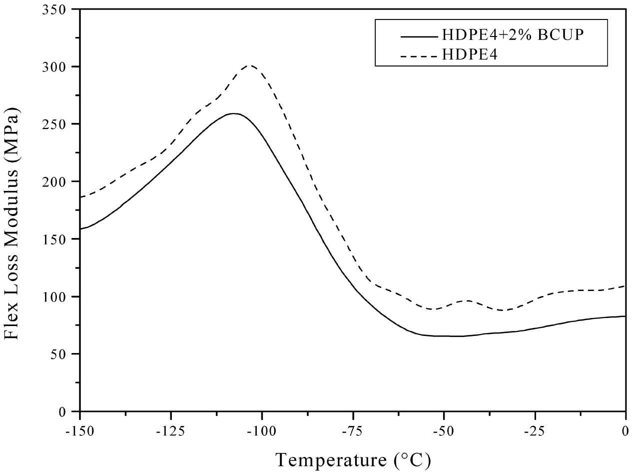


Fig. 2. Effect of crosslinking on the flex loss modulus (E'') of high-density polyethylene.

the amorphous phases. This eases the segmental mobility of the PE chains in the amorphous phase and hence decreases the T_g.

3.3.2. Melting temperature (T_m)

The degree of crystallinity of semi-crystalline polymers has considerable effect on their mechanical and thermal properties. Table 4 shows the melting and crystallization temperatures, heat of fusion (ΔH_m) and degree of crystallinity as determined from DSC measurements, for uncrosslinked and crosslinked HDPE with different percentage of peroxide. The degree of crystallinity was calculated via the total enthalpy method, according to the equation $X_c = \Delta H_m / \Delta H_m^+$, where X_c is the degree of crystallinity, ΔH_m is the specific enthalpy of melting, and ΔH_m^+ is the specific enthalpy of melting for 100% crystalline PE. The ΔH_m^+ value for 100% crystalline PE is taken as 288 kJ/kg as reported in the literature [18,32]. A decrease in the melting and crystallization temperatures, heat of fusion (ΔH_m) and degree of crystallinity was observed with an increase in BCUP content (Table 4). That is, increasing the crosslink density—by increasing the amount of peroxide—reduces the degree of crystallinity of the PE. Crosslinks play the role of defect centers, which impede the folding of macromolecular chains and thus decrease the sizes of the lamellar crystals.

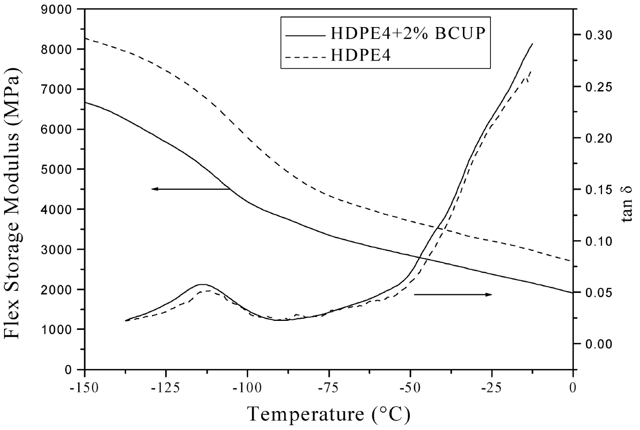


Fig. 3. Effect of crosslinking on the flex storage modulus (E') and tan δ of high-density polyethylene.

Fig. 4, shows that DSC diagram of samples with 0 and 2.5% BCUP. It seems that with increasing of peroxide the melting point, crystallization temperature and crystallinity of the crosslinked HDPE decreases. The melting temperature and total crystallinity are related to the crystal size and amount of crystals revealed as endothermic peak temperature and area under the peak in DSC curves, respectively. Formation of crosslink junctions while the polymer is at melt state (amorphous phase) disturbs the reorganization and chain folding during crystallization process and this results in formation of imperfect crystallite with smaller size and also less in content. Hence the melting point, crystallization temperature and total crystallinity decreases with increase in crosslink density.

3.3.3. Decomposition temperature

Fig. 5 shows TGA curves for the uncrosslinked and crosslinked HDPE samples with various amounts of peroxide content. It is seen that the HDPE does not show a major weight loss up to about 450 °C, beyond which a sharp weight loss is observed. This behavior is almost identical for all the samples, although there is a slight reduced trend in onset of the thermal decomposition with increase in peroxide content. Since the crosslinking introduces tertiary carbons in the system, which are more

Table 4
Melting temperature, heat of fusion (ΔH_m), degree of crystallinity (X_c) and crystallization temperature of crosslinked HDPE with different peroxide (BCUP) content

Peroxide content (%)	ΔH_m (J/g)	X_c (%)	Melting temperature (°C)	Crystallization temperature (°C)
0.0	185.8	64.5	131.6	117.1
0.5	174.2	60.4	130.3	115.2
1.0	166.7	57.9	130.7	114.2
1.5	161.6	56.1	127.0	114.0
2.0	153.3	53.2	123.9	111.9
2.5	151.0	52.4	123.1	110.6
3.0	142.7	49.5	122.6	110.2

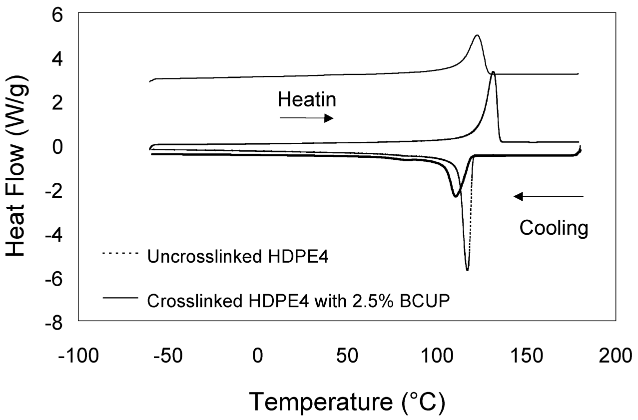


Fig. 4. DSC diagram of uncrosslinked and crosslinked HDPE containing 2.5 wt% BCUP.

prone to thermal decomposition therefore the observed reduced trend is due to increase in number of the tertiary carbon atoms with increase in peroxide content. However, these changes are too small to be considered as a significant effect. This indicates that the thermal stability of the HDPE is independent of the crosslinking. This was also true for the HDPE samples with lower MFI value. Similar results are reported for the uncrosslinked and crosslinked LLDPE/Wax blends by Krupa et al. [33].

3.4. Mechanical properties

3.4.1. Effect of BCUP content and temperature on the tensile behavior

HDPE is ductile and under tension at room temperature usually yields with necking and drawing followed by strain hardening effect and finally ruptures at relatively long elongation. Comparison of the stress–strain behavior of uncrosslinked HDPE with those of the crosslinked polymer containing 0.5, 1.5 and 2.5% BCUP, at room temperature and 90 °C are shown in Figs. 6 and 7, respectively. It is seen that at any specified temperature, the elongation at break, yield strength and tensile strength at break are generally decreased with increased peroxide content. Uncrosslinked HDPE at any specific temperature did not rupture in the measurement range.

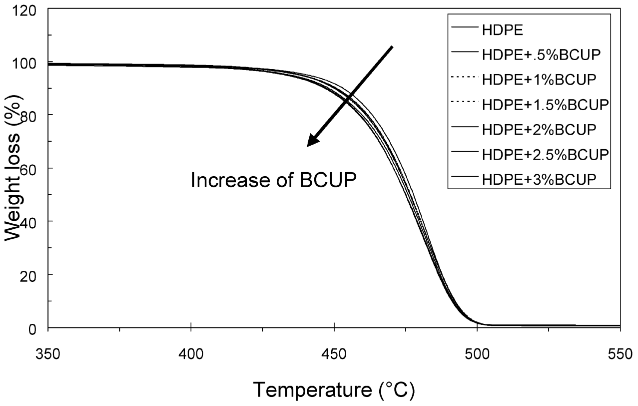


Fig. 5. Effect of crosslinking on the thermal stability of high-density polyethylene.

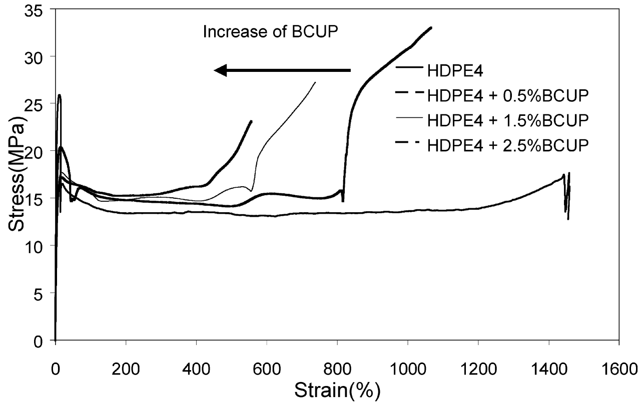


Fig. 6. Stress–strain curves of uncrosslinked and crosslinked HDPE at 25 °C for different BCUP contents.

The data about the effect of temperature and BCUP content on the tensile properties of crosslinked HDPE are summarized in Table 5. As it is seen from Table 5, the Young's modulus decrease with increase in crosslinking level and temperature. The above results can be interpreted as follows:

Due to restriction imposed by crosslink junctions for packing of chains units together in an ordered lattice while cooling from melt, crystallinity of the cooled solid polymer decreases with increase in the crosslinking which takes place in the molten state (as seen from DSC data). These two structural parameters have opposing effect on mechanical properties of the polymer. At room temperature there are both physical crosslinks (crystalline ties) and chemical crosslinks between polymeric chains. With increase in the chemical crosslinks, which are more stronger than the physical crosslinks, the restriction imposed on elongational behavior of the polymer increases. This restriction is due to smaller length of segments available for stretching and lesser the probability of chain slippage resulting in decrease in elongation at break. With increase in temperature, the physical crosslinks are weakened as a result of disappearance of the crystallites. At low peroxide content (0.5 wt%

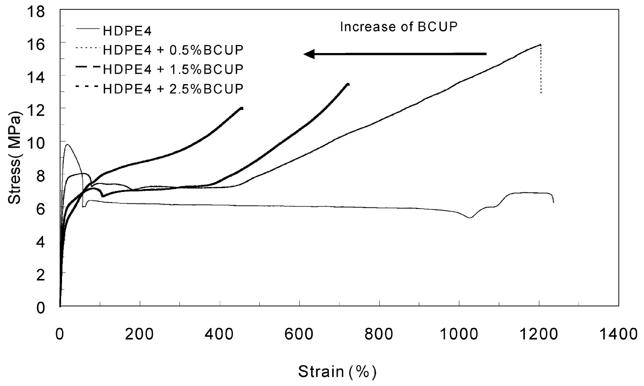


Fig. 7. Stress–strain curves of uncrosslinked and crosslinked HDPE at 90 °C for different BCUP contents.

Table 5
Effect of temperature and peroxide (BCUP) content on the tensile properties of crosslinked high-density polyethylene

Peroxide content (%)	Modulus (MPa)			Tensile strength at break (MPa)			Elongation at break (%)		
	25 °C	90 °C	140 °C	25 °C	90 °C	140 °C	25 °C	90 °C	140 °C
0.0	728.9	155.4	–	25.95	6.26	–	[a]	[a]	–
0.5	542.8	99.9	10.6	32.92	15.86	[a]	1066.2	[a]	[a]
1.5	391.3	74.9	7	27.23	13.42	2.22	737.7	723.3	527
2.5	376.5	56.4	0.8	23	11.92	1.95	556.5	456.3	323

[a] The samples did not rupture in the range of tensile machine.

BCUP), by increase in temperature the physical crosslinks are weakened while the chemical crosslinks are not yet sufficient to hold the structure fully. Therefore, it behaves same as virgin uncrosslinked HDPE. However, with increase in chemical crosslinks and increase in temperature, the chemical crosslinks are more effective although the physical crosslinks are weakening. This reduces the elongation at break at higher temperatures.

Below the crystalline transition temperature, that is in our experiments, the stress–strain behavior obtained below 90 °C (Figs. 6 and 7), values of the Young's modulus and the yield strength are dominated by the amount of hard crystalline regions, unit cells of which are held together by relatively strong forces. This crystalline structure is being weakened and reduced with advancement of crosslinking degree so are the Young's modulus and the yield strength. The tensile stresses are born by larger number of crosslinks resulting in rupture of samples at lower tensile stress. However, with increasing the crosslink points, apart from decreasing of the stress resistant crystalline domains, one reaches a circumstance where no strain hardening occurs and the stress is not born by the oriented backbone chain segment, but only by the single crosslink bonds, where the drop in tensile strength is observed. It is noteworthy that at temperatures higher than the crystalline transition temperature (Table 5), due to fewer or even disappeared crystalline ties, the number of crosslinks upon which the tensile strength is dependent is less than the critical value which would have been reached at the same degree of crosslinking at lower temperatures.

Increasing the temperature and the crosslinking degree both oppose with occurrence of yielding in PE due to diminishing roll of fewer and smaller crystalline regions. At 90 °C (Fig. 7) yielding is only apparent for samples containing 0 and 0.5% BCUP while for samples with higher amount of BCUP (more crosslinks) or samples experiencing higher temperatures (Table 5) the yield points have disappeared and a rubber like behavior has been observed.

3.4.2. Creep behavior of crosslinked HDPE

Creep data were obtained in tension mode on compression molded bars of PE. Tensile creep strain (ε) for uncrosslinked PE in terms of stress (σ) (in MPa) and creep time, t (in hours) at 25 °C is given as follows [25]:

$$\varepsilon = 1.35 \times 10^{-3} \sigma^{1.3} t^{0.11} \tag{7}$$

Thus the creep compliance $J(t)$ can be presented as

$$J(t) = \frac{\varepsilon}{\sigma} = 1.35 \times 10^{-3} \sigma^{0.3} t^{0.11} \tag{8}$$

In hot set tests, stress is maintained at a fixed value of $\sigma =$ 20 MPa. Substituting this value in the above equation, gives the following equation:

$$J(t) = 3.316 \times 10^{-3} t^{0.11} \tag{9}$$

Creep data at 200 °C (the oven temperature in hot set tests) can be obtained by first shifting the data from 25 to -100 °C and then to 200 °C using the time–temperature correspondence expressed as [25]:

$$J(t)_{T_g} = J\left(\frac{t}{a_{T_1}}\right)_{25\ ^\circ\mathrm{C}} \quad \text{and} \quad J(t)_{200\ ^\circ\mathrm{C}} = J\left(\frac{t}{a_{T_2}}\right)_{T_g} \tag{10}$$

The shift factors a_{T_1} and a_{T_2} are calculated from the Williams–Landel–Ferry (WLF) equation

$$\log a_{T_1} = \frac{-17.4(25 - T_g)}{51.6 + (25 - T_g)} \quad \text{and} \quad \log a_{T_2} = \frac{-17.4(200 - T_g)}{51.6 + (200 - T_g)} \tag{11}$$

According to the literature, DMA of PE prior to melting reveals three peaks termed as α, β and γ transitions. For HDPE the γ transition at -100 °C is considered as the glass-transition temperature (Fig. 3). By using above Eqs. (9)–(11), the creep equation for HDPE at 200 °C will be

$$J(t)_{200\ ^\circ\mathrm{C}} = 4.385 \times 10^{-3} t^{0.11} \tag{12}$$

This equation predicts a tensile creep strain of about 0.003 at 200 °C and $t = 15$ min, although the uncrosslinked HDPE fails rapidly at 200 °C in the hot set test. The reason for this disagreement is that at 200 °C, PE is already well above its crystalline melting temperature (130 °C) therefore, it flows freely without any restriction and do not show any tensile creep strain. The above creep Eqs. (7) and (12) are valid only in temperature well below the melting temperature of uncrosslinked HDPE whereas it works well for crosslinked HDPE even at 200 °C. The creep behavior of crosslinked

HDPE samples were determined using hot set measurements. The values of the tensile creep strain and creep modulus (inverse of creep compliance, $1/J(t)$) obtained using the Eq. (8) are reported in Table 2. As it can be seen, at low BCUP content (0.5 wt%), due to its low chemical crosslinks, it behaves same as the uncrosslinked HDPE and fails rapidly after 10–12 min. With increase in crosslinking the number of chemical crosslinks increases and at 200 °C during the hot set measurements, HDPE is able to hold its structure together, even though the crystalline region is melted and lies in a liquid state. With increase in crosslinking level, the tensile creep strain (ε) and creep compliance ($J(t) = \varepsilon/\sigma$) decrease and hence the creep modulus ($1/J(t)$) increases (Table 2).

4. Conclusions

The gel content indicating increase in the degree of crosslinking by addition of peroxide content. The crosslink density calculated by rubber elasticity theory and creep data, increased with increasing of peroxide content. The HDPE densities decreased by increase in crosslinking as a result of decreased crystallinity or enhanced free volume of the system. The crosslinked HDPE showed a rubber like behavior and did not flow under the MFI test conditions. Investigation of the thermal properties of the crosslinked and uncrosslinked HDPE showed that the melting point, heat of fusion (ΔH_m), crystallinity and the temperatures of crystallization (T_c) are reduced by increasing the peroxide content. By increasing the crosslinking, a decrease in glass transition temperature was observed, which was attributed to decreased crystallinity of the system, that enhances the free volume and the molecular motions of the amorphous phase, leading to a lower glass transition temperature (T_g). Correlation between thermal stability and crosslink density was not observed. Both the crosslinked and uncrosslinked HDPE had almost the similar decomposition temperatures.

The elongation at break, stress at break and yield strength decreased with an increase in the BCUP content. By increasing the temperature for slightly crosslinked samples (low BCUP content) the elongation at break was increased, but by increasing the crosslinking level an opposite effect was observed. The Young's modulus showed decreasing trend with an increase in the BCUP content and the temperature. Creep behavior of crosslinked HDPE showed that by increase in crosslinking content, the tensile creep strain and creep compliance decreased while the creep modulus increased.

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