

Preparation of Granular Crosslinkable Medium-Density Polyethylene

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ABSTRACT: Granular crosslinkable medium-density polyethylene (XLPE) without scorch inhibitor was prepared adding organic peroxide [2, 5-dimethyl- 2, 5- di- (t-butyl-peroxy) hexyne-3] through extrusion process, in industrial scale. Twin screw extruder was used to mix the polyethylene and the peroxide. The temperature zones of the extruder were controlled very carefully to prevent unwanted crosslinking during extrusion. Compression molding, rotational molding, and injection molding of XLPE at 155°C made no crosslinking in PE, and then they were exposed to higher temperatures at which the organic peroxide decomposed to

provide free radicals which led to the crosslinking of the MDPE. The thermal properties (using dynamic mechanical analysis, DMA, differential scanning calorimetric analysis, DSC, and thermogravimetric analysis, TGA, techniques) and mechanical properties (including strain at break and stress at break) of virgin PE, crosslinkable PE, and crosslinked PE have been compared. The crosslinked PE and virgin PE were also studied by X-ray diffraction (XRD) technique. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1873–1879, 2007

Key words: polyethylene; crosslinking; thermal properties

INTRODUCTION

Polyethylene is one of the most important polymers and the amelioration of its applied properties is being developed. This polymer has some weaknesses such as against some organic solvents, stress cracking resistance,^{1–5} and limited applications especially above 70°C. Crosslinked polyethylene unlike polyethylene does not have such problems and can be used in pipe industry, cable industry, compression, rotation, and injection molding.¹ Various techniques such as irradiation, addition of crosslinking agents, etc have been used to prepare crosslinked polyethylene. But, in industrial scale, it is important that crosslinked polyethylene products can be produced from granular forms. Among the production of crosslinked PE (e.g., radiation, silans, peroxides ...), thermochemical crosslinking agents and organic peroxides have been widely used due to their minimum side products, controlled decomposition rate, less sensibility to water compared with silans, and economical process.^{6–9}

In this study, a dialkyl peroxide as a crosslinking agent was added in the absence of any scorch inhibitor to decrease the final price of crosslinkable MDPE.

The most important problem in this study was the prevention of unwanted crosslinking during extrusion which needed exact controlling of temperatures.¹⁰ Our group studied production of new grade of polyethylene as a crosslinkable PE via extruder in the shape of granules.

The purpose of the present study is to show how we can prepare crosslinkable PE and compare the thermal and mechanical properties of the virgin polymer, the crosslinkable and crosslinked ones. MDPE is a suitable choice towards HDPE in as much as tertiary radicals are very stable and have a higher rate of production than primary and secondary radicals do; on the other hand spatial hindrance plays an important role in the combination of two radicals, so medium density polyethylene is better than LDPE.

2, 5- Dimethyl- 2, 5- di- (t- butyl- peroxy) hexyne-3 is an aliphatic di alkyl peroxide, so it has no smell. Furthermore, it has a suitable half-life for the production of XLPE.

EXPERIMENTAL

Materials

MDPE (3840 UA, Tabriz Petrochemical, Iran, MFI 190°C, 3.8–4.5 gr/10min, density: 0.938 g/cm³) was mixed with a sufficient amount of [2, 5- Dimethyl- 2, 5- di- (t- butyl- peroxy) hexyne-3 (DYBP; Inter chem. GMBH with half-life of 57 s at 200°C, 85% in white oil)] by a mixer at room temperature. After complete dispersion of peroxide through MDPE the mixture

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TABLE I
Formulation of MDPE Granule

Samples	DYBP (wt %)	Antioxidant (Ir-1010 and 168 ppm)	Ca-st ppm
Sa	2.3	1000–2000	1500
Sb	1.4	1000–2000	1500
Sc	0.8	1000–2000	1500

was introduced into an extruder, which had been reached to a temperature lower than the decomposition temperature of the peroxide, by pure MDPE. As mentioned in Table I, virgin polymer already contained Irganox 1010, Irgafos168 and Ca-St. (Calcium Stearate).

Procedure

Samples were prepared for passing through twin screw extruder (Collin, Germany) with three different DYBP concentrations (2.3, 1.4, and 0.8 phr). The extruder was operated at a speed of 70 rpm with a sequence of segment temperatures at 104, 122, 127, 144, and 148°C from feeder to die, the die temperature was set at 143°C. Fixing these temperatures is very important. Otherwise, PE will be crosslinked during extrusion. Formulations of these samples are summarized in Table I.

Obtained products were crosslinkable polyethylene (XLPE). Compression, rotation, and injection molding of XLPE at 155°C and then the crosslinking was done by increasing the temperature of mold, up to 200°C for 4 min.

Characterization

Determination of gel content

Gel content of the polymer, which could be regarded as the crosslinking degree was measured by ASTM D2765-84 procedure. The portion of MDPE undissolved in boiling xylene for 12 h was dried at 60°C for 7 days, weighed, and compared with the original weight.

Dynamic mechanical analysis

The thermal mechanical properties of the samples were determined by dynamic mechanical analysis (DMA), using a DMA 983 (Dupont Instrument, USA), to determine the visco-elastic properties in PE and PEX. Rectangular bar specimens of dimension $100 \times 10 \times 2 \text{ mm}^3$ were used for the study. Samples were heated from -150 to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$ at a frequency of 1 Hz. The samples were scanned so that their visco-elastic responses including storage moduli (E'), loss moduli (E''), and loss factor ($\tan\delta$) could be determined.

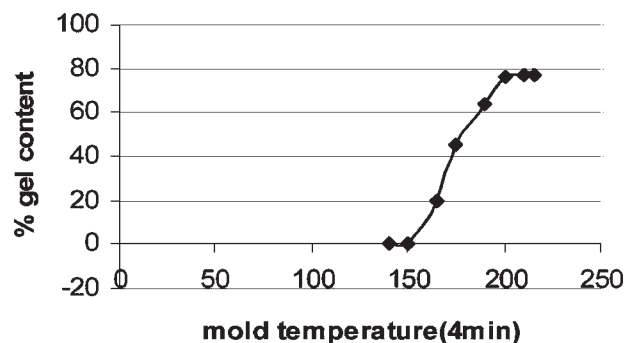


Figure 1 Effect of mold temperature on crosslinking extent in 4 min.

Differential scanning calorimetric

The thermal behaviors of virgin polymer, crosslinkable polyethylene, and crosslinked polyethylene (after molding) were characterized by DSC on a TA DSC Q100 V9.0 equipped with thermal analysis data acquisition software. Polymer samples of 5–7 mg were encapsulated in standard aluminum pans.

Indium standard was used to calibrate the temperature scale and enthalpy of melting. They were measured at a heating rate of $10^\circ\text{C}/\text{min}$ over range of -50 to 320°C . After being heated to 320°C , samples were recrystallized in DSC by cooling at $10^\circ\text{C}/\text{min}$ to -90°C in an Argon atmosphere.

Thermogravimetric analysis

Thermal analysis of virgin PE, crosslinkable PE, and crosslinked PE was done by thermal gravimetric analysis on a TA TGA Q50 V6.3 equipped with ther-

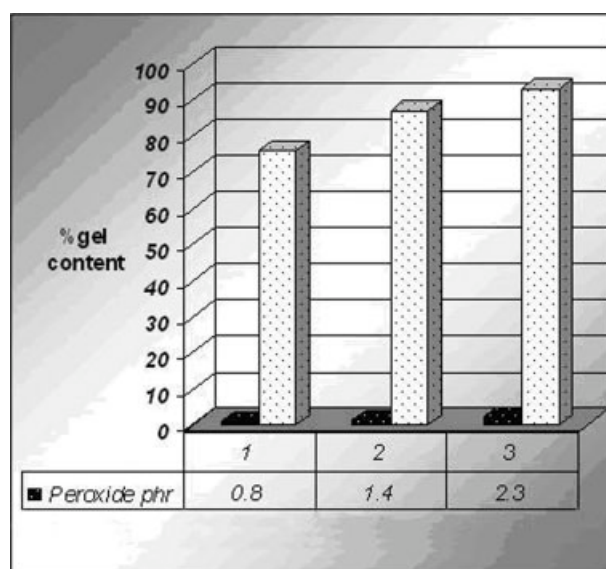


Figure 2 Decomposition of DYBP in MDPE.

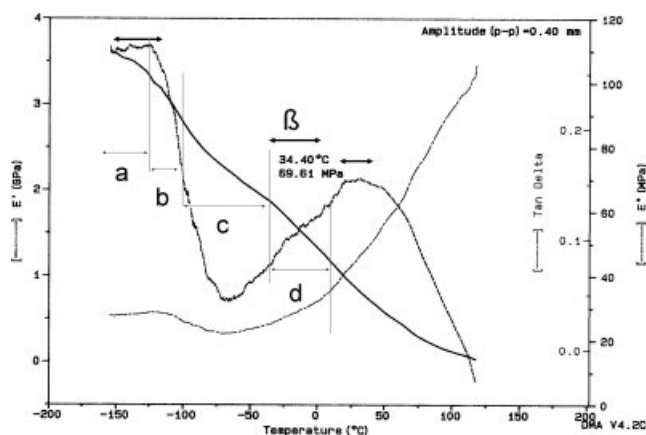


Figure 3 DMA thermograms of PE.

mal analysis acquisition software. The sample weight varied from 10 to 15 mg. The samples were heated from 25 to 590°C at a heating rate of 15°C/min in an Argon atmosphere.

X-Ray diffraction

XRD spectra were used to compare the changes of crystallinity from PE to PEX. X-ray diffraction (XRD) was performed by an Expert Philips diffractometer with a Cu anode. Scanning was done at the wavelength of 1.54 Å.

RESULTS AND DISCUSSIONS

Determination of gel content

Figure 1 shows the effect of mold temperature on crosslinking extent in compression molding. After molding, the polymer, which contained both cross-linked and noncrosslinked parts, was cut to small parts and D2765-84 ASTM gel content test was done and the results showed the crosslinking extent of

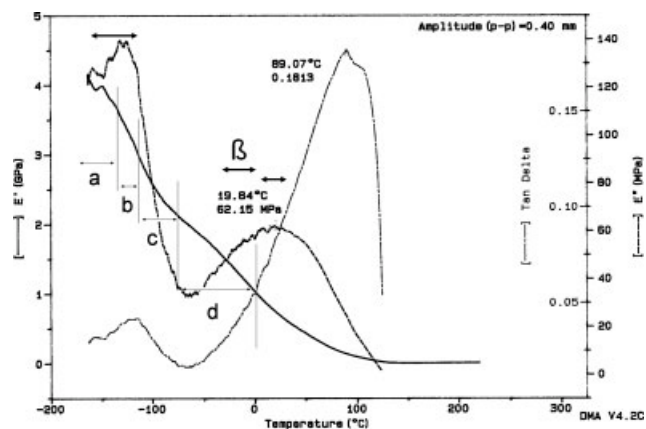


Figure 4 DMA thermograms of PEX.

TABLE II
Transition Temperatures for PE and PEX Measured by DMA

	Transition temperatures (°C)		
	γ	β	α
PE	-119	-12	34
PEX	-130	-21	20

each concentration of peroxide. As DYBP concentration increased, the extent of crosslinking increased, and the controlling of temperature zones became more difficult. Figure 2 shows the results.

Dynamic mechanical analysis

This test was carried out for virgin PE and PEX (crosslinked PE). In this experiment, we used 75% crosslinked PE. Figures 3 and 4 show all the transitions, namely α , β , and γ transitions.

The γ transition occurs in the range of -150 to -100°C. Several controversies still exist about the origin of the γ relaxation¹¹ (amorphous fraction,¹² bulk, and stress-induced reorientation of defects within the PE crystal,¹³ and reorientation of chains in a loose chain-end induced defect within the crystal¹⁴). The original suggestion related to the dynamic mechanical properties of PE and PEX was that the γ relaxation is due to the motion of the polymer chains in the amorphous regions. This suggestion was subsequently assigned to the relaxation of CH₂ groups in the amorphous regions.¹⁵ Scientists studied a detailed molecular mechanism and attributed these relaxations to the hindered rotation of four CH₂ groups.¹⁶ The conformation of these four CH₂ groups has the appearance of a crankshaft, and for this reason the mechanism could occur only in the amor-

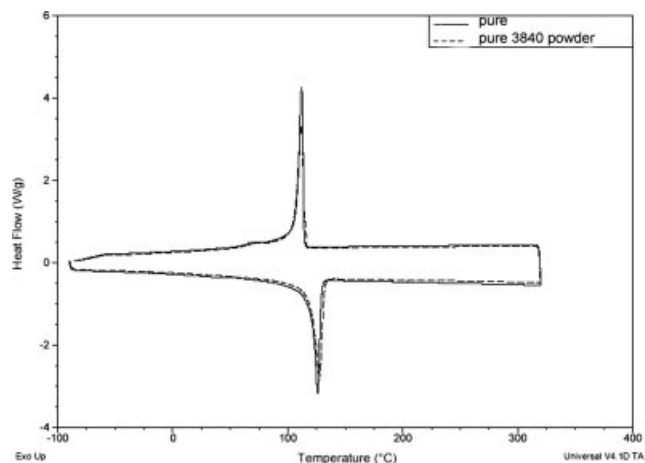


Figure 5 DSC thermograms of pure PE (powder without any additives) and virgin PE with additives.

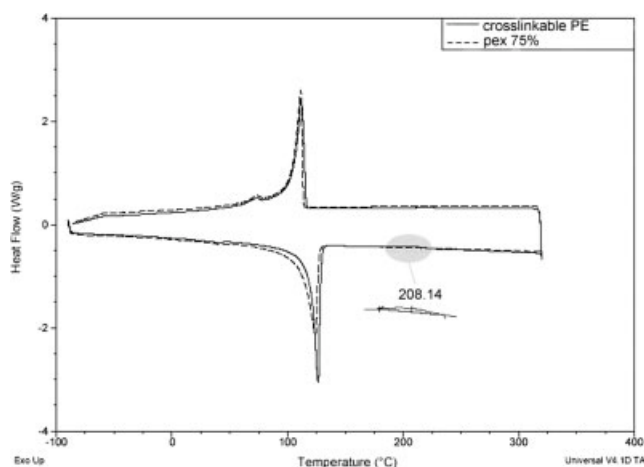


Figure 6 DSC thermograms of crosslinkable PE and PEX.

phous, non crystalline fraction of the solid.¹⁶ The β relaxation occurs between -30°C and $+10^{\circ}\text{C}$. The β transition is attributed to the amorphous phase, which is also confirmed by the fact that single crystals of linear PE do not exhibit a β relaxation. It is generally believed that the β transition is due to the relaxation of chain branches in the amorphous matrix.¹⁷ Furthermore, since the density and degree of crystallinity of PE decreases as chain branching or crosslinking increases, this behavior is consistent with the view that the β relaxation arises from the amorphous domain of the polymer. The α transition is usually seen between 30 and 100°C . The α transition is probably caused by the movement of large sections of the main chains themselves that become possible as the crystallites begin to melt. The α transition also tends to higher temperatures as the branching or crosslinking decreases, as might be expected from the fact that more highly crystalline materials have higher and sharper melting points. It is generally agreed that the α transition is representative of the crystalline phase and originates from several types of motion within crystals. It is well documented that during the α transition the chains within crystal are mobile.¹⁸

Crosslinking reduces the crystallinity significantly and gives a more rubber-like behavior to this PEX, as compared with PE.

Figures 3 and 4 show variations of loss modulus, storage modulus, and loss factor versus temperature for PE and PEX. The results concerning all these transitions are summarized in Table II. It is seen that by the increase of crosslinking extent all the α , β , and γ transitions peak temperatures shift to lower temperatures in PEX. These decreases in transition temperatures are attributed to reduction in crystallinities with crosslinking. The reduction in crystallinity of the system, as a result of crosslinking with organic peroxide, has also been confirmed by DSC results, which are explained in next section. Similar results have been observed for PE and PEX by X-ray diffraction. There is a decrease in storage modulus values with the increase of crosslinking extent, which is attributed to reduction in crystallinity. The curves (Figs. 3 and 4) for both PE and PEX have four of the following regions: (a) glassy region ($T < -120^{\circ}\text{C}$), (b) transition region (γ), (c) rubbery region, and (d) secondary transition region (β). On increasing the crosslinking extent, the crystallinity is reduced and hence the modulus of PEX decreases much faster at higher temperatures.

The value of $\tan\delta$, being ratio of E''/E' , increases with increase of crosslinking extent that is attributed to the increase in value of loss moduli (E'') and the decrease in value of the storage moduli (E'). This increase in the damping behavior is due to the reduction in the crystallinity of the system with an increase in the crosslinking extent, resulting in higher $\tan\delta$ values.

Differential scanning calorimetric

Figures 5 and 6 represent the DSC of the samples. In recrystallized curves, all the samples show a shoulder at about 75°C because of some secondary relaxations.¹⁹

In DSC analysis of crosslinkable MDPE we can see an exothermic signal at $180\text{--}210^{\circ}\text{C}$ which is related to crosslinking of crosslinkable MDPE by peroxide. Peroxide crosslinking of PE is an exothermic reaction. The crosslinked sample begins to melt at lower temperatures and the amount of absorbed energy becomes less than that of the pure one. The reason for this fact is related to lower crystallinity in cross-

TABLE III
Melting and Crystallization Data of Totally Pure Powder PE, Virgin PE, Crosslinkable PE, and Crosslinked PE (75%), Obtained from DSC

Samples	Heating T_c ($^{\circ}\text{C}$)	Cooling (ΔH) (J/g)	Enthalpy of crystallization (ΔH) (J/g)	Enthalpy of fusion (%)	Crystallinity
Pure PE (powder)	119.18	114.54	159.0	143.5	49.82
Virgin PE (granula)	120.94	114.00	157.3	139.2	48.33
Crosslinkable PE	119.80	115.95	160.1	138.9	48.22
Crosslinked PE (75%)	111.78	113.50	152.9	137.3	47.67

TABLE IV
Weight Loss of Virgin PE, Crosslinkable PE, and Crosslinked PE(PEX)
Measured by TGA

Sample	Weight loss at 185°C (wt %)	Weight loss at 250°C (wt %)	Weight loss at 300°C (wt %)
PE	0.0514	0.0723	0.1087
Crosslinkable PE	0.1120	0.2224	0.2807
PEX	0.2882	0.4911	0.7310

linked PE compared with the noncrosslinked one. The crystallization temperature T_c and the ΔH of crystallization correspond to the first cooling and the area under the crystallization exotherms, respectively.

The degree of crystallinity of PE and PEX can be calculated via the total enthalpy method, according to

$$X_c(\%) = \left[\frac{\Delta H_f^\circ(T_m)}{\Delta H_f^\circ(T_m)} \right] \times 100$$

where $\Delta H_f^\circ(T_m)$ is heat of fusion for 100% crystal PE and $\Delta H_f(T_m)$ is heat of fusion for the PE whose crystallinity is X_c . We used a $\Delta H_f^\circ(T_m)$ value of 288 J/g.^{20,21}

The decrease in crystallinity on crosslinking is due to the fact that, crosslinking provides some hindrance to the ordered arrangement of the polymer chain. For DYBP crosslinked PE, crystallinity decreases from 48.40 to 47.81% at 0.8 Phr DYBP concentrations that provides 75% crosslinking in PE. Hence, the PEX, which has been produced, has desirable properties.

To investigate the effect of additives that were mentioned in Table I, the DSC diagrams of totally pure virgin PE, and virgin PE which has antioxidant and Ca-st, were done. Comparison between DSC thermograms of pure PE (powder without any additives) and virgin PE (with additives) in Figure 5

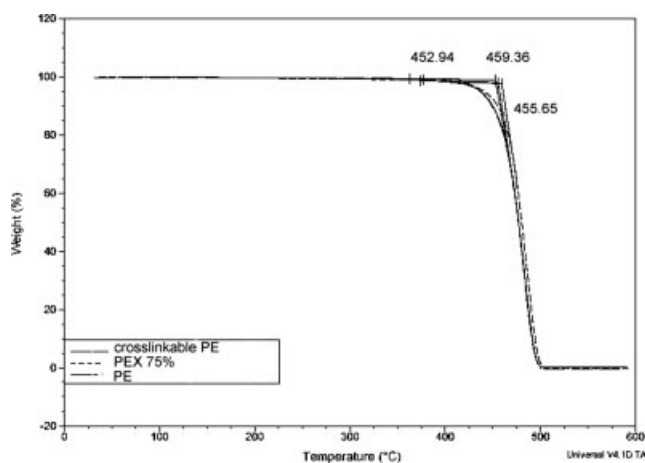


Figure 7 TGA thermograms of crosslinkable PE, PE and PEX.

show that the crystallinity of totally pure PE is 1.49% more than virgin PE that has additives (Table III).

Thermogravimetric analysis

TGA analysis showed that crosslinked sample has higher decomposition temperature than the pure one (Table IV). The presence of covalent bonds between PE chains causes high thermal stability in crosslinked MDPE.

The crosslinked PE was decomposed at 459.36°C while pure PE was decomposed at 452.94°C, and crosslinked PE shows a decrease of weight at 185, 250, and 300°C while pure PE does not show any loss of weight at these temperatures, the reason is related to the by-products of peroxide decomposition reaction which are gas and alcohol²² and can be removed at these temperatures. Figure 7 shows the TGA thermograms of PE, crosslinkable PE, and PEX.

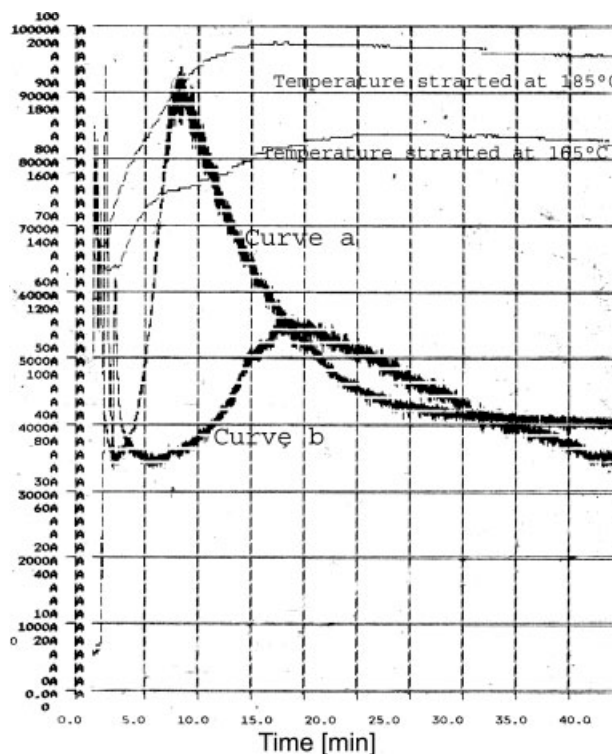


Figure 8 Torque curves of crosslinkable PE granules which are started at 165°C (curve b) and crosslinkable PE granules which is started at 185°C (curve a).

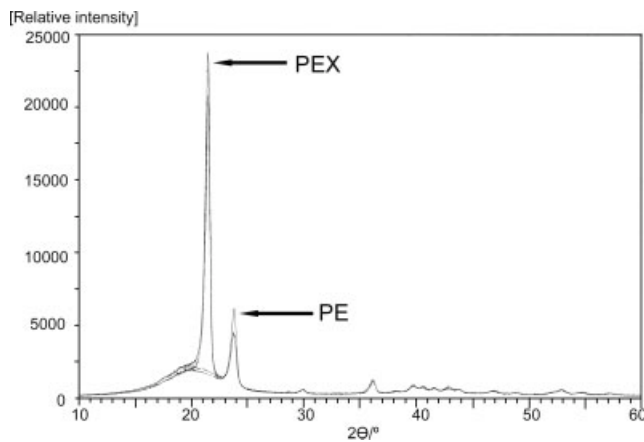


Figure 9 XRD spectra of polyethylene and crosslinked polyethylene.

Torque illustration

Granules of crosslinkable PE were crosslinked by internal mixer at two temperatures 165 and 185°C. In Figure 8, differences between curve a and b relate to start temperatures. In curve a start temperature is 185°C, and at this temperature, the speed of peroxide decomposition is higher than curve b. Thus, crosslinking extent in curve b is lower than in curve a.

X-ray diffraction

The XRD scans of PE and PEX as a function of Bragg angle (2θ) are displayed in Figure 9. The broadened background scattering area of PE suggests the presence of amorphous structure. The diagrams for both PE and PEX are similar because of the same orthorhombic unit cell of PE and PEX.²³ Both PE and PEX give a sharp crystalline and a small peak in the region of Bragg angle (2θ) between 20 and 25, which indicates their semi crystalline nature. The strongest diffraction peak in PE and PEX is located at the diffraction (2θ) of 21.5. The degree of crystallinity, C_r was determined from the integral intensities of the

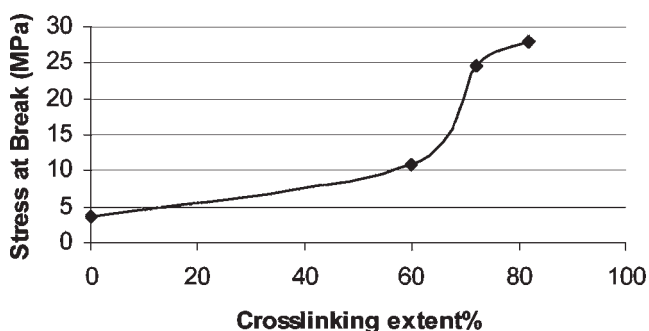


Figure 10 Stress at break changes versus crosslinking extent.

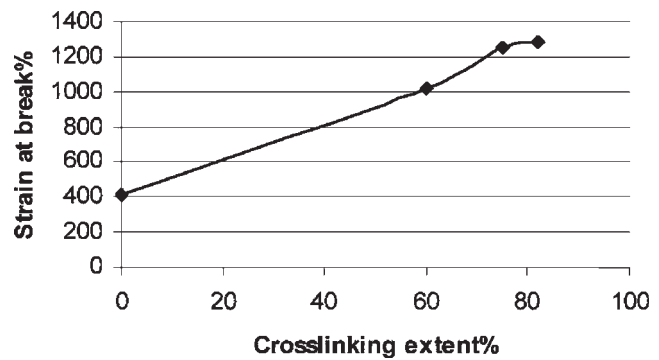


Figure 11 Strain at break changes versus crosslinking extent.

amorphous and crystalline contribution according to Figure 9. Crystallinity of PE and PEX can be calculated by Hermans and Weidinger equation,

$$\text{Crystallinity}(C_r) = A_{cr}/(A_{cr} + 2.17A_{am})$$

where $A_{cr} = A_{total} - 2A_{am}/2$.

The crystallinity decreases continuously with crosslinking from 43.8% (PE) to 41.3% (PEX). Again it indicates that crosslinking reduces crystallinity of the system. By crosslinking the regular arrangement of the crystalline region in the system is blocked.

Mechanical properties

Stress at break and strain at break

Increasing stress at break from 4 MPa for PE to 27 MPa for PEX is due to 75% of crosslinking of PE under this situation, and it is a very good implication for production of PEX pieces (Fig. 10). The increase of crosslinking extent causes the increase of the strain at break about 300% (Fig. 11).

CONCLUSIONS

Production of crosslinkable MDPE needs exact controlling of temperature zones and just the latest zone should have a temperature which is near the safe temperature of the peroxide processing and the other zones should have lower temperatures. The temperature of die should be adjusted lower than the temperature of latest zone and higher than melting point of PE (104, 122, 127, 144, and 148°C from feeder to die; the die temperature was set at 143°C).

By crosslinking of PE all the α , β , and γ transition peak temperatures shift to lower temperatures in PEX. These decreases in transition temperature are attributed to reduction in crystallinities with crosslinking.

Maximum and final torque will increase by the increase of crosslinking extent; in conclusion, 4 min at 200°C is the best situation for producing of PEX.

Crosslinked PE has lower crystallinity, higher strain at break, and higher stress at break than virgin PE does.

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