

SHAPE MEMORY EFFECT OF SLIGHTLY-CROSSLINKED POLYETHYLENE*

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Abstract A series of slightly crosslinked polyethylenes (SXLPE) was prepared by a one-step method using dicumyl peroxide as crosslinking agent in a Haake Mixer. The gel contents G (Soxhlet extracted) of the samples are in the range from 5% to 20% by weight. Their shear viscosity, crystallization and melting behavior, dynamic mechanical properties and shape recovery effect were systematically investigated in terms of the content of the crosslinking agent. It shows that under certain experimental conditions the SXLPE's may exhibit good shape fixation ability and shape memory properties, which are similar to those of the commercially available shape memory polyethylenes prepared by gamma-irradiation technique. However the shape memory behavior of these samples is not very stable due to their low crosslinking degree, or gel content. Thus their application is limited in special cases with fast strain fixing procedures.

Keywords Polyethylenes; Degree of crosslinking; Shape memory behavior

INTRODUCTION

Polyethylene is one of the most important thermoplastics, but its use is restricted in certain applications by its low melting point, solubility in hydrocarbons and a tendency to crack when stressed. In an effort to mitigate these disadvantages, there has been considerable work on the crosslinking of polyethylene. It is also noticed that crosslinked polyethylene deforms easily above its crystalline melting point and this deformation can be fixed by cooling. On heating, it may restore to its original shape. Crosslinked polyethylene, therefore, has been put into practical use as the so-called shape memory material particularly in packaging industry.

High energy radiation has been extensively used to crosslink polyethylene to get shape memory materials^[1,2]. However, both high capital expenditure and complicated techniques are required in these cases, and the use of high energy radiation is also limited to articles of thin cross section.

* This work was financially supported by the National Natural Science Foundation of China and the Science Foundation of Polymer Physics Laboratory, Chinese Academy of Sciences.

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Received March 28, 1997

It is well known that polyethylene can also be crosslinked by using peroxide initiators. This method usually involves two consecutive steps. The peroxide must first evenly dispersed in the polymer, the peroxide-containing polyethylene is then extruded or molded^[3~5]. Special care must be taken in this method so as the peroxide does not react during the mixing step. It is because that a high degree of crosslinking, for example a gel content of more than 60~80%, is usually required in practice, and the early crosslinking will prevent the further dispersion of peroxide in the polymer and also result in poor processibility of the material.

In our previous studies on the shape memory behavior of segmented polyurethanes^[6~9], it was found that very small amounts of hard segments are able to form stable physical crosslinks for ensuring good shape memory property of the specimens. It enlightens us to study the shape memory effect of slightly crosslinked polyethylenes. It is also supposed that the low degree of crosslinking may significantly simplify the preparation, processing and recycling of shape-memory polyethylenes. So, in this paper, a series of slightly crosslinked polyethylenes (SXLPE) were prepared by using dicumyl peroxide as crosslinking agent and their processibility, crystallinity, dynamic mechanical properties and shape memory effect were systematically investigated.

EXPERIMENTAL

Materials

High density polyethylene HDPE (PE-ML-57D075) with $MI = 24\text{ g}/10\text{ min}$, density $0.958\text{ g}/\text{cm}^3$ was obtained from Lia-Yang Petrochemical Corp. Dicumyl peroxide (DCP) as crosslinking agent was purified by recrystallization from ethanol prior to use. Xylene (A.R.) was available from Beijing Chemical Factory. Ir-PE is a commercial sample of shape memory polyethylene used for comparison which was prepared by gamma-irradiation crosslinking technique.

A Haake Rheometer System, Rheocord 90, coupled with a mixer was used for the preparation of the slightly crosslinked polyethylenes. The measurements of torques were controlled by the software of the Haake system. Polyethylene and dicumyl peroxide were melt-blended with a speed of 50 rpm at 180°C for 5 min. The slightly crosslinked polyethylenes were compression molded at

Table 1 The composition of polyethylene/DCP samples

Samples	HDPE (g)	DCP (g)
HDPE	50	0.000
DCP-1	52	0.208
DCP-2	52	0.416
DCP-3	52	0.624
DCP-4	52	0.832

180~ 190°C under 100 kg/cm² pressure into thin films with a thickness around 0.3 mm. The film specimens were kept at ambient temperature for about 10 h before measuring. The composition of the samples is listed in Table 1.

Characterization and Measurements

Steady shear viscosity of the specimens was measured using a Rheometrics Rhios V4.3.0 type DSR at 180°C in air. DSC measurements were conducted using a Perkin-Elmer DSC-4 purged with nitrogen. Dynamic mechanical data were obtained at 10 Hz by using a Dynamic Mechanical Thermal Analyzer MK III of Rheometric Scientific Ltd. Film specimens of 20 mm length and 3 mm width were used, and the heating rate was 2°C/min.

The crosslinked polyethylene samples were Soxhlet extracted in apparatus with xylene for 50 h. The residues were vacuum dried at 80°C to a constant weight. The gel content G was determined gravimetrically by using the following formula:

$$G = \frac{\text{Weight of residues(g)}}{\text{Original weight (g)}} \times 100\% \quad (1)$$

Specimens for shape memory measurements were prepared according to a diagram given in Fig. 1. The compression molded film (point A) is first heated to temperature T_D above the melting temperature of the polyethylene crystals (point B). The film is stretched at this temperature to a strain ε_1 (point C) and then cooled down immediately or after a time period t_D to a setting temperature T_S under constrained conditions of constant length. That is the point D in the graphic. In this work room temperature was chosen as the setting temperature. When the external force is withdrawn, a contraction may occur, and the strain changes from ε_1 to ε_2 , ε_2 is the fixed strain. It means the film specimen moves from point D to point E. The specimen at point E is then used for studying the strain recovery behavior in a process of constant heating rate. The recovery process can be expressed by the temperature dependence of the recovery rate R , the percentage of the recovered strain at temperature T in the total fixed strain, $R(T) = (\varepsilon_2 - \varepsilon(T))/\varepsilon_2$. Some important parameters are usually obtained from these measurements to characterize the shape memory behavior of the samples. The strain fixation S_f expresses the ability of the specimens to fix their strain and is defined as:

$$S_f = \varepsilon_2/\varepsilon_1 \quad (2)$$

Approximately, S_f can be estimated from the modulus ratio by a formula:

$$S_f = 1 - (E_p/E_r) \quad (3)$$

where E_r and E_p are moduli of the specimen before and after the transition temperature, respectively. Parameter R_f , the final recovery rate, shows the recovery ability of the sample. Temperature T_r related with the 50% recovery rate is called the response temperature and a parameter V_r defined as:

$$V_r = (0.8R_f \varepsilon_1 dT/dt) / (T_{90} - T_{10}) \quad (4)$$

is used to characterize the sharpness of the transition in the recovery curve which is an average speed of recovery at T_r . T_{90} and T_{10} are the temperatures corresponding to 90% and 10% recovery rates respectively from the thermal recovery curve. dT/dt is the heating rate of the thermal recovery measurements.

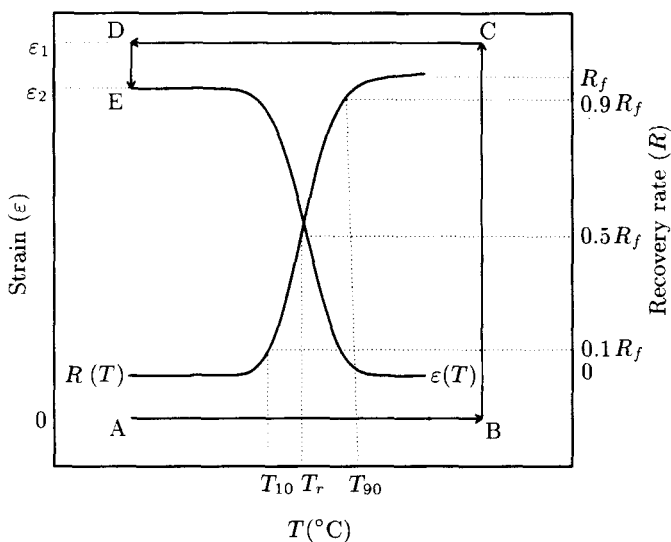


Fig. 1 Diagram for specimen preparation and thermal recovery curves $\varepsilon(T)$ and $R(T)$

Tensile property measurements were carried out on an Instron machine No.1122 at room temperature (29°C). The dimensions of the dumbbell shaped specimens were 4.0 mm in width and 25 mm in effective length. The tensile speed was 50 mm/min.

RESULTS AND DISCUSSION

Fig. 2 demonstrates the torques of different HDPE/DCP systems in the melt-blending processes. The torques start to increase after 2.5 ~ 3 min., indicating that crosslinking reaction happens in the systems. It seems that the crosslinking reaction was well developed within 5 min and the final torques increase with increasing the crosslinking agent in the systems. Fig. 3 gives the experimental results of gel con-

tent of the samples. It is evident that the gel fractions by weight increase with the increase of DCP contents. It should be noted that the crosslinked polyethylenes prepared in this work have very low gel content, less than 20% which is much lower than a value of 73.2% for the commercial polyethylene products crosslinked by irradiation technique. So these samples are really slightly crosslinked polyethylenes.

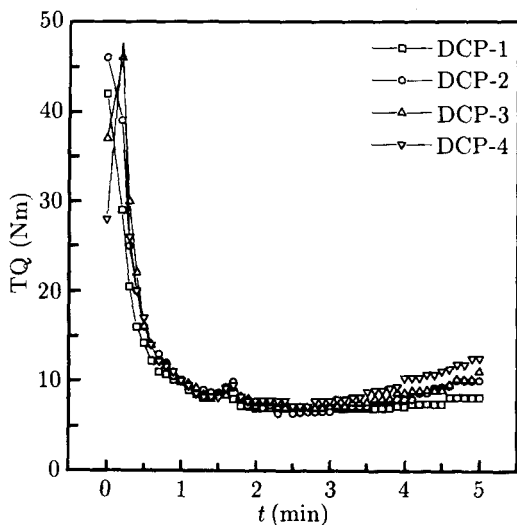


Fig. 2 Time dependence of torques for samples in Haake Mixer at 180°C

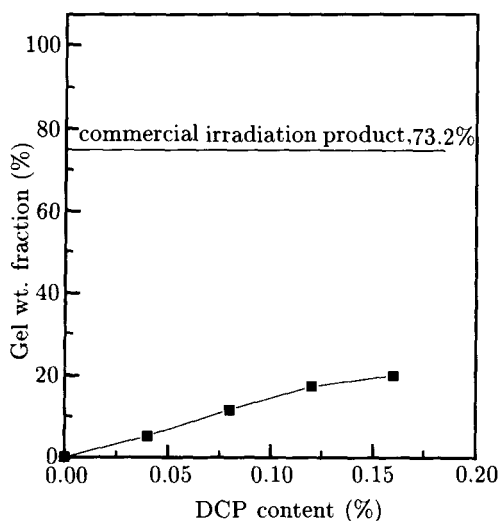


Fig. 3 Gel content of Ir-PE and SXLPE's

Usually, crosslinking degree of samples is closely related with their processibility. The higher the crosslinking degree, the poorer the processibility of the polyethylenes will be. The effect of crosslinking at low levels can be considered as an increase of molecular weight of the samples, which may result in higher melt viscosity and poor processibility. Further increase of crosslinking degree may severely depress the mobility of the molecular chains and finally the samples become inprocessible as thermoplastics. Fig. 4 gives the shear viscosity of our SXLPE specimens at 180°C. The effect of crosslinking on the melt viscosity of our samples is the obvious increase of viscosity value at low shear rates, $\omega < 10^1$ rad/sec, as compared with the viscosity value of the uncrosslinked polyethylene samples, and no Newtonian behavior at low shear rate region was observed. However, at higher shear rate, around $\omega = 2 \times 10^2$ rad/sec, the shear viscosity increase of the SXLPE's becomes not so important as compared with that in the low shear rate range. It indicates that the crosslinks will not evidently affect the rheological properties of the samples, if the crosslinking degree is kept within a proper range.

All of our samples used in this work can be easily compression molded into

films at certain temperatures above the melting point of the samples. Table 2 lists the tensile mechanical properties of the SXLPE specimens prepared by compression molding. With the increase of crosslinking the yield strength σ_y slightly decreases while the tensile strength σ_b and elongation at break ε_b both increase evidently. It means that the mechanical properties are improved by crosslinking of polyethylene molecules. These results may also be considered as an evidence of the processibility of these samples, although they are slightly crosslinked.

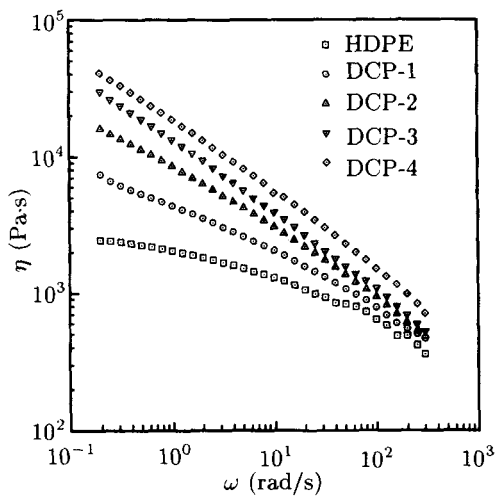


Fig. 4 Shear rate dependence of viscosity for HDPE and SXLPE's

Table 2 Tensile mechanical testing results for HDPE and SXLPE specimens

Samples	σ_y (Pa)	σ_b (Pa)	ε_b %
HDPE	2.73×10^7	1.52×10^7	490
DCP-1	2.53×10^7	1.94×10^7	540
DCP-2	2.60×10^7	2.45×10^7	1600
DCP-3	2.38×10^7	2.12×10^7	1300
DCP-4	2.38×10^7	2.62×10^7	790

According to the understanding of the shape memory behavior of polyethylene and also the results in studies of shape memory segmented polyurethanes the necessary structural

features of our samples to exhibit good shape memory properties are their high crystallinity at room temperature and the formation of a complete crosslinked network. It is well known that HDPE is a well crystallized polymer. Fig. 5 shows the melting temperature of these slightly crosslinked samples and their relative crystallinity with respect to the original HDPE. The crosslinking only results in a 5% decrease of crystallinity and a slight lowering of melting temperature. Dynamic mechanical measurement is a convenient method for estimating the existence and stability of the crosslinked network under deformation. The temperature dependence of dynamic modulus of the samples is given in Fig. 6. The modulus of the samples exhibits a clear drop in the temperature range related with the melting of their crystals. After that the curve of Ir-PE shows a plateau which extends to high temperatures. No obvious trace of flow was observed for Ir-PE in the temperature range up to 250°C. It can be ascribed to its high degree of crosslinking. The curve of the uncrosslinked sample, HDPE, only shows an abrupt decrease of modulus and no plateau was observed, while all the four crosslinked samples exhibit plateau after the sudden drop

of modulus. The plateau of sample DCP-1 is very short, it tends to flow above 170°C. The length of plateau increases with increasing the amount of DCP in the samples. For samples DCP-3 and DCP-4 the modulus plateau may extend up to 200°C. These results indicate that the small amount of crosslinking introduced in these samples is enough to dispatch the samples the network behavior under the deformation conditions of dynamic mechanical measurements.

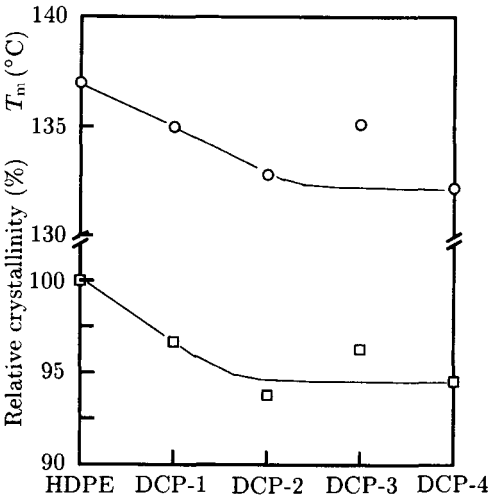


Fig. 5 Dependence of relative crystallinity and melting temperature of SXLPE's on their content of crosslinking agent

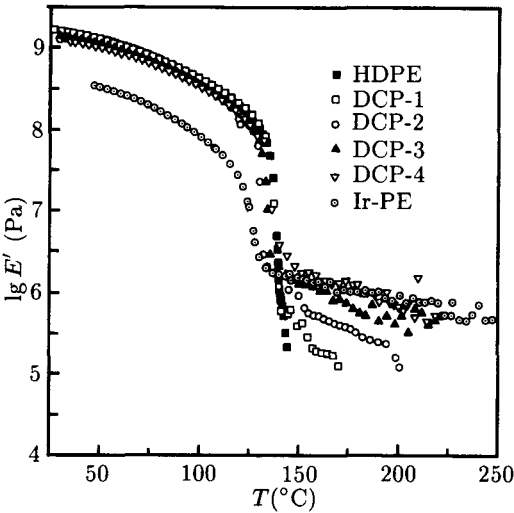


Fig. 6 Temperature dependence of dynamic modulus for HDPE, Ir-PE and SXLPE's

Table 3 The shape recovery results for Ir-PE and SXLPE specimens

Samples	Strain fixation (%)		Draw ratio	T_r (°C)	R_f (%)	V_r (min ⁻¹)
	Estimated	Experimental				
Ir-PE	99.4	96.2	2.00	100.5	94.4	0.29
DCP-1	~ 100	~ 100	2.01	122.7	82.0	0.25
DCP-2	~ 100	99.6	1.99	120.7	93.2	0.25
DCP-3	99.9	99.3	2.00	121.2	93.7	0.23
DCP-4	99.8	99.1	1.97	121.0	94.8	0.29

Fig. 7 gives the thermal recovery curves of the Ir-PE, HDPE and SXLPE specimens, respectively. Data of some important parameters characteristic for their shape memory behavior are listed in Table 3. It shows that HDPE is a typical thermoplastics, and no recovery was detected during heating. Typical shape memory behavior has been observed for Ir-PE and SXLPE samples. They all show high strain fixation value which is very close to the value estimated from the ratio of modulus at 155°C

to that at 30°C. The response temperature for SXLPE's is around 120~122°C, while that for Ir-PE is around 100°C. T_r is mainly determined by the melting temperature of the samples. It implies that Ir-PE is made of LDPE. The final recovery rate R_f of the SXLPE specimens gradually increases as a function of crosslinking degree. All the samples, except DCP-1, have high R_f value, more than 90%, which is almost the same as that of the Ir-PE samples. Data of recovery speed V_r are given in the last column of the Table 3 which show that the recovery speeds of these samples are similar. All the results given in Table 3 indicate that polyethylene samples with low gel content, or crosslinking density, may exhibit good shape memory behavior similar to that of highly crosslinked samples prepared by irradiation technique.

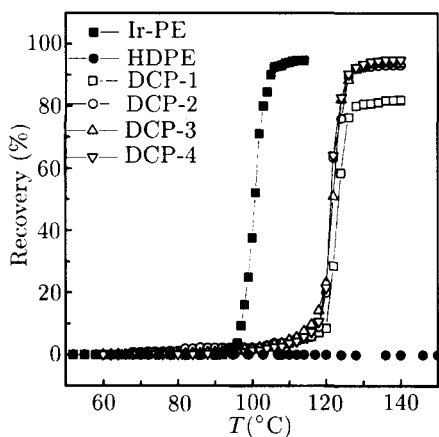


Fig. 7. Thermal recovery curves of HDPE, Ir-PE and SXLPE's

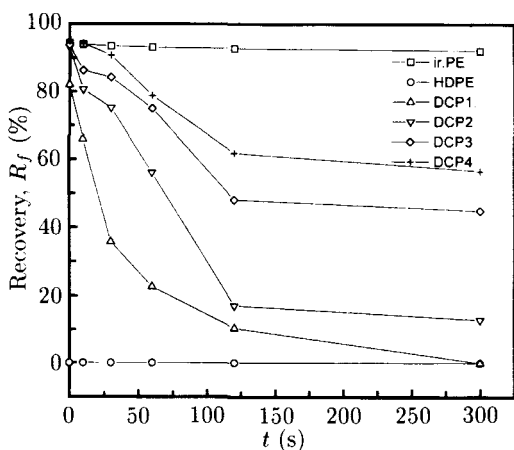


Fig. 8. Influence of t_D at 155°C on the R_f value for different samples

It is expected that the low gel content of SXLPE's may result in poor stability of the polymer network under deformation, and hence the unstability of their shape memory behavior. This can be learned from studies on the influence of t_D , the length of time period the specimen was kept after deformation at temperature T_D , 155°C in our case, on the shape memory behavior (Fig. 8). The final recovery rate R_f evidently decreases with increasing t_D for the SXLPE specimens, while it keeps stable for the commercial Ir-PE. The higher the crosslinking degree of the SXLPE specimens, the better the stability of the shape memory effect will be. A short stay under stress at temperatures above the melting temperature may result in a drastic decrease of their R_f value. It implies that under these conditions some of the unstable crosslinking points can be destroyed. The specimen can no longer be considered as a complete elastic network, and part of its deformation becomes irreversible.

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