

Shape memory effect of polyethylene/nylon 6 graft copolymers

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A series of maleated polyethylene/nylon 6 blends with nylon as the dispersed phase was prepared at 230°C in a batched Haake mixer, and their shape memory effect was investigated. The nylon contents of the blends are in the range from 5 to 20 wt%. The Molau testing was used to verify the *in situ* formation of polyethylene-*g*-nylon 6 graft copolymers bridged by maleic anhydride in the melt-blending process. Differential scanning calorimetry, dynamic mechanical thermal analysis and scanning electron microscopy have been used to investigate the crystallization and melting behaviour, dynamic mechanical properties and phase morphology for all the specimens. The results indicate that the maleated polyethylene/nylon 6 blend specimens are able to show good shape memory effect under normal experimental conditions. The high crystallinity of the polyethylene segments at room temperature and the formation of a network structure in these specimens are the two necessary conditions for their good shape memory effect. The nylon domains, which serve as physical crosslinks, play a predominant role in the formation of a stable network structure for the graft copolymers. The studies show that shape memory materials with thermoplastic characteristics can be prepared not only by segmented copolymers but also by graft copolymers, and the reaction processing method might be a promising and powerful technique for this purpose. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The shape memory effect of polymers is characterized by large value of recoverable strain and high recovery rate, the percentage of recoverable strain in total strain, and is unique for polymers of special structure and morphology. The first shape memory polymer product of commercial importance is made of polyethylene (PE) crosslinked by reaction with ionizing radiation during processing¹. Its response temperature related with the melting temperature of PE is usually near or above 100°C. Various kinds of shape memory polymers are needed to match the requirements of different applications.

According to the mechanism of the shape memory effect of polymers a material design principle can be proposed. A shape memory polymer might be crystalline or amorphous, properly crosslinked with its melting point or glass transition temperature (T_g) sufficiently high above room temperature. The chemical crosslinking of polymer molecules has been extensively studied and can be obtained by various methods. For preparing shape memory polymeric samples with chemical crosslinks special care must be taken to prevent the formation of crosslinking before the shaping of the products, because the high degree of crosslinking will result in poor processibility of the material. For this purpose, usually a two-step or multi-step technology was developed. The crosslinking reaction is arranged to be carried out in the last step of preparation after the shape formation of the products by exposure under high energy radiation or high temperature. Ota¹ and Malloy² have reported the crosslinking of PE and many other polymers initiated by α

and β radiations. We have studied the two-step technique of preparing ethylene/vinyl acetate copolymer based shape memory materials which were crosslinked under the influence of peroxide crosslinking agent in a stage of elevated temperature after the sample formulation³. Shape memory polymers with chemical crosslinks are characterized by their stable three-dimensional network structure. However the two-step or multi-step procedure may greatly complicate the technology and increase the cost, especially when facilities of high capital expenditure are needed. Besides, the chemical nature of the crosslinks makes it impossible to easily reprocess or recycle these materials like the conventional thermoplastics.

It is of great interest to design and prepare shape memory polymers with physical crosslinks. Recently we reported our results^{4–8} in studies of shape memory effect of segmented polyurethanes with 4,4'-diphenylmethane diisocyanate or toluene diisocyanate. The soft segment and extender used were polycaprolactone and 1,4-butanediol respectively. It was found that segmented copolymers can really be used as thermally stimulated shape memory materials with large recoverable strain and high recovery rate. These results strongly support the basic principle for material design of shape memory polymers given above and indicate that the crosslinking could be chemical or physical in nature. The advantages of using segmented copolymers are the ease in controlling the response temperature and the improvement of processing conditions. All the processing techniques for thermoplastics can now be used for these materials and their reuse becomes feasible. Similar results have been obtained for ethylene oxide/ethylene terephthalate segmented copolymers⁹.

In order to expand the idea of using physical crosslinking in preparing shape memory polymers, in this work a series

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of PE/nylon 6 graft copolymers were prepared and their shape memory behaviour was investigated.

EXPERIMENTAL

Materials

High density polyethylene, HDPE (PE-ML-57D075), with melting index of 24 g per 10 min and density of 0.958 g cm⁻³ was from Liao-Yang Petrochemical Corp. Dicumyl peroxide (DCP) as initiator was purified by recrystallization from ethanol prior to use. Nylon 6 was produced by Harbin Nylon Factory.

Preparation of the graft copolymers

A Haake Rheometer system Rheocord-90 coupled with a mixer was used for the preparation of maleated PEs (M-PEs) and their blends with nylon 6. The M-PEs were first prepared in the mixer at 180°C for 5 min with DCP as the initiator. Four M-PE samples with different content of

maleic anhydride (MAH) were used in this work (Table 1). They were prepared in systems of different DCP content, but the same content of MAH. The raw product of PE grafted with MAH was extracted by acetone to eliminate unreacted MAH monomers and homopolymers. The purified M-PE was analysed by Fourier transform infrared (FTi.r.) with a Perkin-Elmer 2000 spectrometer. I.r. bands of 1787 and 2018 cm⁻¹ were used, which are characteristic bands of anhydride and methylene groups, respectively. The absorbance ratio of the two bands was used to characterize the content of MAH in these M-PEs¹⁰, which was found to increase with increasing DCP content in the reaction system (Table 1). Then the M-PEs were reacted with nylon 6 in a melt blending process at 230°C for 5 min to obtain the PE-g-nylon 6 graft copolymers. The extrudates were compression moulded into thin films at 230°C. The film specimens were kept at ambient temperature for about 10 h before use. The composition of the melt-blended samples of M-PE with nylon 6 used in this work is given in Table 2.

Specimens for strain recovery measurements were prepared according to a diagram given in Figure 1. The compression moulded film (point A) is first heated to temperature T_D (155°C in this work), above the melting temperature of the PE crystals (point B). The film is stretched at this temperature to a strain ε₁ (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 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 ε₁ to ε₂. ε₂ 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 behaviour in a process of constant heating rate.

Table 1 The MAH content of maleated polyethylenes

Samples	DCP (hpr)	MAH (hpr)	A ₁₇₈₇ /A ₂₀₁₈
M-PE-1	0.04	1.5	1.75
M-PE-2	0.08	1.5	4.10
M-PE-3	0.12	1.5	5.05
M-PE-4	0.16	1.5	7.88

Table 2 The composition of the polyethylene/nylon 6 blends

Samples	Polyethylene		Nylon 6 (wt%)
	No.	Wt%	
PE-0-90	HDPE	90	10
PE-1-90	M-PE-1	90	10
PE-2-90	M-PE-2	90	10
PE-3-90	M-PE-3	90	10
PE-4-90	M-PE-4	90	10
PE-2-95	M-PE-2	95	5
PE-2-85	M-PE-2	85	15
PE-2-80	M-PE-2	80	20

CHARACTERIZATIONS

Differential scanning calorimetry (d.s.c.) measurements were carried out using a Perkin-Elmer DSC-4 purged with

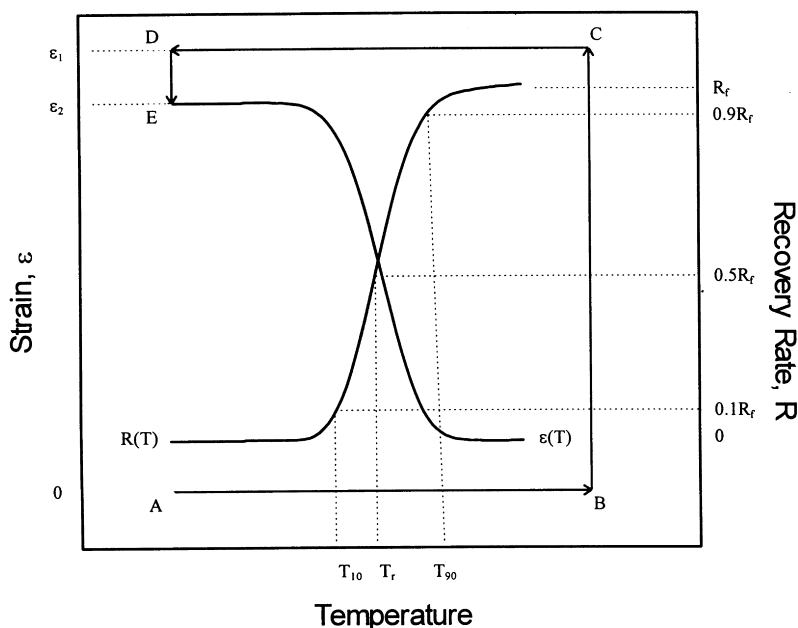


Figure 1 Diagram of preparation procedure of specimens for strain recovery measurements and recovery curves

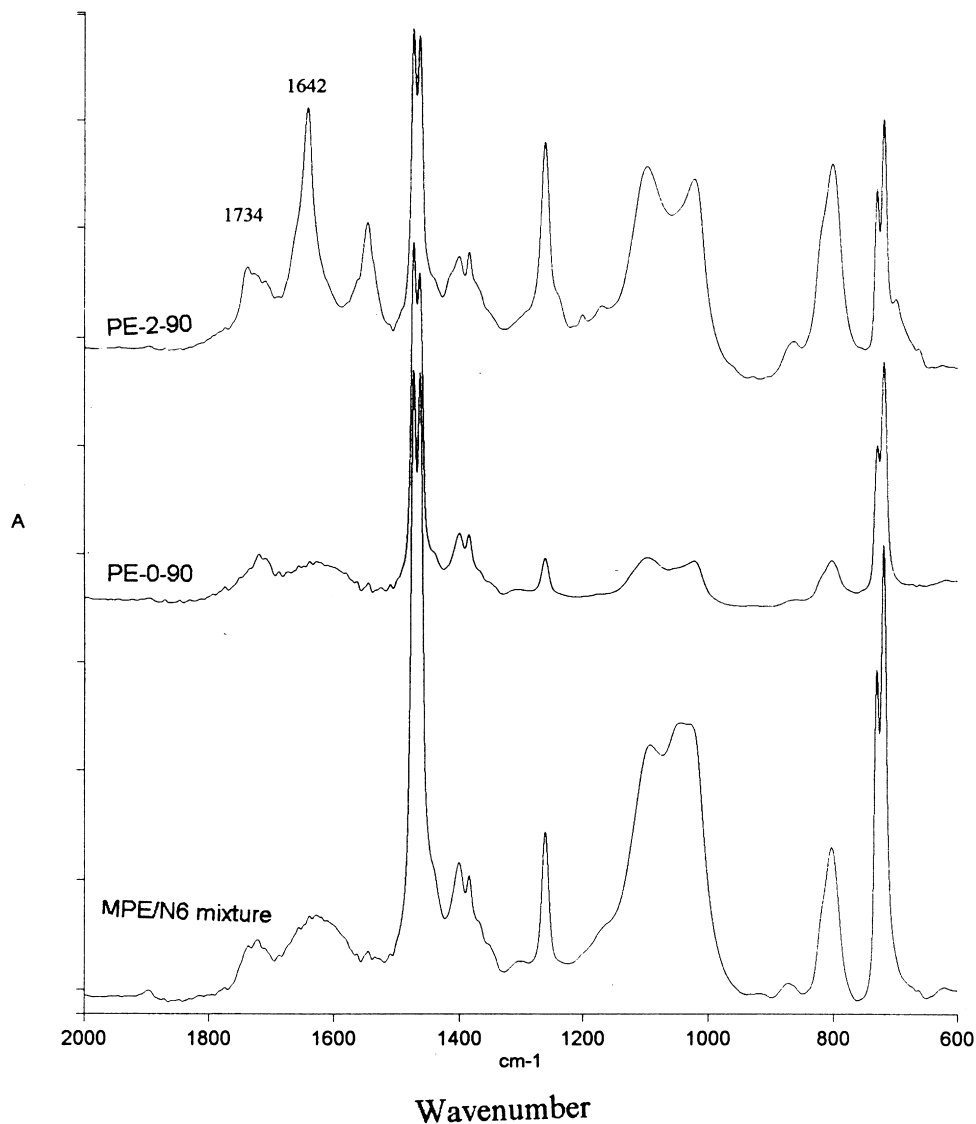


Figure 2 I.r. spectra for specimens from liquid phase in Molau testing

nitrogen. Dynamic mechanical data were obtained at 10 Hz by using a dynamic mechanical thermal analyser (DMTA) MKIII of Rheometric Scientific Ltd. Film specimens of 20 mm length and 3 mm width were used, and the heating rate was $2^{\circ}\text{C min}^{-1}$.

The fracture topograph as well as the dispersed structure of the fractured specimens were studied using a scanning electron microscope, SEM (S-530). The surfaces of the specimens were coated with gold to avoid charging under an electron beam.

The strain recovery effect of the specimens in a heating process was directly measured under an Olympus BHSP microscope equipped with a hot stage. The heating rate used was around $2.7^{\circ}\text{C min}^{-1}$. The recovery process can be expressed by the temperature dependence of the strain $\varepsilon(T)$, or the recovery rate $R(T)$, the percentage of the recovered strain at temperature T in the total fixed strain, $R(T) = \varepsilon_2 - \varepsilon(T) / \varepsilon_2$ (Figure 1). Some important parameters are usually obtained from these measurements to characterize the shape memory behaviour of the samples. The strain fixation S_f expresses the ability of the specimens to fix their strain and is defined as $S_f = \varepsilon_2 / \varepsilon_1$. As shown in Figure 1 the final recovery rate R_f shows the recovery ability of the sample. The temperature T_r related with 50% R_f is called

the response temperature, and a parameter V_r is used to characterize the speed of the recovery process, defined as:

$$V_r = 0.8R_f\varepsilon_2(dT/dt)/(T_{90} - T_{10})$$

where T_{10} and T_{90} are the temperatures corresponding to the recovery rate of $0.1R_f$ and $0.9R_f$ on the recovery curve respectively, and dT/dt is the average heating rate of the recovery measurement.

RESULTS AND DISCUSSION

First, it is interesting to learn whether PE-g-nylon 6 graft copolymers were obtained during the melt-blending process. In many studies of the polyolefin-toughened nylon 6 systems, the Molau test was well accepted as a good method to verify the presence of graft copolymers of the components in the systems¹¹⁻¹³. Since PE is the major component in our samples, xylene was chosen as the testing agent. The PE tends to crystallize in its xylene solutions at temperatures below 100°C . Therefore all the tests were conducted at 120°C . For the HDPE/nylon 6 blends and simple mixtures of M-PE and nylon 6, PE was seen to dissolve into xylene within 3-5 h, while nylon 6

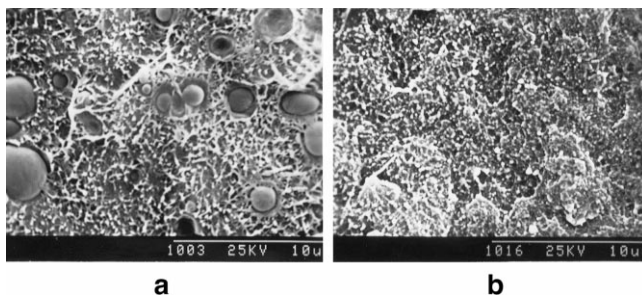


Figure 3 SEM photographs of cryogenically fractured surfaces for: (a) HDPE/nylon 6 (90/10); and (b) PE-3-90 specimens

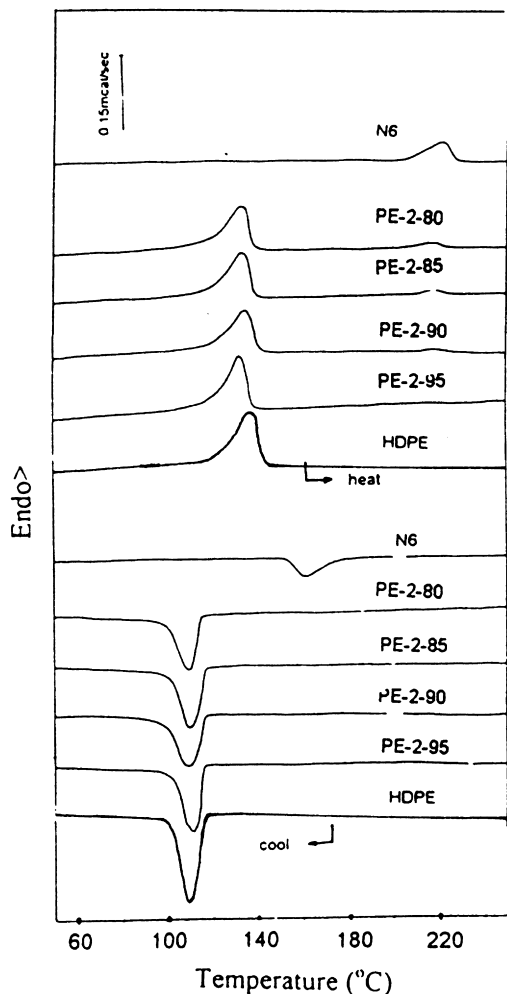


Figure 4 D.s.c. thermographs for M-PE/nylon blend specimens

precipitated in the form of white flakes; the solutions were transparent. When the same experiment was repeated for the M-PE/nylon 6 blends, besides some precipitated gels, a light milky-white emulsion was obtained and this emulsion was able to keep stable at 120°C. This positive Molau test indicates that PE-g-nylon 6 graft copolymers do exist after the melt-blending process. Furthermore, the liquid parts in these experiments were separated from the precipitates and the solvent was evaporated. The residues were analysed by FTi.r. measurements. Figure 2 gives the FTi.r. spectra of the samples. In the spectrum of the M-PE/nylon 6 blend, the band 1640 cm⁻¹ clearly shows that there really exists nylon 6 in the xylene based stable emulsions.

The formation of PE-g-nylon 6 graft copolymers is able to influence its bulk phase morphology. Figure 3 presents the SEM photographs of cryogenically fractured surfaces for HDPE/nylon 6 and M-PE/nylon 6 specimens of the same nylon 6 content, respectively. Because of large differences in chemical structure, clear phase separation of the components was observed for all the blends. In the case of HDPE/nylon 6 specimens large spherical nylon particles with diameters of several μm were dispersed in the PE matrix. The interfaces between nylon particles and the PE matrix are clear, and this may suggest there is no strong interaction between the two phases. However in M-PE/nylon 6 blends, due to the formation of chemical bonding between the two phases, the nylon particles become finely dispersed with sizes less than 0.3 μm, and the interface between the nylon particles and the matrix was obscure.

It was clear in our previous studies of segmented copolymers⁴⁻⁹ that a sufficiently high crystallinity at room

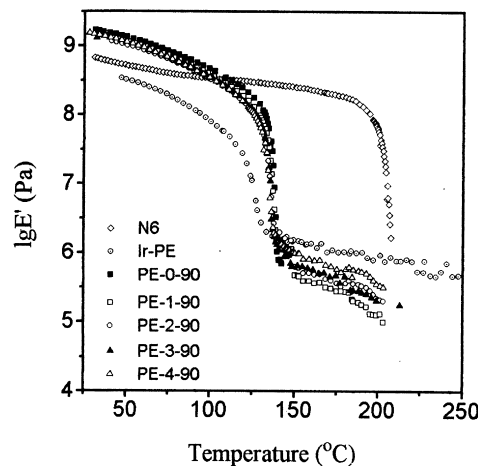


Figure 5 The temperature dependence of dynamic modulus for the M-PE/nylon blend specimens with different MAH content

Table 3 The strain recovery results for polyethylene/nylon blends

Samples	Draw ratio	Strain fixation (%)	T _f (°C)	R _f (%)	V _r (min)
HDPE	2.02	100	—	—	—
Ir-PE	2.10	96.2	100.5	94.4	0.32
PE-0-90	2.03	100	—	—	—
PE-1-90	1.99	99.4	122.3	94.9	0.26
PE-2-90	2.00	99.5	120.4	95.2	0.23
PE-3-90	2.10	99.0	121.3	96.0	0.27
PE-4-90	2.07	99.0	120.2	96.9	0.16
PE-2-95	2.06	99.8	118.8	95.0	0.27
PE-2-85	2.00	98.9	121.0	96.0	0.24
PE-2-80	2.04	98.6	120.3	96.6	0.26

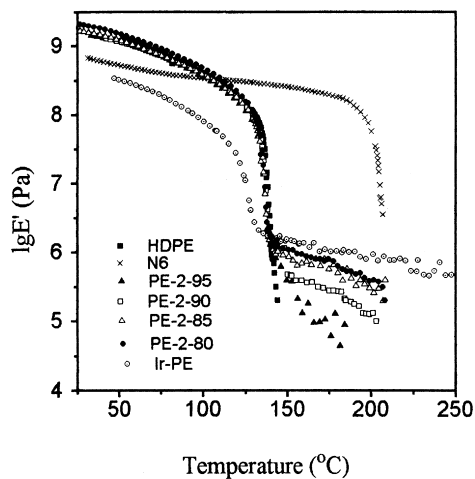


Figure 6 The temperature dependence of dynamic modulus for the M-PE/nylon blend specimens with different nylon content

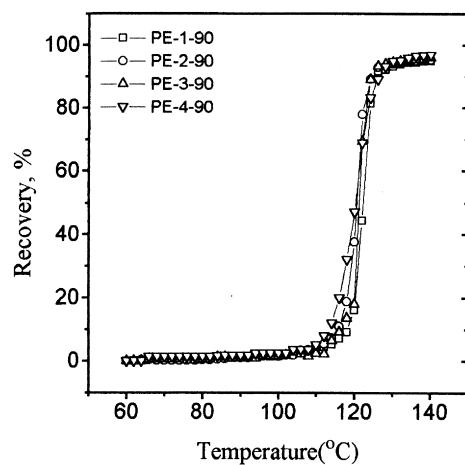


Figure 7 Strain recovery curves for the M-PE/nylon blend specimens with different MAH content

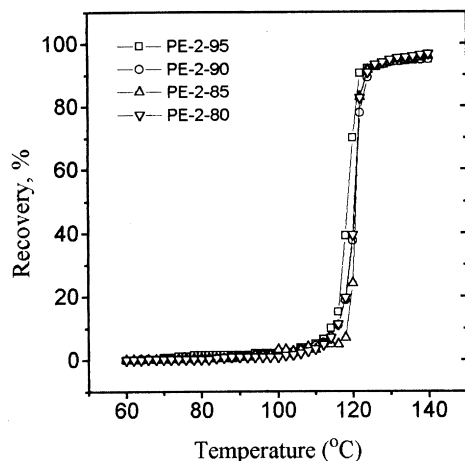


Figure 8 Strain recovery curves for the M-PE/nylon blend specimens with different nylon content

temperature and the formation of stable network structure with physical crosslinks are the two important factors for a polymer to exhibit good shape memory effect. The crystallization and melting behaviour of the samples is given in Figure 4. The d.s.c. experiments do not show large influence

of blending on the crystallization and melting behaviour of PE in the blends. Only a small lowering of the melting temperature of PE crystals was observed, and the decrease of crystallinity of PE was consistent with its content in the blends.

The formation of a network structure in the specimens can be detected by the dynamic mechanical measurements. Figures 5 and 6 present the temperature dependence of dynamic modulus for HDPE, HDPE/nylon 6 and M-PE/nylon 6 blends, respectively. The results for a commercial shape memory sample, Ir-PE, are also given in these figures for comparison. Ir-PE is made of low density PE crosslinked by reaction with ionizing radiation. The modulus at ambient temperature is about 1×10^9 Pa. With the melting of PE crystals, the modulus of the M-PE/nylon 6 blends abruptly decreases and then forms a plateau. The modulus keeps quite stable up to about 200°C or more corresponding to the melting of the nylon 6 crystals. While specimens of HDPE and HDPE/nylon blend tend to flow at temperatures above the melting point of PE crystals, no modulus plateau was observed. The modulus in the plateau region of the M-PE/nylon 6 blends increases with increasing the nylon content or the amount of DCP used in preparing the M-PE samples. All these results indicate that an elastic network structure is formed in these M-PE/nylon 6 blends, and the nylon domains dispersed in the PE matrix may act as physical crosslinks due to the chemical bonding between the nylon segments in the dispersed domains and the PE chains in the matrix region. The modulus of all these samples in the plateau regions was lower than the plateau modulus of Ir-PE specimens. This implies that the apparent degree of crosslinking of these blend systems is clearly lower than that of Ir-PE samples.

Figures 7 and 8 are the thermal recovery curves for the M-PE/nylon 6 blends. The results are summarized in Table 3, and data for HDPE, Ir-PE and a HDPE/nylon 6 sample are also given for comparison. It shows that all the M-PE/nylon 6 blend specimens exhibit typical good shape memory behaviour, having final recovery rates, R_f , more than 95% and high recovery speeds comparable to those of Ir-PE, the commercial sample with high degree of chemical crosslinking. The response temperature, around 120°C, is believed to be related with the melting temperature of the PE crystals in these specimens. At the same time the HDPE and HDPE/nylon 6 specimens did not show any strain recovery effect, although both of them have high strain fixation values. This means that no elastic network structure was formed in these specimens, and all the fixed strain after the stretching process was irreversible.

It can be supposed that at 155°C the PE crystals are melted and the M-PE/nylon 6 blend specimens are in the high elastic state. The flexible and long PE segments offer the ability of large deformation, and the finely dispersed nylon domains, acting as physical crosslinks, may keep the deformation in a reversible regime. It is obvious, then, that after fixing the high elastic deformation by crystallization of the PE segments in a cooling process the specimens will show typical strain recovery effect during reheating.

According to the preparation method of the M-PE/nylon 6 blends the formation of chemical crosslinking between PE chains due to the initiation of DCP in the process of grafting MAH onto the PE chains should be considered in addition to the physical crosslinking in the form of nylon domains. For this purpose, PE samples were melt processed with DCP in the same conditions, including the content of DCP in the system, used for preparing the M-PE samples. Figure 9

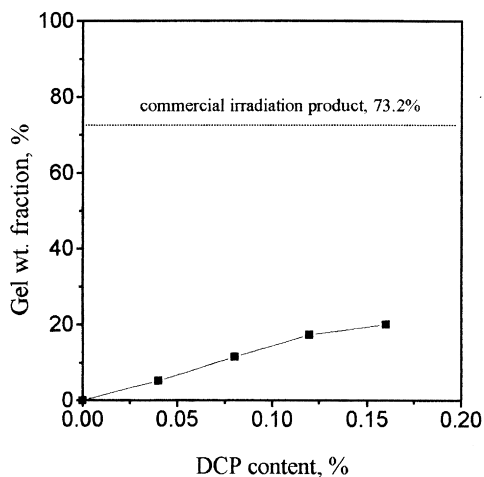


Figure 9 Gel content of Ir-PE and slightly crosslinked PE samples

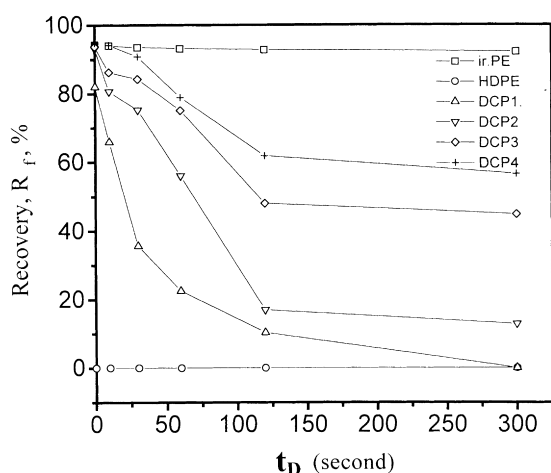


Figure 10 Influence of t_D on the R_f value for slightly crosslinked polyethylene samples

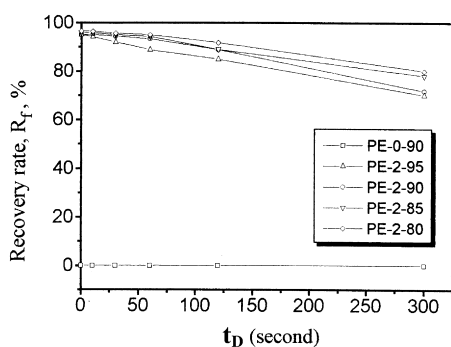


Figure 11 Influence of t_D on the R_f value for the M-PE/nylon blend specimens with different nylon content

shows the gel content of these samples (DCP1–4) obtained by Soxhlet extraction with xylene. The gel content was found to be less than 20%, and to increase with increasing the DCP content in the system. At the same time the Ir-PE sample has a gel content of about 73%. This means that our M-PE/nylon 6 blend specimens do have some chemical crosslinks, although the content is quite low.

The strain recovery effect of these slightly crosslinked PE

samples has been investigated and reported¹⁴. It was found that the low gel content, or the low degree of crosslinking, of the samples may result in the poor stability of the network structure under deformation and hence the unstability of their shape memory behaviour. Figure 10 shows the influence of t_D , the length of time period the specimen was kept after deformation at temperature T_D , on the shape memory behaviour. The final recovery rate evidently decreases with increasing t_D for all these slightly cross-linked samples. A drastic decrease of R_f after a short time period under stress implies that under these conditions the specimen can no longer be considered as a complete elastic network, and most of its deformation becomes irreversible.

The same measurements have been made for M-PE/nylon 6 blend specimens. Figure 11 gives the results for samples of different nylon content. It is clear that the final recovery rate of these samples keeps quite stable with increasing t_D up to several minutes. By comparing with the results of sample DCP-2 in Figure 10 it can be concluded that the good shape memory behaviour of the M-PE/nylon 6 blends is mainly related with the formation of nylon domains as physical crosslinks due to the grafting structure of nylon 6 on PE.

All the results given in this work indicate that graft copolymers, like the block copolymers, can also be used to develop good shape memory materials with physical crosslinks. It should be noted that these graft copolymers were obtained just by melt blending of two commercially available polymers. This means many polymer pairs can be used to prepare shape memory materials by using the reaction processing technique.

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