

Review

THERMALLY STIMULATED SHAPE MEMORY BEHAVIOR OF POLYMERS WITH PHYSICAL CROSSLINKS*

Mao Xu** and Feng-kui Li

*Polymer Physics Laboratory, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, China*

Abstract The shape memory effect of polymers was investigated for the purpose of improving the processing conditions of their preparation and broadening the list of polymers for shape memory applications. Emphasis was put on the possibility of using polymers with physical crosslinks as shape memory materials and their structure-function relationships. Segmented block polyurethanes and polyethylene/nylon 6 graft copolymers were used as examples of polymers with physical crosslinks. It was found that these copolymers can really be used as thermally stimulated shape memory materials with large recoverable strain and high final recovery rate. The main advantage of using copolymers is their improved processing conditions as compared with polymers with chemical crosslinks. As only physical crosslinks are introduced, all conventional processing techniques for thermal plastics can be used, and the materials become easily reusable. The results indicate that the high crystallinity of these copolymers at room temperature and the formation of stable physical crosslinks are the two prerequisites for these polymers to exhibit shape memory effect. The successful use of block and graft copolymers imply the possibility of using polymers of various structure and properties as shape memory materials.

Keywords Shape memory effect, Segmented polyurethanes, Polyethylene/nylon graft copolymers

INTRODUCTION

Shape memory polymers are materials that may remember their original shape, when they are deformed and fixed. This means that they are able to recover their original shape almost completely at appropriate conditions, for example, under heating. So this is a thermally stimulated shape memory effect. The shape memory effect is a special kind of thermal shrinkage that is unique to polymers of specific structure and morphology and is characterized by its large recoverable strain and high recovery rate, that is the percentage of the recoverable strain to the total strain. For a shape memory polymer, its recoverable strain must be equal to or larger than 100% and its recovery rate higher than 80% ~ 90%.

The first shape memory polymeric material commercially available was a special product of polyethylene which is modified by using ionizing radiation during processing, and whose critical response temperature is around 100°C^[1]. Much research has been done since then in industrial laboratories in preparing new materials with shape memory effect and for exploiting their applications^[2, 3]. However very few contributions concerning the structure and property relationships of shape memory polymers are found in the existing literature. Tobushi *et al.*^[4]

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** Corresponding author: Mao Xu (徐 懋), E-mail: xumao@pplab.icas.ac.cn

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studied the mechanical properties of two polyurethane samples, which were supposed to be shape memory materials, but no data regarding their structure, composition and shape memory properties were given.

Our research project was mainly focused on the possibility of developing new routes to prepare shape memory polymers. The purpose was to improve processing conditions, because it is not convenient to use ionizing radiation during processing. Another aim was even more general in nature: it is desirable to have a variety of shape memory polymers of different structures and properties, so as to match the needs of various applications. It was presumed that the best way to solve these problems is to learn the mechanism of the shape memory effect of polymers, or the structure-function relationship. Once we have acquired the knowledge of the mechanism, we can solve these problems on the level of the so-called molecular design or material design.

MECHANISM AND MATERIAL DESIGN PRINCIPLE^[5]

By comparing and analyzing the shape memory behavior of the polyethylene product and the phenomena of thermal shrinkage and rubber elasticity, we are able to find out the differences and similarities among them. On the basis of these studies and considerations, a model was proposed to explain the mechanism of the shape memory effect of polyethylene samples. This can be schematically shown in Fig. 1. The original specimen at room temperature is crystalline. The crystallites and the crosslinking points randomly distributed within the specimen without macroscopic anisotropy. The specimen becomes high-elastic at temperatures above the melting point of the polyethylene crystals. In this state the specimen can be highly stretched, or deformed, and can recover its original shape after withdrawing the external force. However if the stretched specimen is cooled down to lower temperatures under constrained conditions, the elastic deformation can be frozen and retained after withdrawing the external force due to the crystallization of polyethylene. When the specimen is reheated, the melting of the crystals occurs, and the stored elastic energy will prompt the specimen to almost completely recover its original shape. So by using this model we can understand the shape memory behavior of the polyethylene specimens. What is important here is that this model clearly indicates a material design principle of

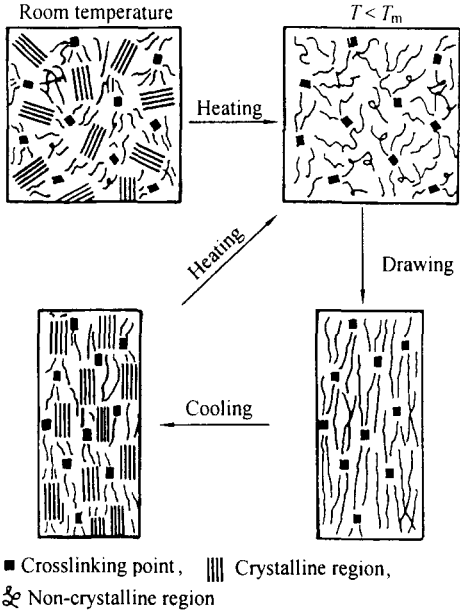


Fig. 1 Model for shape memory effect of polymers

shape memory polymers in general. That is they might be polymers properly crosslinked and with their melting point or glass transition temperature appropriately higher above the room temperature.

According to this model, a crosslinking structure is necessary for the polyethylene products. It is well known that the introduction of chemical crosslinkings will severely lower the extent of molecular motion and results in poor processibility of the samples. So in these cases a two-step or multi-step processing technology was eventually developed. The crosslinking reaction was intentionally arranged to be carried out in the last step of preparation after the shape formation of the products by exposing the products under high energy radiation as in the case of polyethylene or elevated temperature^[6]. However, these two-step or multi-step procedures may greatly complicate the technology and increase the productive cost, especially when expensive facilities are needed.

In order to improve the processing conditions and vary the structure of shape memory polymers we have attempted to develop shape memory polymers with physical crosslinks instead of chemical ones. It was proposed that these studies would also be very important and necessary for checking the validity and the versatility of the model for shape memory polymers. For this purpose two kinds of polymers, segmented block copolymers and graft copolymers, were chosen in our studies.

MEASUREMENTS OF SHAPE MEMORY EFFECT

A special experimental procedure was adopted for preparing samples and for measuring the shape memory effect. This is schematically given in Fig. 2. The original film specimen at room temperature, point A, is first heated to temperature T_D , point B in the graph T_D is a chosen temperature above the melting temperature of the crystals. The specimen is then stretched to a strain ϵ_1 , point C, and then cooled down immediately, or after a time period of t_D , to a setting temperature T_s under constrained conditions of constant length. Usually room temperature is chosen as the setting temperature. So the specimen is situated at point D in the graph. After keeping at T_s for a period of time t_s the external force is withdrawn. A contraction may occur at this moment, the strain may change from ϵ_1 to ϵ_2 . This means the position of the 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 strain remains unchanged in the beginning and decreases suddenly in the temperature range near the melting temperature, and then it decreases slowly approaching a limiting value. The recovery process can also 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.

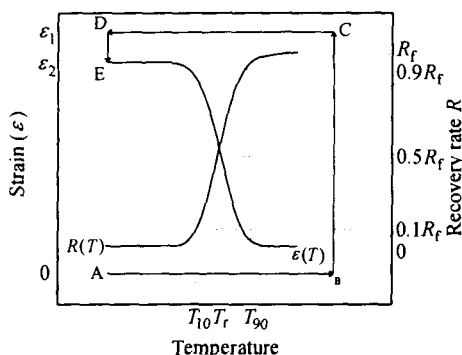


Fig. 2 The diagram of preparation procedure of specimens for strain recovery measurements and recovery curves

Several parameters from these measurements are used to describe the characteristic features of the shape memory behavior of the specimens. The degree of fixation, $\varepsilon/\varepsilon_i$, denotes the ability of the samples to fix their strain. The final recovery rate R_f gives the recovery ability of the specimen. The temperature corresponding to 0.5 R_f on the thermal recovery curve is the response temperature. A parameter V_r is proposed to characterize the speed of the recovery process. It can be considered as the slope of the central part of the recovery curve.

SEGMENTED BLOCK COOPOLYMERS^[5, 7-12]

A series of segmented polyurethanes were prepared for studying the relationship between structure and shape memory effect of polymers. The soft segment used was polycaprolactone (PCL). The molecular weight of PCL diols was in the range of 1600~7000. The diisocyanates were 4, 4'-diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI), respectively and 1, 4-butanediol was used as the chain extender. The hard segment content varied from about 8% to 45%. The composition and structure of polyurethane samples (with MDI as diisocyanate) as well as their intrinsic viscosity data measured in N, N'-dimethylformamide at 30°C are given in Table 1.

According to the model given above, the high crystallinity of the soft segment regions at room temperature and the formation of stable hard segment domains acting as physical crosslinks up to temperatures above the melting temperature of the soft segment crystals should be the two prerequisites for a segmented polyurethane sample to exhibit shape memory behavior. So it was interesting to study these two properties of segmented polyurethanes and their dependence on the structure and composition of the polyurethane molecules.

Polycaprolactone is a well crystallizable polymer. The used PCL diols of different molecular weight may crystallize near or above the room temperature during cooling from the melt state. These PCL diols have a melting temperature around 55°C, and a crystallinity around 60%. When these PCL diols are introduced into segmented copolymers, their crystallization ability is significantly depressed due to the connection with the hard segments. This is evident from the lowering of the crystallization temperature and the decrease of crystallinity (Table 1). The results can be illustrated more clearly in Fig. 3. It was found that the crystallization ability of soft segments in copolymers was mainly dependent on the molecular weight of the PCL segments. No crystallinity was observed for samples with soft segments of low molecular weight. The crystallinity of PCL segments increases abruptly after a critical molecular weight value, then it approaches a constant. This critical molecular weight is in the range of 2000~3000 in this case, and increases slightly with increasing hard segment length. Besides, for polyurethanes of the same soft segment length, the crystallinity of PCL segments decreases with increasing hard segment content of the samples. It means that sufficiently high molecular weight and content of soft segments are important for segmented polyurethanes to exhibit the high crystallinity of their soft segments.

It is well known that the microphase separation of hard and soft segments is usually far from complete. So it is very interesting to learn whether the hard segments are still able to aggregate and form individual domains at such low contents, which are important for the crystallization of the soft segments, especially when these hard segments are separated far apart from each other by the long soft segments with a molecular weight of several thousands. It was found that the important evidence for the formation of hard segment domains acting as physical crosslinks can be obtained from the temperature dependence of the dynamic modulus. Figure 4 shows the results for samples with PCL segments of molecular weight 7000. The modulus of these samples remains almost unchanged with temperature until the melting of PCL crystals. Then the curves may form a plateau which indicates the existence of physical crosslinks in these samples. The extent of the plateau increases with increasing hard segment content of the samples. For the sample with low hard segment content, 8%, the modulus drops abruptly, and no plateau was observed. Similar results

Table 1. Parameters and DSC results for segmental polyurethanes

Sample	Mol ratio PCL/MDI/BDO	M_n of PCL prepolymer	Hard segment (wt%)	$[\eta]$ (dL/g)	T_c (°C)	ΔH_c (cal/g-soft)	Crystallinity (%)	T_m (°C)
M-121-1.6	1/2/1	1600	26.97	0.30	-	0	0	-
M-132-1.6	1/3/2	1600	36.79	0.20	-	0	0	-
M-143-1.6	1/4/3	1600	44.28	0.40	-	0	0	-
M-121-2.0	1/2/1	2000	22.80	-	-	0	0	-
M-132-2.0	1/3/2	2000	31.70	-	-	0	0	-
M-143-2.0	1/4/3	2000	38.81	-	-	0	0	-
M-154-2.0	1/5/4	2000	44.60	-	-	0	0	-
M-121-4.0	1/2/1	4000	12.95	0.41	8.7	13.52	41.7	50.3
M-132-4.0	1/3/2	4000	18.99	0.36	-0.8	9.89	30.5	47.8
M-143-4.0	1/4/3	4000	24.25	0.40	-4.3	3.62	11.2	45.2
M-121-5.0	1/2/1	5000	10.56	0.60	11.9	12.74	39.3	50.3
M-132-5.0	1/3/2	5000	15.68	1.04	-0.8	9.78	30.2	48.0
M-143-5.0	1/4/3	5000	20.26	0.95	-0.4	6.48	20.0	44.9
M-121-7.0	1/2/1	7000	7.77	1.11	15.3	12.99	40.1	50.7
M-132-7.0	1/3/2	7000	11.73	0.77	12.9	12.70	39.2	50.7
M-143-7.0	1/4/3	7000	15.36	0.97	7.3	11.02	34.0	50.7
M-154-7.0	1/5/4	7000	18.70	0.98	8.4	9.98	30.8	49.5

were obtained for all other polyurethane samples with different soft segment molecular weight. These dynamic mechanical measurements are also consistent with the results from electron microscopy observations. Clear hard segment rich domains randomly distributed in soft segment rich matrix can only be observed for samples of relatively high hard segment content, for example more than 10%. All these results indicate that there is a lower limit of hard segment content. Only above that limit do the polyurethanes have enough hard segment domains acting as physical crosslinks at temperatures above the melting temperature of the PCL crystals.

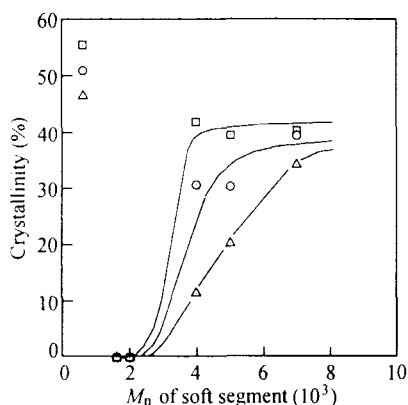


Fig. 3 Dependence of PCL crystallinity of polyurethanes on the molecular weight of soft segments

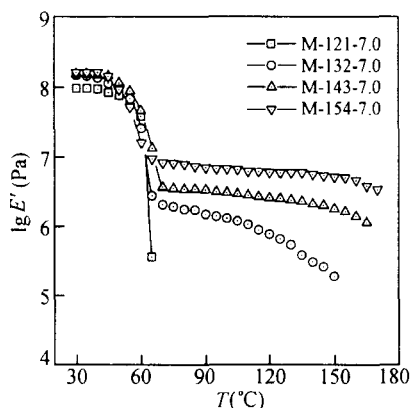


Fig. 4 Temperature dependence of dynamic modulus for polyurethanes with PCL segments of molecular weight 7000

According to the model of shape memory effect, it is possible now to predict the shape memory behavior of these segmented polyurethanes, because we are acquainted with the abilities of PCL soft segment crystallization and the formation of hard segment domains and how these abilities are related with the composition and structure of the copolymer molecules. All the polyurethane samples are characterized by their structure and composition and can be put in a graph with the molecular weight and content of the PCL soft segment as the two parameters (Fig. 5). As has been shown above, only high molecular weight PCL segments are crystallizable; the dashed line in Fig. 5 shows the crystallization limit. For samples under this line their soft segments are unable to crystallize under conditions of conventional processing procedures. The solid line in Fig. 5 gives the limit of hard segment domain formation. Only samples in the left part of this line may have stable hard segment domains acting as physical crosslinks. It is clear now that only samples in region I may fulfill the two necessary conditions at the same time and exhibit typical shape memory behavior according to the principles of the proposed model.

The results obtained from the measurements of all the polyurethane samples show that the prediction of the shape memory behavior of the samples according to their composition and structure given in the graph is correct. It implies that this model really reflects the basic principles governing the shape memory behavior of polymers. Figure 6 gives the data for samples with same mole composition, but different soft segment length. They are located in regions I and II respectively. The sample of PCL molecular weight 4000 in region I exhibits behavior typical of a good shape memory polymer: high degree of fixation, more than 98%, high final recovery rate, near 98%, and narrow recovery temperature range or high recovery speed. By contrast the sample of PCL molecular weight 1600, located in region II, only shows very small deformation recovery effect during heating. The final recovery rate is about 20%. This means that only about 4% of the strain are thermally recovered, if the low degree of fixation, about 20%, is also taken into

consideration. Figure 7 shows the results of samples with the same PCL segment length, but different composition. In the graph there are three samples in region I and one sample outside of it. The samples in region I exhibit typical memory shape behavior with almost complete fixation, high final recovery rate and recovery speed, while the sample outside region I shows poor recovery effect.

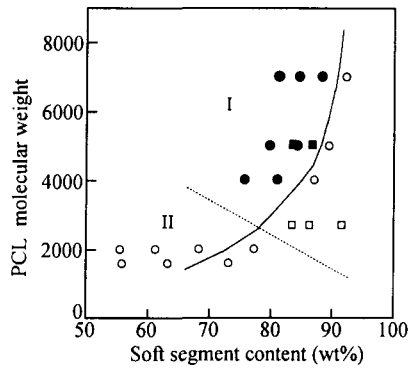


Fig. 5 Graph predicting the shape memory effect of segmented polyurethanes

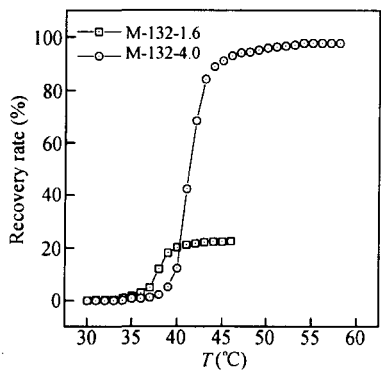


Fig. 6 Thermal recovery curves of polyurethanes with PCL segments of molecular weight of 1600 and 4000

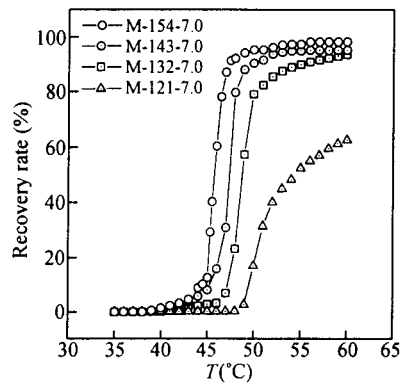


Fig. 7 Thermal recovery curves of polyurethanes with PCL segments of molecular weight of 7000

The data of all the MDI-polyurethane samples are summarized in Table 2. The degree of fixation of good shape memory samples is more than 98% and is believed to be related to the PCL segment crystallization ability of the samples. The response temperature was in the range of 43 ~

Table 2. Shape recovery results for polyurethanes with different length of soft segments					
Samples	Draw ratio	Strain fixation (%)	T_f (°C)	R_f (%)	V_f (min ⁻¹)
M-132-1.6	1.73	21.8	38.0	22.2	0.02
M-132-4.0	1.81	98.4	43.0	97.7	0.44
M-121-5.0	1.77	100	54.3	50.1	0.11
M-132-5.0	1.76	99.3	43.7	96.0	0.99
M-143-5.0	1.80	98.9	43.0	98.4	1.13
M-121-7.0	1.79	100	51.8	60.0	0.15
M-132-7.0	1.76	99.5	48.6	93.3	0.38
M-143-7.0	1.78	98.8	47.3	94.9	0.47
M-154-7.0	1.81	98.0	45.7	97.9	0.61

49°C and seems to be dependent on the melting temperature of the PCL segment crystals. The final recovery rate and the average recovery speed both increase with increasing hard segment content of the samples. All these results are consistent with the principles of the model.

Similar results have been obtained for TDI-based polyurethanes and ethylene oxide/ethylene terephthalate segmented copolymers.

GRAFT COPOLYMERS^[13]

The sample of graft copolymers we used was polyethylene grafted with polyamide, nylon 6. The graft copolymer samples were prepared by melt blending of maleated polyethylene (M-PE) with nylon 6. It is verified that in this process the polyamide molecules are grafted onto polyethylene chains via the anhydride groups. Table 3 gives the compositions of the polyethylene/nylon 6 blends used in our studies. M-PE-*n*, *n* = 1 ~ 4, are maleated polyethylenes of different anhydride group content, and M-PE-1 has the lowest content. It was postulated that for these graft copolymers the high crystallinity of polyethylene segments and the formation of micro-domains of nylon segments, acting as physical crosslinks, would fulfill the necessary conditions for shape memory polymers.

Table 3. The compositions of the polyethylene/nylon 6 blends

Samples	Polyethylene		Nylon 6 (wt%)
	No.	Content (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

The crystallization and melting behavior of the samples were studied. There is no large influence of grafting on the crystallization and melting of the polyethylene. Only a small lowering of the melting temperature of the polyethylene crystals was observed, and the decrease of crystallinity was consistent with the composition of the samples.

The formation of a network structure in these specimens can also be detected by the dynamic mechanical measurements, as shown in Fig. 8. With the melting of the polyethylene crystals the modulus of the graft copolymers decreases abruptly and then exhibits a plateau. The modulus remains quite stable up to about 200°C or higher, corresponding to the melting of the nylon 6 crystals. In contrast, the specimens of polyethylene and polyethylene/nylon 6 blends tended to flow at temperatures above the melting point of the polyethylene crystals, and no plateau was observed. The extent of the plateau increases with increasing anhydride group content of the maleated polyethylene molecules and nylon content.

All these results imply that the polyethylene/nylon 6 graft copolymers might exhibit good shape memory effect according to the model. The examples of their thermal recovery curves are given in Fig. 9. The graft copolymer samples show typical shape memory effect as expected. The data for all the blend samples are given in Table 4. The high final recovery rate, more than 95%, and high recovery speed are comparable to those of the commercial polyethylene product with high degree of chemical crosslinking. At the same time the polyethylene and polyethylene/nylon 6 blends 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 was irreversible.

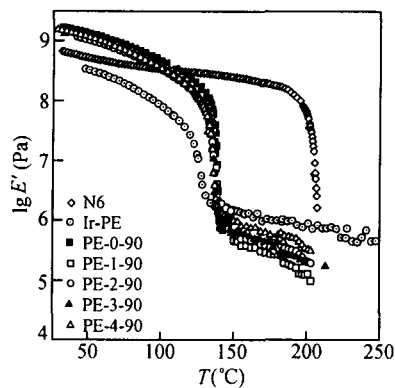


Fig. 8 Temperature dependence of dynamic modulus for M-PE/nylon blend specimens

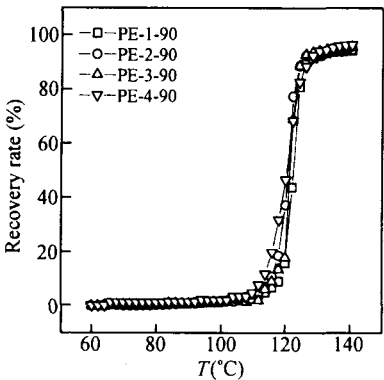


Fig. 9 Thermal recovery curves of M-PE/nylon blend specimens

Table 4. The strain recovery results for polyethylene/nylon blends

Samples	Draw ratio	Strain fixation (%)	T_r (°C)	R_r (%)	V_r (min ⁻¹)
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

INSTABILITY OF PHYSICAL CROSSLINKS AND SHAPE MEMORY EFFECT^[13, 14]

Our studies on segmented block copolymers and graft copolymers shown above indicate that it is possible to use physical crosslinks in shape memory polymers instead of chemical crosslinks. However, physical crosslinks are usually not as strong or as stable as chemical ones. So it is of great interest and importance to find out whether the unstable nature of the physical crosslinks will influence the shape memory effect of these samples and to what extent this influence will be.

For this purpose the dependence of the final recovery rate on t_D , the length of the time period the deformed specimen has stayed before cooling, was studied. Some polyethylene samples slightly crosslinked under interaction of organic peroxide were used for comparison. Their degree of crosslinking in terms of gel content is given in Fig. 10. Their gel content is less than 20%, while the commercial polyethylene product has a high gel content more than 70%. The commercial product is very stable with respect to the duration of time under strain at high temperatures, while the final recovery rate of these slightly crosslinked samples decreases significantly with an increasing duration of time (Fig. 11). This means that after a short period under stress the specimen can no longer be considered as a complete elastic network. These results show clearly the influence of weak or unstable network structures on the shape memory effect of polymers.

The same measurements were taken for our segmented polyurethanes and polyethylene/nylon 6 graft copolymers. Figure 12 gives the results for one of the segmented polyurethanes. A slow decrease of the final recovery rate was observed. The final recovery rate was still more than 90% within 2 min, and more than 80% up to about 5 min. Similar results were obtained for the polyethylene/Nylon 6 graft copolymers (Fig. 13). It seems that the behavior of shape memory

polymers with physical crosslinks is usually not as stable as that of polymers with a high degree of chemical crosslinking. However it should be noted that a time period of one to two minutes is long enough to cool down the specimen away from the stretching temperature in the practical process, so in practice the influence of the unstable nature of the physical crosslinks could be minimized or even ignored after careful design of the material.

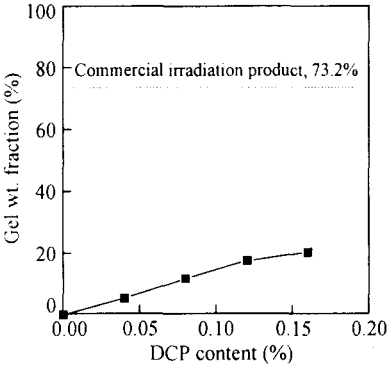


Fig. 10 Gel content of slightly crosslinked polyethylene samples

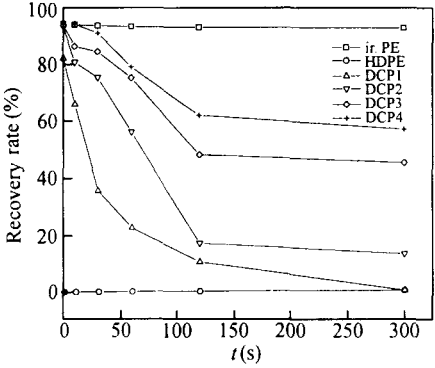


Fig. 11 Influence of t_D on the R_f value for slightly crosslinked polyethylene samples

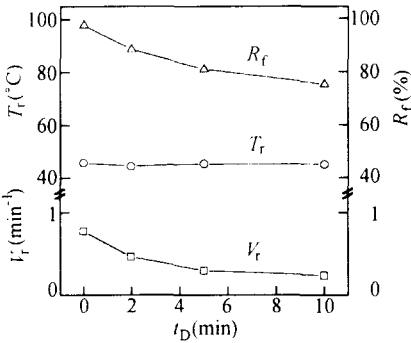


Fig. 12 Influence of t_D on the R_f value for a polyurethane sample

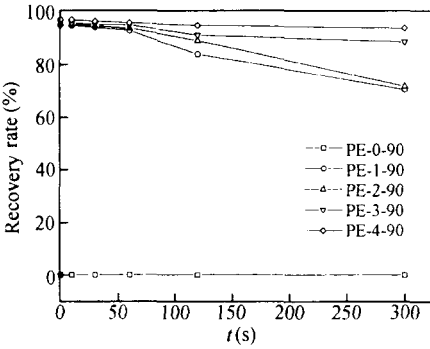


Fig. 13 Influence of t_D on the R_f value for M-PE/nylon blend specimens

There are several points should be noted from these studies. First our results indicate that copolymers including block and graft ones can be used as thermally stimulated shape memory materials with large recoverable strain and high final recovery rate. The main advantage of using copolymers is the improved processing conditions. All conventional processing techniques for thermal plastics can now be used without relying on ionizing radiation. As only physical crosslinks are introduced, the materials now become easily reusable. The second point is that these results strongly support the basic principle for material design of shape memory polymers, that is they are polymers properly crosslinked, with melting point and/or glass transition temperature appropriately high above the room temperature, and we know now that the crosslinking could be chemical or physical in nature. In addition, the successful use of block and graft copolymers can greatly broaden the list of polymers for shape memory applications, and the reaction processing technique might be a promising and powerful method for preparing these copolymers. All these are the prerequisites for the wide application of shape memory polymers in various areas.

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