Shape Memory Effect of Ethylene–Vinyl Acetate Copolymers

FENGKUI LI, WEI ZHU, XIAN ZHANG, CHUNTIAN ZHAO, MAO XU

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

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ABSTRACT: Crosslinked ethylene-vinyl acetate (EVA) copolymers with VA content of 28% by weight were prepared by a two-step method by evenly dispersing the crosslinking agent (dicumyl peroxide) into the EVA matrix and then crosslinking at elevated temperatures. The crosslinking features of the samples were analyzed by Soxhlet extraction with xylene and dynamic mechanical measurements. All the samples were crystalline at room temperature, and the chemical crosslinks seemed to have little effect on the melting behavior of polyethylene segment crystals in the EVA copolymers. The shape recovery results indicated that only those specimens that had a sufficiently high crosslinking degree (gel content higher than about 30%) were able to show the typical shape memory effect, a large recoverable strain, and a high final recovery rate. The degree of crosslinking can be influenced by the amount of the peroxide and the time and temperature of the reaction. The response temperature of the recovery effect (about 61°C) was related to the melting point of the samples. The EVA shape memory polymer was characterized by its low recovery speed that resulted from the wide melting range of the polyethylene segment crystals. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1063-1070, 1999

Key words: ethylene–vinyl acetate (EVA) copolymers; crosslinking; shape memory effect

INTRODUCTION

Shape memory polymer is a special kind of functional material that may remember its original shape when it is deformed. This means that the strain of shape memory polymers can be fixed after deformation and then recovered almost completely under appropriate conditions, for example, under heating. In this sense they are thermally stimulated shape memory materials. The first shape memory polymer material of practical importance was made of polyethylene crosslinked by the reaction with ionizing radiation during processing.¹ Its response temperature related to the melting temperature of polyethylene is usually near or above 100°C. Various kinds of shape memory polymers are needed to match the requirements of different applications.

An interesting topic is to lower the response temperature of the shape memory effect. Shape memory polymers of low response temperature may find applications in daily life and might be important for applications of special biological or medical considerations where the use of high temperature should be avoided. An important approach to solve this problem is to use segmented copolymers. Tobushi et al.² studied the mechanical properties, including the cyclic tensile test, of two polyurethane samples, which were supposed to have shape memory features; but no data about their structure, composition, and shape memory behavior were given. Recently we reported our

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studies of a series of segmented polyurethanes with polycaprolactones of different molecular weights as the soft segment.^{3–8} The hard segment was composed of 4,4'-diphenylmethane diisocynate (MDI) and 1,4-butanediol. It was found that segmented polyurethanes of particular structures and compositions may exhibit an excellent thermally stimulated shape memory effect with a large value of recoverable strain and a high recovery rate. Their response temperature was around 40-50°C. The shape memory behavior was clearly related to the crystallinity of the polycaprolactone segments and the stability of the hard segment domains acting as physical crosslinks, and a model was used to explain the mechanism of the shape memory effect of segmented copolymers. Similar results were obtained for toluene diisocynate based segmented polyurethanes⁹ and also for ethylene oxide/ethylene terephthalate segmented copolymers.¹⁰ The advantage of using segmented copolymers is the possibility of controlling the response temperature by selecting the structure and length of the soft segment. Besides, the thermoplastic nature makes them guite convenient to process.

Another possible method to lower the response temperature of polyethylene is copolymerization. It is supposed that the introduction of the comonomers into the polyethylene chains will depress the melting temperature of polyethylene crystals, depending on the structure and content of the comonomers. Ethylene-vinyl acetate (EVA) copolymers are the random incorporation of VA comonomer units into polyethylene backbones. It was long ago discovered that the melting points of polyethylene crystals in the copolymers decreases almost linearly with the increase of the VA content and approaches 40°C at a VA content of about 50%.¹¹ It is clear that EVA can be crosslinked like the polyethylene homopolymers by electron beam, γ ray, or organic peroxides such as dicumyl peroxide (DCP). However, only few results about crosslinked EVA can be found¹² and no studies on the shape memory behavior of EVA have been reported in the open literature. In this study a series of crosslinked EVA samples were prepared by using DCP as the crosslinking agent, and their shape recovery behavior and its relationship with the structure and the preparation conditions were investigated.

Table IComposition and Gel Contentof Crosslinked EVA Copolymers

Samples	EVA (g)	DCP (g)	$\begin{array}{c} T_{\rm cross} \\ (^{\circ}{\rm C}) \end{array}$	$t_{ m cross}$ (min)	$G \ (\%)$
	50	0.00	0	0	0
EVA	50	0.00	0	0	0
EVA-1-170-10	50	0.02	170	10	3.2
EVA-2-170-10	50	0.04	170	10	10.5
EVA-3-170-00	50	0.08	170	0	0
EVA-3-170-05	50	0.08	170	5	5.5
EVA-3-170-10	50	0.08	170	10	33.5
EVA-3-170-20	50	0.08	170	20	41.4
EVA-3-1905	50	0.04	190	0.5	18.3
EVA-3-190-01	50	0.08	190	1	36.7
EVA-3-190-02	50	0.08	190	2	34.1
EVA-3-190-05	50	0.08	190	5	38.2
EVA-3-190-10	50	0.08	190	10	37.8
EVA-3-2105	50	0.04	210	0.5	30.1
EVA-3-210-01	50	0.08	210	1	37.1
EVA-3-210-02	50	0.08	210	2	38.0
EVA-3-210-05	50	0.08	210	5	40.9
EVA-3-210-10	50	0.08	210	10	39.9

 $T_{\rm cross}$ and $t_{\rm cross}$ are the temperature and time of the crosslinking reaction, respectively.

EXPERIMENTAL

Materials

EVA copolymer (28 wt % VA; melt index, 25 g/10 min; density, 0.955 g/cm³) was a product from Beijing Organic Factory. DCP was produced by the Beijing Midwest Chemical Factory. It was purified by means of recrystallization from ethanol solution prior to use. Xylene (AR grade) was made in Beijing Chemical Factory.

A Haake Rheometer System-Rheocord 90, coupled with a batch mixer, was used for the preparation of the crosslinked EVA samples. The measurements of torque were controlled by the software of the Haake system. EVA and DCP were melt blended at a speed of 50 rpm at 100°C for 5 min. The mixtures were compression molded into films of around 0.3 mm thickness at 100°C. Then the film specimens were subjected to elevated temperatures for crosslinking. The crosslinking temperatures used were 170, 190, and 210°C, respectively. The specimens are summarized in Table I.

Specimens for strain recovery measurements were prepared according to the diagram given in Figure 1. The compression molded film (point A) is first heated to temperature $T_{\rm D}$ (80°C in this



Figure 1 The diagram of the preparation procedure of specimens for strain recovery measurements and recovery curves.

work) 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 to a setting temperature T_s under constrained conditions of constant length. That is point D in the graphic. In this work the 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. This 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.

Characterization and Measurements

DSC measurements were performed with a Perkin–Elmer DSC-4 purged with nitrogen. Dynamic mechanical data were obtained at 10 Hz by using a dynamic mechanical thermal analyzer (MKIII, 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 specimens were Soxhlet extracted with xylene. The residues were vacuum dried at 60°C to a constant weight. The gel content G was determined gravimetrically by using the following relation:

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

The strain recovery effect of the specimens in a heating process of constant rate was directly measured under an Olympus BHSP microscope equipped with a hot stage. The heating rate used was around 2.7°C/min. 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, $R(T) = (\varepsilon_2 - \varepsilon(t))/\varepsilon_2$ (Fig. 1). Some important parameters are usually obtained from those 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 $= \varepsilon_2/\varepsilon_1$. 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 and is 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

We mentioned in our previous studies on segmented copolymers that a sufficient crystallinity at room temperature and the formation of stable network structure are the two important factors for a polymer to exhibit a good shape memory effect. EVA copolymer has lower melting points compared to polyethylene that are due to the introduction of the VA component. So it is easy to make crosslinked EVA copolymers by a two-step method by first evenly dispersing the crosslinking agent in the EVA matrix and then crosslinking at elevated temperatures. Figure 2 is the torque versus time during the melt blending of EVA and DCP at 100°C. The curves show a sharp peak within 1 min followed by a slow decrease, and the torque values are almost unchanged after a period of about 4 min. The overlap of all the curves with different DCP contents and the absence of a torque increase in the process indicate that the crosslinking reaction initiated by the decomposi-



Figure 2 The torque versus time during the melt blending of EVA and DCP at 100°C.

tion of DCP does not happen during the melt blending process. This can be confirmed by the complete solubility of the extrudates in good solvents, for example, xylene. These facts might be the result of the very low decomposition rate of the DCP molecules at 100°C.

The crosslinking reaction was subsequently conducted at elevated temperatures. The gel contents of the samples after the crosslinking process are listed in Table I. It was found that the crosslinking reactions were influenced by DCP content and the crosslinking temperature and time. Table I shows that the gel content is low for samples with low DCP content (0.04 and 0.08% for EVA-1 and EVA-2, respectively). The gel content of the sample with 0.16% DCP content (EVA-3) crosslinked at 170°C increased with crosslinking time, and an abrupt increase was observed at about 10 min. The final gel content was around 40%. The results of sample EVA-3 crosslinked at 190 and 210°C indicate that raising the crosslinking temperature does not influence the final degree of crosslinking, but it may clearly accelerate the crosslinking reaction that almost finishes in 1 min at 210°C. These results are similar to those of crosslinked EVA copolymers having less VA content (9 and 16%).¹² At the same level of DCP content and crosslinking conditions our samples may have more gel content due to the higher VA content, because most of the reactive points in the crosslinking process were the acetate groups.¹²



Figure 3 Temperature dependence of the dynamic modulus for the specimens with different DCP contents crosslinked at 170° C for 10 min.

The formation of a network structure in the specimen can also be confirmed by dynamic mechanical measurements. Figures 3 and 4 present the temperature dependence of the dynamic modulus for the EVA samples prepared under different crosslinking conditions. At room temperature, the modulus of the specimens was about 1×10^7 Pa. As the temperature increased a transition occurred at around 70°C. It was not a sharp tran-



Figure 4 Temperature dependence of the dynamic modulus for the specimens with different crosslinking times at 170°C.

sition as in the crosslinked polyethylene; the modulus gradually decreased in a wide temperature range. It was mainly due to the broad melting process of polyethylene segment crystals in the EVA copolymers and will be discussed later. After the melting of the polyethylene segment crystals, the specimens of low crosslinking degree or low gel content tended to flow as shown by the sharp decrease of the dynamic modulus at about 100°C in Figures 3 and 4. Only specimens of high gel content (over a level of about 30%) were able to show an elastic plateau after the melting of polyethylene segment crystals, which is a clear evidence of the formation of a network structure that is stable under deformation.

Figure 5 shows the DSC thermograms of some of the crosslinked EVA samples, and data from these measurements are given in Table II. All the EVA samples crystallized during cooling, having an exothermal peak at about 45°C (T_c). It seems that the introduction of crosslinking did not influence the melting temperature of crystals formed in these samples but resulted in a slight decrease of crystallinity expressed in terms of the enthalpy change given in Table II. A characteristic feature of these thermograms is the broad melting temperature range, which might be the origin of the wide transition in the same temperature range observed in the dynamic mechanical measurements. This phenomenon can be attributed to the existence of a wide distribution of the polyethylene segment length in these EVA copolymer samples. As a result, polyethylene crystals with different melting temperatures were formed.¹³

Figures 6 and 7 give the strain recovery curves for the EVA specimens prepared under different crosslinking conditions. The strain recovery usually occurs at about 40°C and approaches a constant value after 80°C. The results are summarized in Table III. The strain fixation of all the samples showed a high value of more than 95%. For linear and crosslinked EVA samples with low gel content the final recovery rate R_f was very low, usually below 50%. This means that in these cases the large fixed strain was mainly composed of the plastic, or irreversible, strain. Only when the gel content of the samples was high enough (e.g., more than about 30%) can the final recovery rate reach 90% or more, indicating the importance of the formation of a network structure for a polymer sample to exhibit the typical shape memory effect. It was also found that the response temperature of the samples was around



Figure 5 DSC thermograms for specimens with different DCP contents crosslinked at 170°C for 10 min: (1) EVA, (2) EVA-1-170-10, (3) EVA-2-170-10, and (4) EVA-3-170-10.

61°C, which was closely related to their melting temperature. It should be noted that the strain recovery temperature range of these EVA samples was quite wide compared to that of polyeth-ylene and segmented copolymers.^{3-5,8-10,14} This is clearly expressed by their low recovery speed V_r as shown in Table III. The recovery speed, $V_r = 0.03-0.08 \text{ min}^{-1}$, for these samples was much lower than those of other polymers, which were in the range of 0.2–1.0 min⁻¹. The recovery of the fixed elastic strain happened only during the melting of the crystals. The observed slow recovery process of EVA samples was the result of the

Samples	T_c (°C)	$\Delta H_c \; ({\rm cal/g})$	T_m (°C)
EVA	45.5	12.64	71.4
EVA-1-170-10	45.4	11.24	71.2
EVA-2-170-10	44.2	11.06	71.5
EVA-3-170-00	44.1	12.64	71.2
EVA-3-170-05	45.0	11.24	70.5
EVA-3-170-10	43.9	10.61	71.5
EVA-3-170-20	44.4	10.54	68.6

Table II DSC Results for Crosslinked EVA Copolymers

broad melting range of the crystals of the polyethylene segments. Besides, a slight increase of the recovery speed with increasing gel content of the crosslinked EVA samples was also observed. A similar result was reported for shape memory segmented polyurethanes of different hard segment content.⁸

The stability of the shape memory effect is of great significance in practical applications. Figures 8 and 9 give the plot of the final recovery rate versus cyclic testing time for the EVA samples crosslinked at 170°C. For specimens of low gel content due to their short crosslinking time or DCP content, the final recovery rate decreased with the cyclic testing experiments; in some cases



Figure 6 Strain recovery curves for EVA-3 specimens crosslinked at 170°C for different times.



Figure 7 Strain recovery curves for specimens with different DCP contents crosslinked at 170°C for 10 min.

 R_f values as low as 10–20% were observed. When the crosslinking degree was high enough, for example, in samples EVA-3-170-10 and EVA-3-170-20, the final recovery rate was able to keep high values during the cyclic testing; a tendency to a slight increase of R_f value with increasing testing time could be detected. This phenomenon was even more clearly expressed for samples crosslinked at higher temperatures (Fig. 10). The high value of the final recovery rate resulted from the formation of an elastic network structure in the specimens, and the deviation of R_f value from unity implies that the specimen cannot be considered as an ideal elastic network during deformation. This means that the specimen is not com-

Table IIIStrain Recovery Resultsfor Crosslinked EVA Copolymers

Samples	$S_f \ (\%)$	Draw Ratio	T_r (°C)	$egin{array}{c} R_f \ (\%) \end{array}$	V_r (min^{-1})
EVA EVA-1-170-10 EVA-2-170-10 EVA-3-170-00 EVA-3-170-05 EVA-3-170-10	99.0 98.5 97.7 98.6 97.5 96.1	$2.01 \\ 2.10 \\ 1.98 \\ 2.03 \\ 2.00 \\ 1.97$	$\begin{array}{c} 63.7 \\ 58.7 \\ 61.8 \\ 61.6 \\ 61.5 \\ 61.9 \end{array}$	34.8 40.0 68.3 46.0 50.0 94.2	.046 .036 .056 .049 .050 .076
EVA-3-170-20	95.0	2.01	61.4	98.3	.085



Figure 8 Final recovery rate for EVA-3 specimens crosslinked at 170°C in repeating tests.

pletely involved in the network or there are some weak crosslinking points in the network that are unstable under stress. In these cases it is clear that the strain fixed after deformation will not be completely elastic but may include a fraction of a



Figure 9 Final recovery rate in repeating tests for specimens with different DCP contents crosslinked at 170°C for 10 min.



Figure 10 Final recovery rate in repeating tests for EVA-3 specimens crosslinked at 190°C.

plastic one, which is not recoverable under heating. Because the plastic strain in previous testing is excluded in the following testing of the cyclic experiments, the increase of R_f value for wellcrosslinked samples in cyclic testing is reasonable. Similar results were reported for shape memory segmented polyurethanes.^{8,9}

CONCLUSION

It is possible to prepare good shape memory polymers with large recoverable strain and high final recovery rate by introducing a sufficient amount of crosslinks and a gel content higher than about 30% into EVA samples with a two-step method. The response temperature is lower than 100°C, and it can be controlled continuously in principle by using EVA copolymers of different compositions. The EVA shape memory material is characterized by its low recovery speed. This resulted from the wide melting range of the polyethylene segment crystals due to the random copolymerization nature of EVA copolymers.

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