

Thermostimulative Shape-Memory Effect of Reactive Compatibilized High-Density Polyethylene/Poly(ethylene terephthalate) Blends by an Ethylene–Butyl Acrylate–Glycidyl Methacrylate Terpolymer

Shu-Cai Li, Li-Nong Lu, Wei Zeng

College of Material Science and Chemical Engineering, Tianjin University of Science and Technology, Tianjin 300457, China

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ABSTRACT: High-density polyethylene (HDPE)/poly(ethylene terephthalate) (PET) blends were prepared by means of melt extrusion with ethylene–butyl acrylate–glycidyl methacrylate terpolymer (EBAGMA) as a reactive compatibilizer. The effects of the EBAGMA and PET contents, recovery temperature, and stretch ratio on the thermostimulative shape-memory behavior of the blends were studied. The results show that the addition of EBAGMA to the HDPE/PET blends obviously improved

the compatibility and the shape-memory effects of the blends. The response temperature was determined by the melting point of HDPE, and the shape-recovery ratio of the 90/10/5 HDPE/PET/EBAGMA blend reached nearly 100%. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3341–3346, 2009

Key words: blends; compatibilization; functionalization of polymers; polyethylene (PE)

INTRODUCTION

Shape-memory polymers (SMPs) are a novel class of important smart materials that can recover their original shape after they are deformed into a temporary shape when they are heated or receive any other external stimuli, such as light, electric fields, magnetic fields, chemicals, moisture, and pH changes.^{1–3} Among them, thermostimulative shape-memory polymers (TSMPs), whose shape can be easily stimulated under an expected and wide range of switch temperatures, have developed rapidly and have attracted great interest in recent years because of the advantages of their rich variety, large deformation, light mass, low cost, high shape recoverability, and easy processability compared to conventional shape-memory alloys.^{4–6} This makes TSMPs desirable for a multitude of applications, including biosensors, actuators, robotics, microelectromechanical systems, biomedical devices, and fabrics.^{7–12} Furthermore, their potential value in the autodisassembly of electronic products, medical instruments, and intelligent materials is very outstanding, especially in the autodisassembly of electronic products and the recycling of plastic waste.

TSMPs basically consist of two phases, that is, a fixed phase and a reversible phase.¹³ The fixed phase can be chemical or physical crosslinks, which impart a level of rigidity, dimensional stability, and thermal resistance, whereas the reversible phase can be either crystalline or amorphous and provides the properties of the elastomer's primary recovery and energy absorption.¹⁴

Compared to that for SMPs with chemical crosslinks, the preparation procedure of SMPs with physical crosslinks may simplify the technology, decrease the cost, and make it possible to easily reprocess or recycle these materials like conventional thermoplastics. Therefore, it is of great interests to design and prepare SMPs with physical crosslinks by melt blending; those SMPs investigated so far include polyethylene/nylon 6 graft copolymers blends,¹⁵ poly(vinyl chloride)/thermoplastic polyurethane blends,¹⁶ and ethylene/vinyl acetate copolymer-g-maleic anhydride/nylon 6 ((E/VAC)-g-MAH/PA6) blends.¹⁷

It is well known that the melting point of poly(ethylene terephthalate) (PET) is more than 100°C higher than that of high-density polyethylene (HDPE). According to the shape memory mechanism effect of polymers, the melt HDPE crystals above the melting point can act as the reversible phase, whereas the dispersed PET domains as the physical crosslinks can be designed as the fixed phase. So it is possible to obtain a new shape-

Correspondence to: S.-C. Li (lishuc@tust.edu.cn).

memory system composed of HDPE and PET if the interfacial adhesion of their blends is improved. The ethylene component of the ethylene-butyl acrylate-glycidyl methacrylate terpolymer (EBAGMA) is similar to HDPE in structure, and the polarity of the butyl acrylate(BA)-glycidyl methacrylate (GMA) component of EBAGMA is near to one part of PET. Moreover, the epoxy groups of the GMA of EBAGMA may react with the hydroxyl and carboxyl groups of PET. We suggest that EBAGMA could reactively improve the compatibility of the HDPE/PET blends. In view of this idea, we prepared HDPE/PET blends by means of melt extrusion with EBAGMA as a reactive compatibilizer, and the shape-memory effect of these blends was investigated.

EXPERIMENTAL

Materials

In this study, the HDPE used was DGDA6098 produced by Qilu Ptro-Chemical Corp. (tibo, China). The melt flow rate of this polymer was 1.58 g/10 min (at 190°C/10 kg), and the density was 0.95 kg/m³. PET with an intrinsic viscosity of 0.67 dL/g was supplied by Yanshan Ptro-Chemical Corp. (Beijing, China). EBAGMA consisted of 66.75 wt % ethylene, 28 wt % BA, and 5.25 wt % GMA and was supplied by DuPont (Mechelen, Belgium) under the trade name Elvaloy PTW. The main characteristics of the terpolymer were a melt flow rate of 12 g/10 min, as measured by the method of ASTM 1238, and a melting point of 72°C.

Preparation of the blends

Before use, PET and EBAGMA were dried in a drying cabinet at 130°C for about 4 h and at 50°C for about 6 h, respectively. HDPE/PET blends with and without the EBAGMA were prepared by melt extrusion, which was carried out in a single-screw extruder (PLE330 Brabender OHG, Duisburg, Germany) with a diameter of 19 mm and a length-to-diameter ratio of 25. HDPE, PET, and EBAGMA in a given ratio were introduced into the hopper of the extruder at a screw speed of 35 rpm and barrel temperatures (from the feeding zone to the die) of 200, 245, 265, and 250°C. The screw profile was made up of conveying and kneading elements to ensure melting, mixing, shearing, and good dispersal of the components. The strands obtained from the extruder were cooled in air, then cut into small granules in a granulator, and dried (8 h at 80°C). Finally, the HDPE/PET/EBAGMA blends were injection-molded into standard dumbbell specimens with a JPH50 injection-molding machine. The compositions of the samples are shown in Table I.

TABLE I
Compositions of the HDPE/PET/EBAGMA Blends

Sample	HDPE (phr)	PET (phr)	EBAGMA (phr)
P0-0	100	0	0
P0-10	90	10	0
P3-10	90	10	3
P5-10	90	10	5
P8-10	90	10	8
P5-5	95	5	5
P5-15	85	15	5
P5-20	80	20	5
P5-30	70	30	5

Measurements and characterization

The dynamical mechanical properties of the blends were measured with a dynamic mechanical thermal analyzer (DMA2980, TA Instruments, New Castle, DE) in a tensile mode at a constant frequency of 1 Hz as a function of temperature with a heating rate of 3°C/min.

The morphology of the blends was examined with scanning electron microscopy (SEM; JSM-6380 scanning electron microscope, JEOL Ltd., Tokyo, Japan). The samples were freeze-fractured in liquid nitrogen and sputter-coated with gold before analysis.

Differential scanning calorimetry (DSC) measurement was carried out with a differential scanning calorimeter (DSC141, Setaram Ltd., Caluire, France) at a heating rate of 10°C/min in the range 50–250°C.

The shape-memory effect was examined by a stretching test as follow. First, two distance lines of approximately 20 mm were drawn at two sides of the center of a dumbbell specimen, the distance between the two lines was measured accurately, and it was recorded as L_0 . Second, the specimen was clamped on a self-made shape-memory instrument, which then was placed into an oil bath at constant temperature for 5 min. After that, the specimen was stretched to the required length with one stretch ratio; then, it was taken out and quickly cooled to the room temperature to keep the deformation. The distance between the two lines in the stretch state was measured and marked as L_1 . Finally, the specimen was put into the oil bath again at the response temperature without constraint. The recovery time was recorded when the deformed sample maximally reverted to the original shape; then, the sample was taken out, and the distance was marked as L_2 . The shape-recovery ratio (R_v) was defined as follows:

$$R_v = \frac{L_1 - L_2}{L_1 - L_0} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

Effects of the compatibilizer on the compatibility and morphology of the HDPE/PET blends

The effect of the compatibilizer content on the compatibility of the HDPE/PET blends was detected by

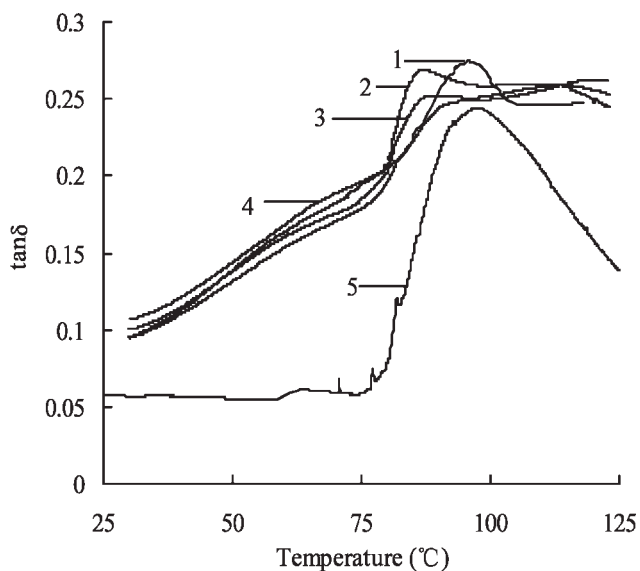


Figure 1 Dynamic mechanical behavior of pure PET and the HDPE/PET blends: (1) 90/10/0, (2) 90/10/3, (3) 90/10/5, and (4) 90/10/8 HDPE/PET/EBAGMA and (5) PET.

dynamic mechanical measurements. Figure 1 shows the relationship between the $\tan \delta$ and temperature for pure PET and the blends. The glass-transition temperature (T_g) of the PET component in the HDPE/PET binary blend was consistent with pure PET, which implied that the blend was incompatible. With the addition of EBAGMA, the T_g of the PET component in the blends moved to a low-temperature region; the glass-transition peaks of the PET component descended and deteriorated gradually as the EBAGMA content increased, which indicated that the EBAGMA effectively improved the compatibility of the HDPE/PET blends.

Furthermore, this was also confirmed by the SEM photographs of the fracture surfaces of the HDPE/PET/EBAGMA blends, as shown in Figure 2. It was obvious that all the blends displayed a two-phase structure. The droplets of PET dispersed in the continuous HDPE phase. The uncompatibilized blend [Fig. 2(a)] showed a typical morphology of phase segregation and poor interfacial adhesion with the

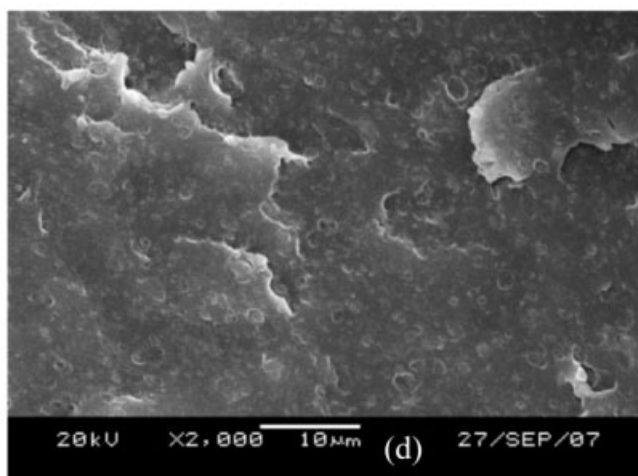
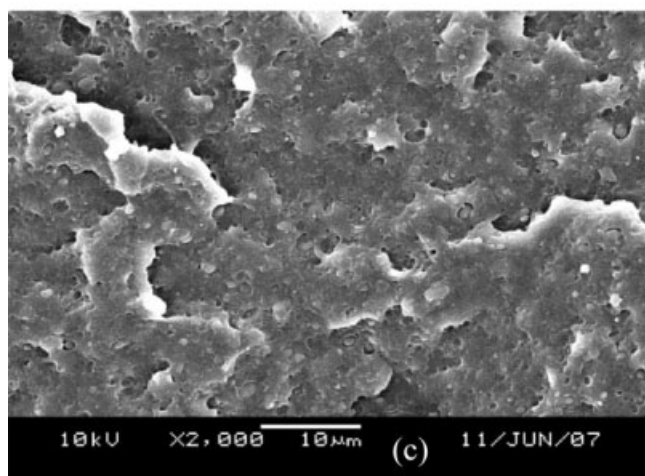
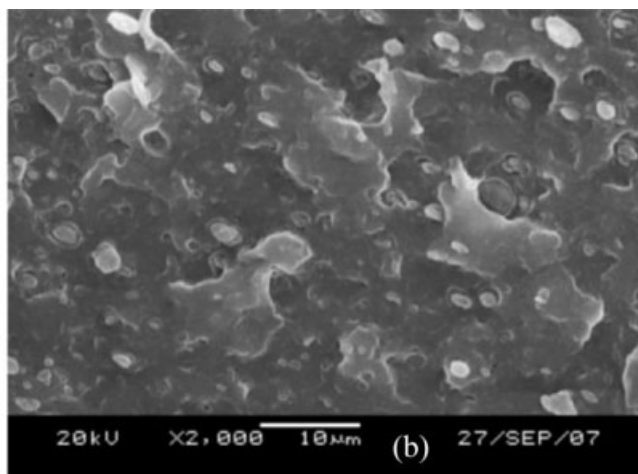
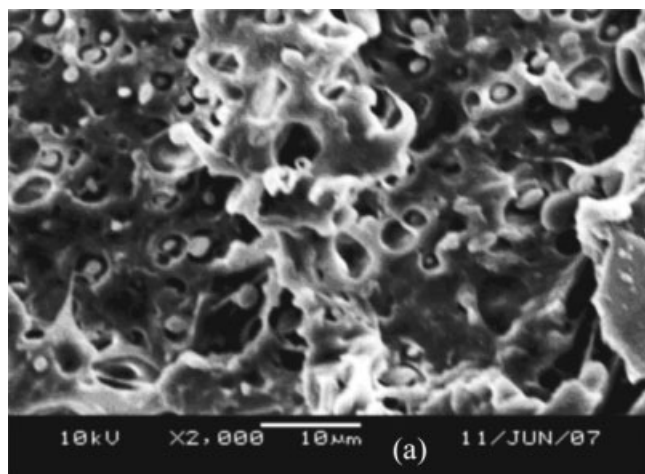


Figure 2 SEM photographs of the fracture surface of the (a) 90/10/0, (b) 90/10/3, (c) 90/10/5, and (d) 90/10/8 HDPE/PET/EBAGMA blends.

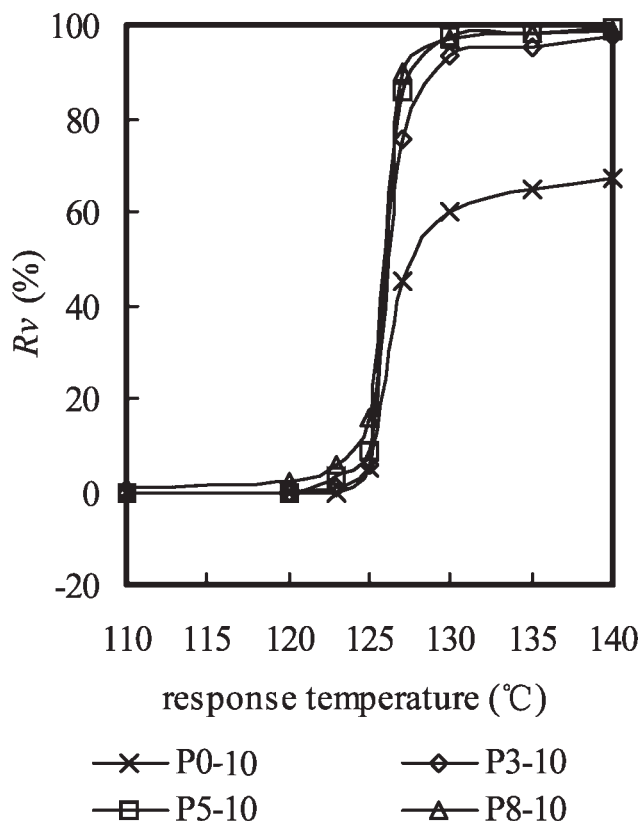


Figure 3 Variation of the R_v values with temperature for the HDPE/PET/EBAGMA blends with different EBAGMA contents.

appearance of a discrete interface between the two phases. With the introduction of EBAGMA, the compatibility of the blends was improved. The PET particle size decreased, and adherence between the two phases was promoted with increasing content of EBAGMA, as illustrated in Figure 2(b-d). This was ascribed to the reaction of the hydroxyl and carboxyl groups of PET with the epoxy groups of the GMA of the EBAGMA during melt mixing.¹⁸

R_v

Effect of the compatibilizer

Figure 3 shows the effect of the EBAGMA content on R_v of the HDPE/PET (90/10) blends at 130°C. It was evident that the R_v value of the pure HDPE/PET blend was low. With increasing content of EBAGMA, the R_v value raised rapidly, and it almost reached 100% when the blends contained 5 phr EBAGMA. In the blends, the HDPE phase with the soft molecular chains that possessed relatively low T_g and melting temperature (T_m) values acted as the reversible phase; the PET phase, with relatively high T_g and T_m values due to the molecular chains' rigidity, was designed as the fixed phase. Therefore, the strong interaction between the reversible phase and

fixed phase was the key to the good shape-memory effect of the HDPE/PET blends. However, HDPE and PET were incompatible because of their different molecular structures, so the HDPE/PET binary blend without EBAGMA did not possess good shape-memory effects. After the addition of the reactive compatibilizer EBAGMA to the blends, the interfacial adhesion between PET and HDPE was enhanced evidently, which is shown in Figure 2. As a result, the PET phase in the HDPE matrix was able to play the important role of the fixed phase on the shape-memory behavior, and hence, R_v increased largely.

Effect of the PET content

As shown in Figure 4, R_v of the blends increased at first and then decreased with increasing content of PET. With the content of EBAGMA fixed at 5 phr, the shape-memory effect of the blends was better when PET content was between 5 and 20 phr. It demonstrated that the reactive compatibilized blend possessed good shape-memory effects just at the appropriate ratio of the reversible phase and the fixed phase. Pure HDPE in melting state at the response temperature had a certain R_v , but the ratio

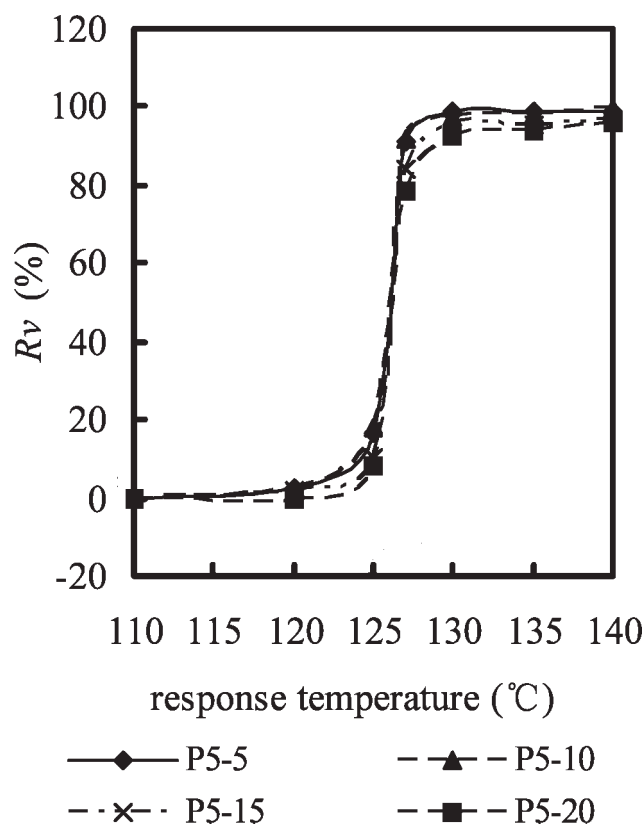


Figure 4 Variation of the R_v values with temperature for the HDPE/PET/EBAGMA blends with different PET contents.

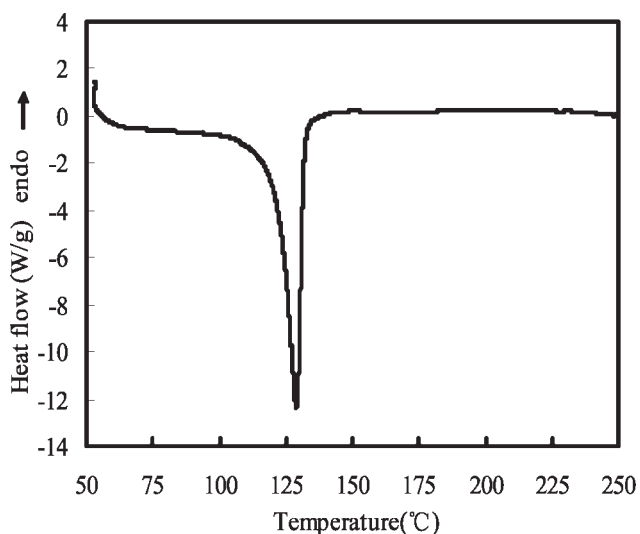


Figure 5 DSC thermograph of pure HDPE.

was low. This was because the melt of pure HDPE did not possess the function of the fixed shape. However, the primarily recovery of the reversible phase HDPE could be restricted if the content of the PET component was too high, which led to a decrease in R_v .

Shape-response temperature

The shape-response temperature is the external stimulus condition of the deformation process of TSMPs, which can be defined as the temperature when a SMP its basic original shape. Figures 3 and 4 display the variation of R_v values with temperature for the HDPE/PET/EBAGMA blends. The R_v values were

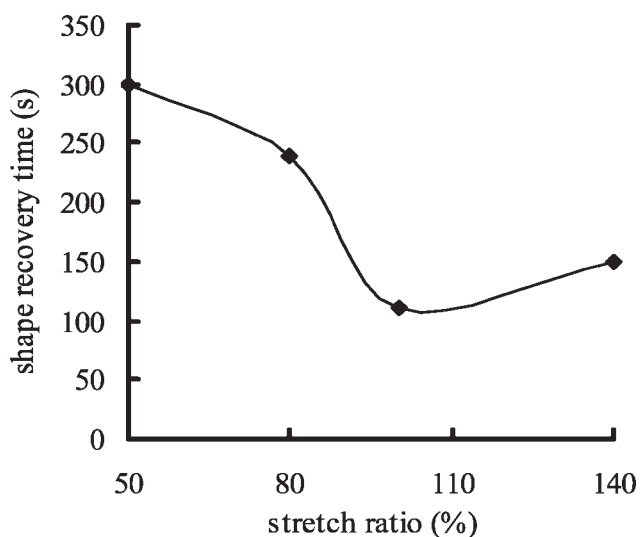


Figure 6 Relationship between the stretch ratio and shape-recovery time at the response temperature.

very low and almost remained constant below 125°C and then ascended sharply at about 127–130°C. The R_v values were high and once again remained constant above 130°C. Figure 5 shows the DSC thermograph of pure HDPE; it can be seen from the thermograph that the melting point of HDPE was 127°C. So the best shape-response temperature was determined by the melting point of the reversible phase of the blends and little more than that temperature.

Shape-recovery speed

The shape-recovery speed was expressed by the time when SMP reached the maximum recovery ratio. The relationship between the stretch ratio and shape-recovery time of specimen P5-10 is shown in Figure 6. The shape-recovery time of the specimen decreased with increasing stretch ratio. When the stretch ratio achieved 100%, the recovery time was the shortest, and the recovery speed was the fastest. However, the recovery time became prolonged when the stretch ratio increased further. The shape-recovery process was the chain segment relaxation process of the macromolecular chain of the reversible phase in a high elastic state. The orientation of molecular chains was low when the stretch ratio was small, so the entropy elasticity deformation that could be recovered and the recoverable stress were low, and hence, the shape-recovery time was longer. As the stretch ratio increased, the recoverable stress increased, and the shape-recovery time shortened. When the stretch ratio increased further and achieved a certain value, because of the overlarge tensile deformation of the specimen, the molecular chains slipped, and the degree of irreversible deformation increased. As a result, the shape-recovery speed slowed down accordingly.

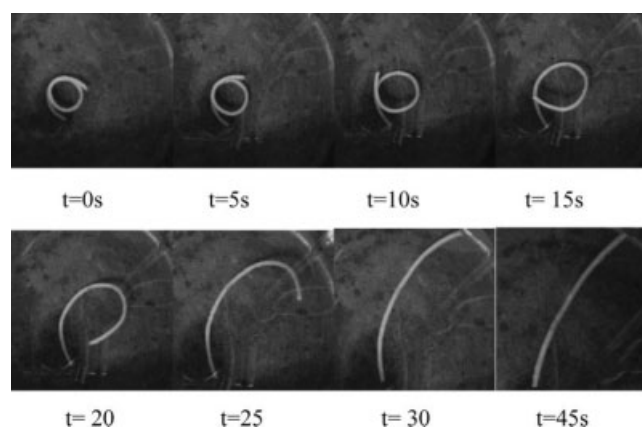


Figure 7 Thermostimulative shape-memory recovery process of the HDPE/PET/EBAGMA blends. t , the shape-recovery time.

Shape-recovery process

Figure 7 shows the snap shots of the thermostimulative shape-memory recovery process of the HDPE/PET/EBAGMA blends. As shown in the photographs, the permanent shape of the blend was like a rod with a length of about 10 cm and a diameter of about 30 mm. When the sample was heated above the T_m of HDPE, the sample became soft and was easily deformed to a spiral (temporary shape) under external forces. Then, the deformed sample was cooled to room temperature, and the temporary shape was fixed without loading. However, if the temperature was raised to 130°C, the sample quickly recovered its initial shape in basically 45 s.

CONCLUSIONS

HDPE/PET thermostimulative shape-memory blends with good combined properties were prepared with EBAGMA as the reactive compatibilizer. The following conclusions were obtained:

1. The reactive compatibilizer EBAGMA improved the compatibility of the HDPE/PET blends; as a result, the interfacial adhesion between the PET and HDPE phases was evidently enhanced.
2. R_v of the HDPE/PET blends was evidently increased with the addition of EBAGMA.
3. The shape-memory effect of blends with 5 phr EBAGMA was best when the ratio of HDPE/PET was 90/10.
4. The shape-recovery speed accelerated at first and then slowed with increasing stretch ratio,

and it was fastest when the stretch ratio was 100%.

5. The shape-response temperature of the HDPE/PET/EBAGMA blends was determined by the melting point of HDPE and little more than the melting point of HDPE.

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