Thermo-responsive shape memory polymer blends based on alpha olefin and ethylene propylene diene rubber

Tuhin Chatterjee, Pranab Dey, Golok Behari Nando, Kinsuk Naskar*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur, 721302, West Bengal, India

ABSTRACT

Thermally stimulated novel shape memory polymer blend of ethylene octene copolymer (EOC) and ethylene propylene diene terpolymer (EPDM) has been developed. This novel polyolefinic blends possess superior shape memory behaviour in presence of heat. Shape memory behaviour study at 60 °C of the blends shows that the blends containing higher fraction of EPDM exhibits superior shape memory behaviour in terms of shape fixity (f) and shape recovery ratio (RR). Structural similarities of the pristine components lead to higher degree of compatibility which also results better physicomechanical behaviour. Lower modulus value followed by low relaxation ratio of the blend containing higher proportion of EPDM also supports the superior shape memory behaviour of the EPDM rich blend. Thus EPDM rich blend shows better shape memory effect among the various blends.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

In the field of modern scientific and industrial research smart materials (SMs) are gaining much more scientific and technological importance due to their ability to sense and respond to external stimuli (such as temperature, chemicals, light, pH, electric or magnetic field) that enables these materials to change their properties such as shape, colour, electrical conductivity etc. [1,2]. Shape memory polymers (SMPs), a promising class of smart materials have achieved significant importance due to their proficiency of executing unique functions in response to changes in stimuli [3–5]. On demand, SMPs can change their shape in a predefined way from a less-constrained shape/configuration to a strained temporary shape/configuration and then again reverts back to the memorized shape/configuration upon triggering by an external stimulus [6]. Unlike gradual and linear response of regular polymers to external stimulus, SMPs exhibit a significant change even in presence of small magnitude of external stimulus and that response of SMPs to external stimuli is very rapid and nonlinear in nature [7]. Depending upon the response of SMPs to external stimulus, SMPs can be of various categories, namely a) thermo-responsive (temperature dependent) [8], b) chemo-responsive (chemicals, including water, ethanol and pH dependent) [9], c) photo-

responsive (light dependent) [10], d) electro-responsive (electricity dependent) [11,12] e) magneto-responsive (magnetic field dependent) [13] etc. Among the afore mentioned different groups thermal-responsive SMPs are the most focused and concerned system because thermally actuated SMPs have found broad applications in actuators, coatings, cable applications, sporting goods and also in biomedical devices [14–16]. It is already reported that polymers like polyester [17,18], poly (ether-ether-ketone) [19], polynorbornene [20], cross-linked polyethylene [3,21] and polyurethane [22,23] exhibit shape memory phenomenon. Apart from polymer blending offers a much simpler way to fabricate SMPs in order to improve the properties or to achieve newer functions (such as improvement of mechanical properties, improvement in thermal conductivity to reduce the shape recovery induction time) of SMPs shape memory polymer blends is a matter of concern [24,25]. Existence of the separate phases which are related to the coiled structure, presence of crosslinks (covalent bonds), hydrogen or ionic bonds or physical intermolecular interactions between the polymers are the key factors for the shape memory effects (SMEs) of SMPs [26]. Formation of covalent crosslinks takes place during suitable crosslinking of the polymer whereas polymer morphology consist of segregated domains (such as hard and soft segments) generates the physical crosslinks [27]. In multiphase polymer blend systems, hard segments provide stiffness and reinforcement to the material whereas the soft segments are responsible for the thermoelastic behaviour of polymers and the shape memory behaviour is produced by the reversible phase transition of the soft segments

[26]. Although glass transition temperature (T_g) or melting temperature (T_m) of the soft segment may be the shape transition temperature (T_{trans}) for this kind of blends but melting temperature are preferred because of the sharpness of the transition rather than the glass transition temperature. As a result, shape recovery temperature of the blends can be better determined [28]. Upon deformation at high temperature ($T > T_{trans}$) the materials transform to temporary shape in which chain segments get altered and this temporary and dormant shape can be fixed by cooling below the transition temperature ($T < T_{trans}$). Again trigerring to higher temperature ($T > T_{trans}$) allows the material to revert back to its original shape [29]. Polymer blends based on polyethylene/polycyclooctene [5], PVDF/PMMA [30], PVDF/PVAc [30], PLA/PVAc [30], SBS/PCL [31], PCL/PLLA polyurethane [32] etc. have been reported to exhibit shape memory effects.

In the present investigation a novel heterogeneous polyolefinic blend system based on ethylene octene copolymer (EOC) and ethylene propylene diene terpolymer (EPDM) rubber has been developed to study the shape memory behaviour. Both the pristine polymers contain higher percentage of ethylene. EOC acts as hard domain and therefore provides adequate stiffness and reinforcement. On the other hand, EPDM being softer is responsible for the thermoelastic behaviour of the blends. In order to study the shape memory behaviour of the EOC-EPDM blend, five different blends in uncrosslinked state having different blend ratios have been prepared and subsequently thermal and mechanical behaviour of various blend have been studied in details. Finally shape memory behaviour of EOC-EPDM blend is optimized and it has been found that shape memory character is highest at an optimum blend ratio.

2. Experimental

2.1. Materials

Polyolefin elastomer, EOC (Engage 8440), with an ethylene content of 77 wt% and co-monomer content of 23 wt% was procured from Dow Chemical. EOC has the density of 0.897 gm cm^{-3} and it has glass transition temperature (T_g) of ($-33\ ^\circ$C) and melting (T_m) at 93 $^\circ$C. The melt flow index of EOC, measured at 190 $^\circ$C and 2.16 kg loads is 1.6 dg min^{-1}. Ethylene propylene diene rubber EPDM (Keltan 5508), with an ethylene content of 70 wt% and an ethylidenenorbornene content of 4.5 wt%, procured from DSM Elastomers, Netherlands was chosen as the second blend component. EPDM has the density of 0.87 gm cm^{-3} and it has Mooney viscosity, $ML_{(1+4)}$ at 125 $^\circ$C of 55. Glass transition temperature (T_g) of EPDM is ($-40\ ^\circ$C) whereas the melting of crystal takes place at around 31 $^\circ$C.

2.2. Preparation of the blends

All the blends of EOC and EPDM at five different blend ratios have been prepared in a batch process using a Haake Rheomix (model Rheomix 600 OS) having a mixing chamber volume of 85 cm^3. The batch sizes were nearly 60 gm. Blends were prepared at a rotor (cam type) speed of 60 rpm and at a temperature of 120 $^\circ$C. Details of the blend compositions are given in Table 1.

Table 1
Various blend composition.

Blend no	EOC (phr)	EPDM (phr)	Designation
1	25	75	$P_{25}R_{75}$
2	40	60	$P_{40}R_{60}$
3	50	50	$P_{50}R_{50}$
4	60	40	$P_{60}R_{40}$
5	75	25	$P_{75}R_{25}$

2.3. Testing procedure

2.3.1. Differential scanning calorimetry (DSC)

The thermal properties, such as glass transition temperature (T_g), melting temperature (T_m) and crystallinity of the soft segment, were determined using a differential scanning calorimeter (DSC 204F1, NETZSCH, Germany) coupled with an auto-sampler. Tests were carried out from $-80\ ^\circ$C to $+120\ ^\circ$C at a heating rate of 10 $^\circ$C min^{-1} under nitrogen atmosphere. In the first thermal scan the specimens were heated at a heating rate of 10 $^\circ$C min^{-1} to $+120\ ^\circ$C and then quenched to $-80\ ^\circ$C at an average cooling rate of 20 $^\circ$C min^{-1} using liquid nitrogen. The second thermal scan was taken over a temperature range of $-80\ ^\circ$C to $+120\ ^\circ$C with a heating rate of 10 $^\circ$C min^{-1}. Degree of crystallinity of the soft segment (EPDM) was determined from the heating curve by using the following equation

$$X_C = \frac{\Delta H_f}{\Delta H_{c100\%} \times W_i} \times 100 \tag{1}$$

where

X_c = Percentage of crystallinity (%)
ΔH_f = Apparent melting enthalpy of crystallization (J/gm)
$\Delta H_{c100\%}$ = Extrapolated value of enthalpy of crystallization of 100% crystalline polyethylene is 290 (J/gm)
W_i = Weight fraction of individual polymer in the blend [33].

2.3.2. Dynamic mechanical analysis (DMA)

Dynamic mechanical analyser, Metravib 50 N, France was used to perform the DMA measurements. Temperature sweep of the samples were carried out in tension mode over a temperature range of $-80\ ^\circ$C to $+100\ ^\circ$C, at a rate of 2 $^\circ$C min^{-1}. The samples were scanned at a frequency of 10 Hz and a strain level of 10 mm, which was well within the linear viscoelastic region (LVR). The storage modulus (E'), loss modulus (E''), and the loss tangent (tanδ) were determined as a function of temperature.

2.3.3. Shape memory property (SMP) test

Shape fixation of the sample to a deformed shape or temporary shape and the recovery from deformed shape to permanent shape are the main criteria for the quantification of shape memory functionality of SMPs. The so called and most widely used cyclic thermomechanical tensile test which consists of a programming module where the temporary shape is fixed and recovery module where the permanent shape is recovered was performed to characterize the shape-memory functionality of the blends. The typical test protocol of strain-controlled programming with stress free recovery (ε-σ) diagram has been schematically represented in Fig. 1 [34].

Tensile testing machine (Hounsfield H10KS) with a temperature controlled chamber was used to determine the shape memory properties. Sample deformation at different stages of shape memory cycle has been schematically represented in Fig. 2.

Usually cyclic thermomechanical test of a polymer is carried out at a temperature which is at least 20 $^\circ$C higher than that of transition temperature [35,36]. During programming module, a sample of original length (l_o) was heated to a higher temperature ($T \geq T_{trans}+20$) and 100% elongated to a length of (l_e) in the tensile tester with a constant force ($F_{tensile}$) at a crosshead speed of 50 mm min^{-1} [37]. The new shape is then fixed by cooling the constrained specimens below the transition temperature ($T \leq T_{trans}-20$).

Afterthat, upon release of the load instantaneous shrinkage of