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Shape memory properties of polyethylene/ethylene vinyl acetate /carbon nanotube composites

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Abstract

The safe operation of electrical equipment relies on advanced polymer insulation to contain electrical pathways. Polymer sheath materials should be mechanically robust and chemically stable in order to protect the internal metal wiring from environmental attack. Polyethylene (PE) and ethylene vinyl acetate (EVA) have often been used as electrical cable jacket materials for electrical power industry. Partially crosslinked PE is able to shrink and wrap tightly around the metal wires upon stimulated by external heat, exhibiting shape memory behaviour. In this work, multiwalled carbon nanotubes (MWCNTs) were introduced to partially crosslinked linear medium density polyethylene (LMDPE) and EVA blend in order to enhance the shape memory performance at lower temperature by promoting the thermal transfer and antistatic properties of the polymer nanocomposite. The morphologies of the partially crosslinked and non-crosslinked composites are analysed. The MWCNTs preferentially resided in the EVA phase while the peroxide crosslinking process drastically altered the morphology and electrical properties. The addition of 3 wt.% of MWCNTs resulted in a percolation transition and enhanced the **alternating current (AC) conductivity** by 10 orders of magnitude for non-crosslinked LMDPE/EVA and by 3 orders of magnitude for crosslinked LMDPE/EVA composites. LMDPE/EVA (80/20) containing 3 wt.% MWCNTs possessed excellent shape recovery of 100% and **shape fixing** of 82%. The addition of MWCNTs can not only promote the shape memory efficiency of the polymer sheath material, but also introduce antistatic properties to avoid electrical shocking or sparking.

Keywords: shape memory; polyethylene; carbon nanotube; electrical cable insulation.

1. Introduction

Smart polymers are materials that can adapt their shape and physical properties by responding to external stimuli. Shape memory polymers (SMPs) can recover their original shape from a temporarily deformed state upon responding to an external stimulus such as temperature, light, chemical, electrical or electromagnetic field[1]. SMPs are desirable for electrical cabling protection due to their combined insulation, anticorrosion, mechanical protection and strain relief. Notable advances in the field of SMPs have occurred in recent years which have changed the conventional view of SMPs and led to more opportunities for advanced applications such as aerospace, biomedical, industrial and textile.

Achieving shape memory properties in a polymer typically involves the formation of a polymer network via physical or chemical crosslinking reactions. For semi-crystalline polymer blends, the crystalline structures act as physical crosslinks. The polymer can be deformed in the rubbery state when the temperature is above the glass transition temperature (T_g). However, for covalently crosslinked polymer networks, the material changes shape when it is heated above its crystalline melt point. At this point, the polymer can be deformed into a temporary shape and subsequently recovered to its original shape when properly thermally activated, either through the glass transition temperature (T_g) or the melting temperature (T_m) [2, 3]. The melting transitions are commonly used in crosslinked semi-crystalline polymers such as polyethylene, polyesters or nylon [3]. Glass transition based SMPs are commonly found in chemically crosslinked thermosets and physically cross-linked thermoplastics.

The polymer structure plays an important role in providing permanent **shape fixing** and shape recovery [4], through two distinct phases within the polymer. The first is the stable phase which determines the original shape of the polymer and is formed through strong molecular bonds from either crosslinking or crystalline regions [5]. Distorting the polymer from its stable phase while heating above then cooling below its switch temperature, creates the second phase. The second phase can be controlled by an external trigger once the polymer has been distorted. This phase is temporary but holds its shape until an external trigger returns the SMP to its stable phase.

SMPs can be classified into five different categories based on their triggering mechanisms a) thermo-responsive b) electro-responsive c) photo-responsive d) chemo-responsive and e) magneto-responsive [6]. Thermo-responsive shape memory behaviour, either by direct or indirect heating is the most common triggering method for SMPs. Direct thermal activation

can be by conduction, convection and radiation and indirect thermal activation can be via joule heating or infrared lasers.

This paper focuses on shape memory characteristics of LMDPE/EVA blends and their performance improvements through the introduction of MWCNTs. Most shape memory polymers are electrically insulating and the electrical conductivity of polymers is between 10^{-16} to 10^{-12} $\text{S}\cdot\text{m}^{-1}$ [7]. By incorporating electrically conductive fillers in SMPs, activation can be achieved via resistive/Joule heating. Recent examples have demonstrated electricity as a triggering mechanism for shape memory polymer composites [8-10]. The electrical properties of shape memory polymers can be modified by incorporating electrically conductive particles or fibers such as carbon black, carbon nanotubes, graphene or nanowires into the polymer system. Of these nanoparticles, MWCNTs possess excellent properties such as high thermal and electrical conductivity over 3000 W (mK)^{-1} and $10^4 \text{ S}\cdot\text{m}^{-1}$, respectively. MWCNTs can act as functional fillers in polymer nanocomposites, reinforcing the mechanical strength and improving the shape recovery stress effectively [11].

The combination of high electrical and thermal conductivity behaviour from MWCNTs allows their utilisation as electrical heating elements, which has many industrial applications such as de-icing of aircrafts, engine preheater and heated seats [12]. It was reported that the maximum surface temperature of a polyethylene/carbon nanotube composite film reached 125°C within less than 100 seconds when 1.73 W of power was applied to the composites[13]. A polydimethylsiloxane/MWCNT composite film generated a maximum of 150°C when 0.8 W of power was applied to the composite[14]. These studies have shown that MWCNTs can be used as a highly efficient electrical heater due to its quick heating behaviours. Alternatively, the effect of carbon black nanoparticles on shape memory in polyethylene was reported [15]. The addition of 0.5 vol.% of carbon black lowered the response/switch temperature range of the polymer. Carbon black also improved the tensile modulus of the polymer without affecting the crystallinity during cooling under tension however the shape memory properties were lost with the addition of more than 20 volume% due to disruption of the crystal structure.

The percolation threshold for polymer nanocomposites is generally in the range of 0.1 ~ 3 wt.%, depending on the type and morphology of the fillers. It was previously reported that the electrical triggering method is more efficient and convenient compared to external heat triggering methods [16]. Using electricity as a triggering mechanism eliminates the need for using external heat which is not desirable for many applications. The dependence of the rate of shape recovery on voltage applied across the sample depends on the electrical resistivity of the composites[17].

In this work, the effect of MWCNTs on the electrical conductivity, shape fixity and shape recovery of a chemically crosslinked LMDPE/EVA nanocomposite was investigated. The morphology and thermal-triggered shape memory behaviour are studied.

2. Experimental

2.1 Materials

LMDPE with melt flow rate of 3.5g/10 mins at 190 °C and density of 0.941 g·cm⁻³ was sourced from Polimeri Europa. EVA with a density of 0.93 g·cm⁻³ and melt flow rate of 1.2 g/10 mins at 190 °C was provided by DuPont Industrial Polymers. Luperox 101 (2, 5-Bis(tert-butylperoxy)-2,5-dimethylhexane) was sourced from Arkema for crosslinking the polymer. The non-functionalised MWCNTs produced by catalytic carbon vapour deposition (NC7000TM) were purchased from Nanocyl S.A., Belgium. The MWCNT has the diameter and average length of 10 nm and 1.5 μm respectively with density 1.8 g·cm⁻³.

2.2 Melt-processing

The polymer composites were melt processed using a ThermoFisher Scientific PolyLab Mixer. The LMDPE/EVA (80/20) blend containing 0, 1 and 3 wt.% of MWCNTs were processed at 165 °C, 60 rpm for 10 minutes. For chemically crosslinking the polymer blend, 0.5 wt.% of organic peroxide was added after mixing for 9 minutes, and further mixed for 1 min for a uniform dispersion. The resultant composites were compression moulded using a Rondol manual hot press at 170 °C and 10 kN with cure time of 10 minutes for the crosslinking of peroxide containing formulations.

2.3 Characterisation

The shape memory behaviour of neat polymer blend and MWCNTs modified blends were analysed using PerkinElmer DMA8000. The experiments were conducted in stress control mode using Pyris software. Through DMA analysis, the percentage shape fixing and shape recovery were determined. The samples analysed were prepared by cutting the compression moulded films into strips having length of ~5mm, width of ~5mm and thickness of ~0.6 mm respectively. Contact angle measurements were performed using an Attension Theta Lite, using H₂O and CH₂I₂ as the wetting solvents. The impedance spectroscopy was carried out using an Ametek Scientific Instruments PARSTAT® MC Multichannel Potentiostat. The experiment was conducted with a custom two probe measurement cell attach to the PMC2000 card. Carl Zeiss Sigma Field SEM was used to analyse the cryo-fractured samples to study the dispersion

of MWCNTs within the polymer and the morphology of different polymer phases. The cryo-fractured samples were sputter coated using an Au/Pd target for approximately 45 seconds.

3. Results and Discussion

3.1 Mechanical and electrical properties

Fig. 1 shows the stress-strain analysis for the non-crosslinked and crosslinked LMDPE/EVA/MWCNT composites. The strain at break of the LMDPE/EVA blend was ~550% and after crosslinking, it decreased to ~450%. A similar effect was noticed for crosslinking composites containing 1wt.% and 3 wt.% of MWCNTs. The strain at break for the crosslinked nanocomposites decreased due to the formation of three-dimensional network structures restricting the movement of the polymer chains.

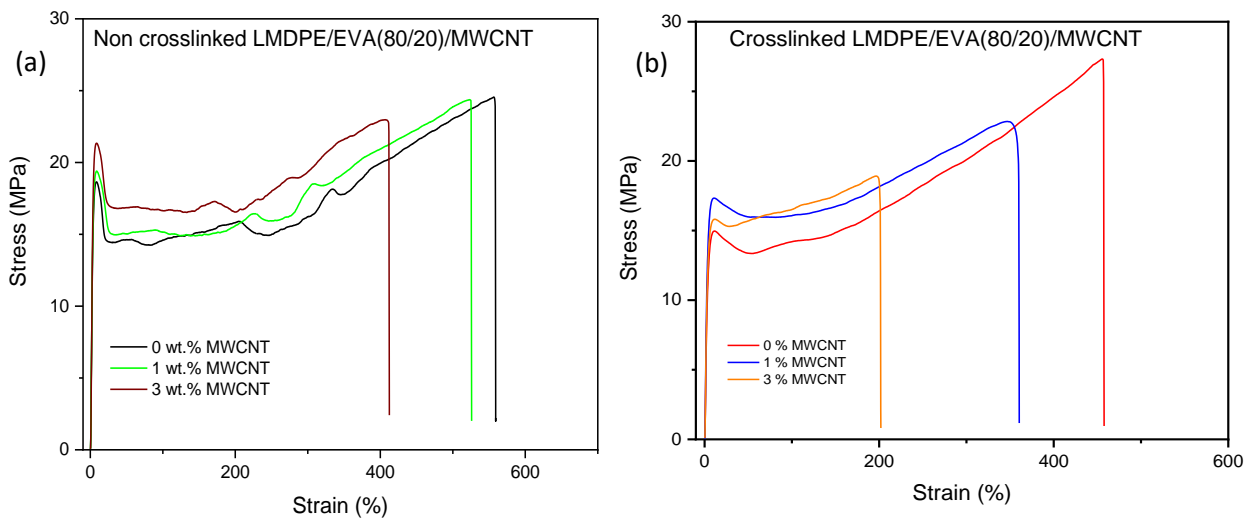


Fig. 1 Stress-strain analysis of (a) non-crosslinked and (b) crosslinked LMDPE/EVA/MWCNT composites

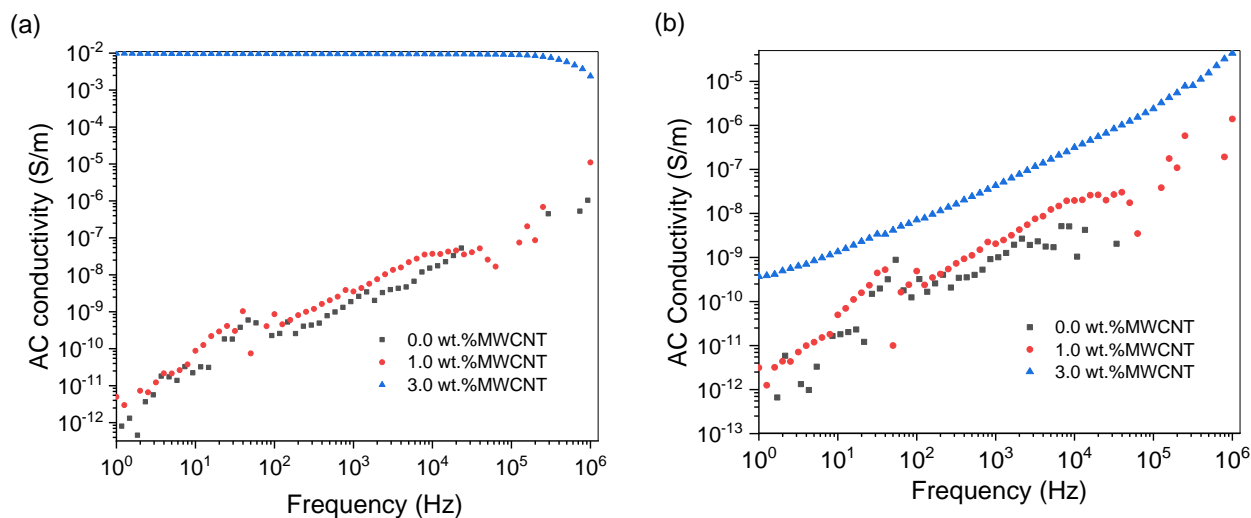


Fig. 2 AC Conductivity of (a) LMDPE/EVA/MWCNT composites; (b) crosslinked LMDPE/EVA/MWCNT composites

The AC conductivity, where AC is defined at the alternating current, of the LMDPE/EVA/MWCNTs composites was measured using impedance spectroscopy, as shown in Fig. 2. The addition of 1 wt.% of MWCNTs had a minimal influence on the AC conductivity of the composites due to no percolation network formation. The addition of 3 wt.% of MWCNTs resulted in percolation and enhanced the AC conductivity by ten orders of magnitude in non-crosslinked LMDPE/EVA and by three orders of magnitude for crosslinked LMDPE/EVA. Due to the significant differences in conductivity of the non-crosslinked nanocomposite and crosslinked nanocomposite, it indicates that the formation of MWCNT conductive networks was impeded by crosslinking LMDPE/EVA, thus hindering the percolation threshold of the crosslinked composites.

3.2 Distribution of MWCNTs in LMDPE/EVA composites

The surface properties and interfacial interactions of MWCNTs in the nanocomposites are evaluated by contact angle measurements. To determine the electrostatic interaction between the MWCNTs and the LMDPE/EVA blend, the wetting coefficient (ω_a) was calculated from the interfacial surface tensions between the blend & MWCNTs and interfacial surface tension between LMDPE & EVA, as shown in Eqn 1 [18, 19].

$$\omega_a = \frac{\gamma_{MWCNTs-polymer1} - \gamma_{MWCNTs-polymer2}}{\gamma_{polymer1,2}} \quad (1)$$

where, $\gamma_{MWCNT-polymer1}$ is the interfacial tension between MWCNTs and polymer 1 (EVA), $\gamma_{MWCNT-polymer2}$ is the interfacial tension between MWCNTs & polymer 2 (LMDPE) and $\gamma_{polymer1,2}$ is the interfacial tension between polymer 1 and 2. Eqn 2, shown below, was used to measure interfacial tension between the two polymers according to the geometric mean [19].

$$\gamma_{1,2} = \gamma_1 + \gamma_2 - 2 \left(\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p} \right) \quad (2)$$

where γ^d and γ^p are the dispersive and polar parts of surface energy respectively. Eqn 3 and 4 below shows the geometric mean method is used to calculate the surface energy [19, 20].

$$\gamma_{LV}(1 + \cos\theta) = 2 \left(\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \gamma_{LV}^p} \right) \quad (3)$$

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p \quad (4)$$

where γ_{LV} and γ_{SV} are interfacial liquid-vapour and interfacial surface-vapour respectively, θ is the observed contact angle and the superscripts in the equation, d and p , represents the disperse and polar components of surface tension. Table 1 shows the contact angle of LMDPE and EVA in both H₂O and CH₂I₂.

Table 1. Contact angle measured for LMDPE & EVA.

Material	Contact angle (θ) for H ₂ O [°]	Contact angle (θ) for CH ₂ I ₂ [°]
LMDPE	96.9	71.7
EVA	94.2	63.9

The calculated wetting coefficient (ω_a) of the polymer system is shown in Eqn 5 and the preferred residence of MWCNTs are explained below. The interfacial tension between each component was calculated based on Eqn (2 – 4).

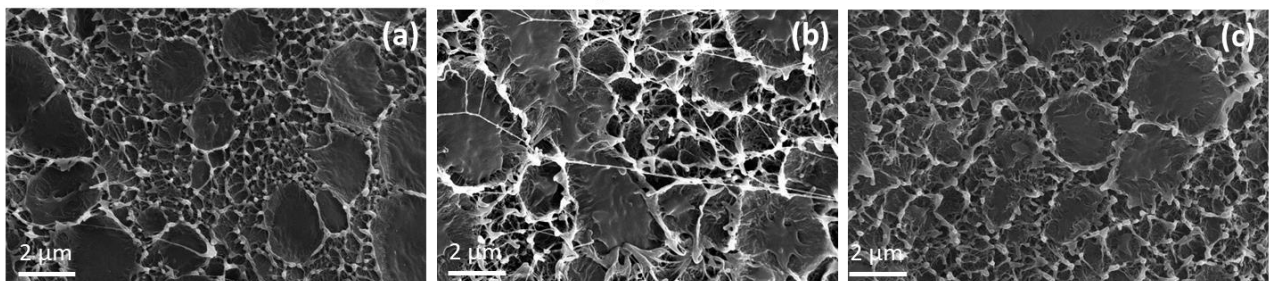
$$\omega_a = \frac{2.668 - 3.376}{0.231} \quad (5)$$

When the wetting coefficient ω_a is larger than 1, the MWCNTs prefer to stay in polymer 2, if ω_a is smaller than -1, MWCNTs prefer to be in polymer 1, the MWCNTs stay at the interface

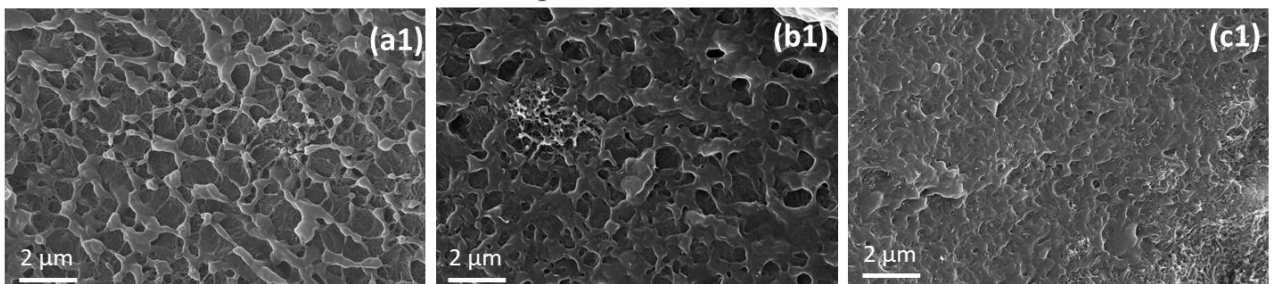
between LMDPE and EVA when ω_a is between -1 and 1 [18]. From the above measurements, it can be concluded that the MWCNTs preferentially reside in the EVA matrix.

The cross-section morphology of the LMDPE / EVA / MWCNTs composites was observed under SEM and seen in Fig. 3. Both LMDPE and EVA phases were micrometer sized and distinct phase separation is seen from the images of non-crosslinked composites. The regions with the dark colour indicate the LMDPE phase and the bright areas indicate the dispersion of MWCNTs in the EVA phase of the polymer matrix. The MWCNTs are more visible in the non-crosslinked LMDPE/EVA blend compared to the crosslinked polymer which can be attributed to the distinct phase separation and the homogeneous dispersion of MWCNTs in the EVA phase. However, for crosslinked composites, there is only one phase visible from the SEM images. After crosslinking, the LMDPE and EVA demonstrate good phase mixing and remained as a single continuous phase. There is no visible agglomeration of MWCNTs, indicating homogeneous dispersion of nanotubes in the polymer matrix. The continuous structure altered the distribution of MWCNTs in the LMDPE/EVA blend and affected the electrical conductivity of the nanocomposite. This explanation matches the AC conductivity results and contact angle measurements.

Non-crosslinked LMDPE/EVA/MWCNT composites



Crosslinked LMDPE/EVA/MWCNT composites



(a) MWCNT 0 wt.%

(b) MWCNT 1 wt.%

(c) MWCNT 3 wt.%

Fig. 3 Phase morphology of non-crosslinked and crosslinked LMDPE/EVA/MWCNT composites containing different MWCNT concentrations: (a) 0 wt.%, (b) 1 wt.%, and (c) 3 wt.% (Scale: 1 μm).

3.3 Shape memory analysis

The shape memory properties of the nanocomposites were studied using DMA analysis. The DMA cyclic stress-temperature-strain tests [21] were carried out in tensile mode by the following cyclic procedure. The sample was initially heated from 25 °C to 140 °C at a heating rate of 5 °C min⁻¹. The sample was then kept isothermally at 140 °C for 10mins. Force was uniaxially applied (0.5 N, 1 N, 1.5 N etc.) until the strain reached ~30%. The sample was kept at 140 °C for 5 minutes in the strained state before it was cooled to ambient temperature (23 °C) at a rate of 10 °C/minute. The applied force was unloaded and the sample was maintained at 23 °C for 5 minutes to fix the temporary shape. The sample was then heated to 140 °C at a heating rate of 5 °C min⁻¹ and kept at this temperature for 10 minutes to recover the original shape. The above cycle was repeated twice, the % shape fixing and % shape recovery were measured using the Eqn 6-7 [21].

$$\% \text{ Fixation} = \frac{\varepsilon_u - \varepsilon_i}{\varepsilon_s - \varepsilon_i} \times 100 \quad (6)$$

$$\% \text{ Recovery} = \frac{\varepsilon_u - \varepsilon_r}{\varepsilon_u - \varepsilon_i} \times 100 \quad (7)$$

Where ε_i is the initial strain before stretching, ε_s is the strain after stretching, ε_u is the strain after unloading and ε_r is the recovered strain after heating.

The shape memory of LMDPE/EVA nanocomposites was achieved by temporarily locking the stretched polymer chains by cooling to below the crystalline melt temperature. Once heated above the crystalline melting point, the crosslinked amorphous phase released the stored energy and provide enough force for shape recovery to happen. Shape fixing and shape recovery are important parameters to explore the mechanical properties of SMPs. These parameters are affected by the crystallization of the switchable segments and the melting of crystalline domains respectively. The three-dimensional shape memory cycle displaying the cyclic shape memory behaviour of the neat LMDPE/EVA blend and MWCNT based nanocomposites is shown in Fig. 4.

The calculated shape recovery and shape fixing ratios are summarized in Table 2. The crosslinked polymer blend has exhibited 74.1% shape fixing with 98.9% shape recovery

compared to composite with 3 wt.% MWCNTs showed 81.9% shape fixing and 100% shape recovery.

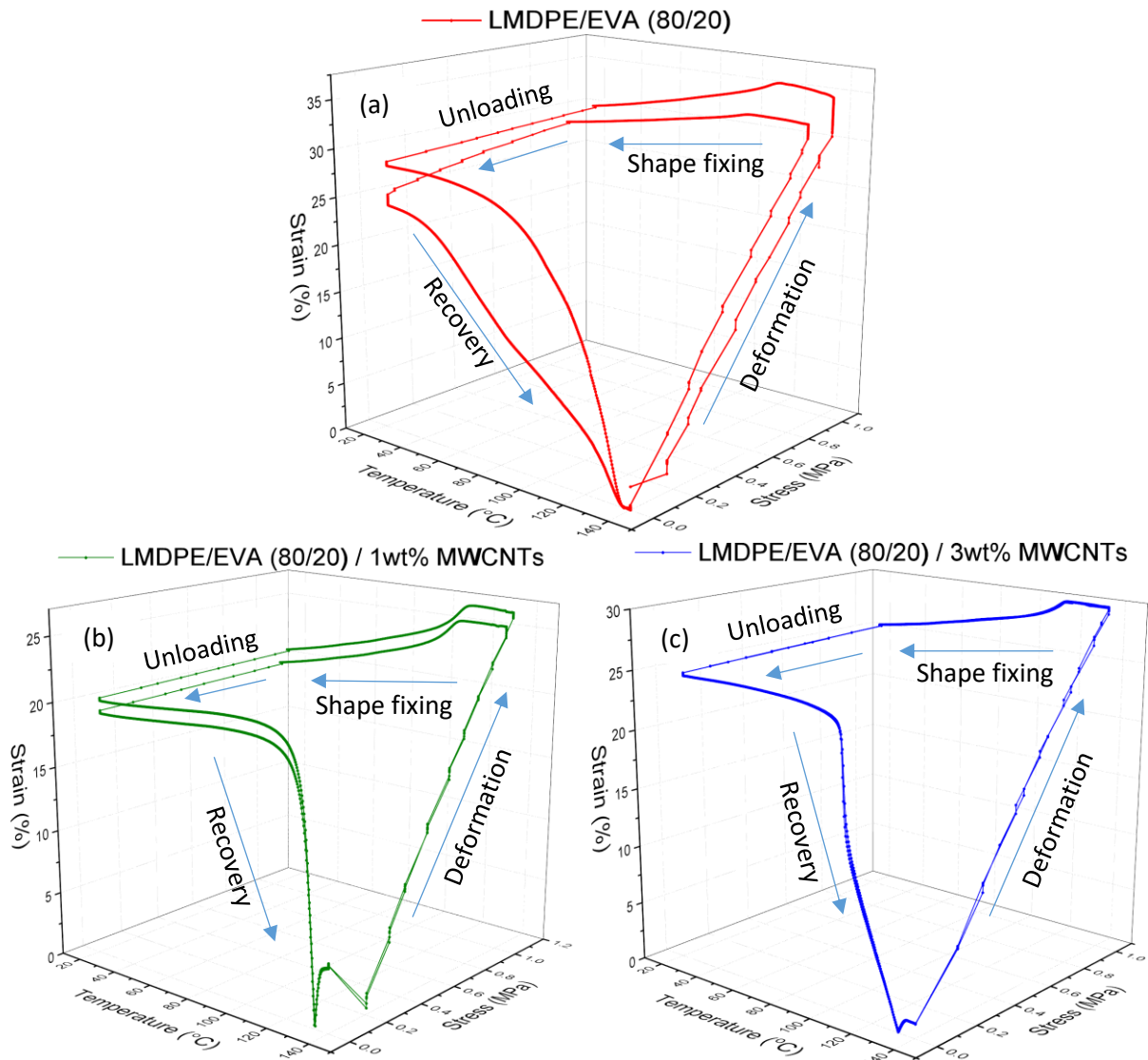


Fig. 4 shape memory stress-strain-temperature curve(two consecutive cycles) of the crosslinked LMDPE/EVA (80/20) /MWCNT composites with MWCNT concentration of (a) 0 wt.%, (b) 1 wt.% and (c) 3 wt.%.

A sharp change in % strain, above the switch temperature $\sim 80\text{ }^{\circ}\text{C}$ during the shape recovery stage was noticed with the incorporation of MWCNTs in the LMDPE/EVA blend. A reduction of % strain in the cooling step between $100\text{ }^{\circ}\text{C}$ and $80\text{ }^{\circ}\text{C}$ was evident on all the three graphs, which could be due to recrystallization and shrinkage of the polymer blend. Excellent shape

recovery (> 98%) was observed for all the three samples which indicates that high levels of chemical crosslinking has been achieved within the samples. The introduction of MWCNTs improved the **shape fixing** and the shape recovery of the nanocomposites, especially with the addition of 3wt% MWCNTs.

Table 2. Percentage of shape fixity and recovery for each sample

MWCNT concentration (wt. %)	Shape fixing (%)	Shape recovery (%)
0	74.1	98.9
1	69.2	99.6
3	81.9	100

Fig. 4 shows an improvement in recovery speed was achieved with the incorporation MWCNTs. This was noticed with the sharp change in % strain, above the switch temperature (~80 °C) during the shape recovery stage. The crosslinked nanocomposite showed a faster thermal response to the applied heat compared to the crosslinked neat polymer blend. This could be due to the improved thermal conductivity and homogenous heating of the nanocomposite with the incorporation MWCNTs. **Fig. 5 shows the shape memory response curve of the LMDPE/EVA composite with 3 wt.% MWCNTs. Shape fixing and shape recovery in response to stress, strain, temperature and time were observed from the graph.**

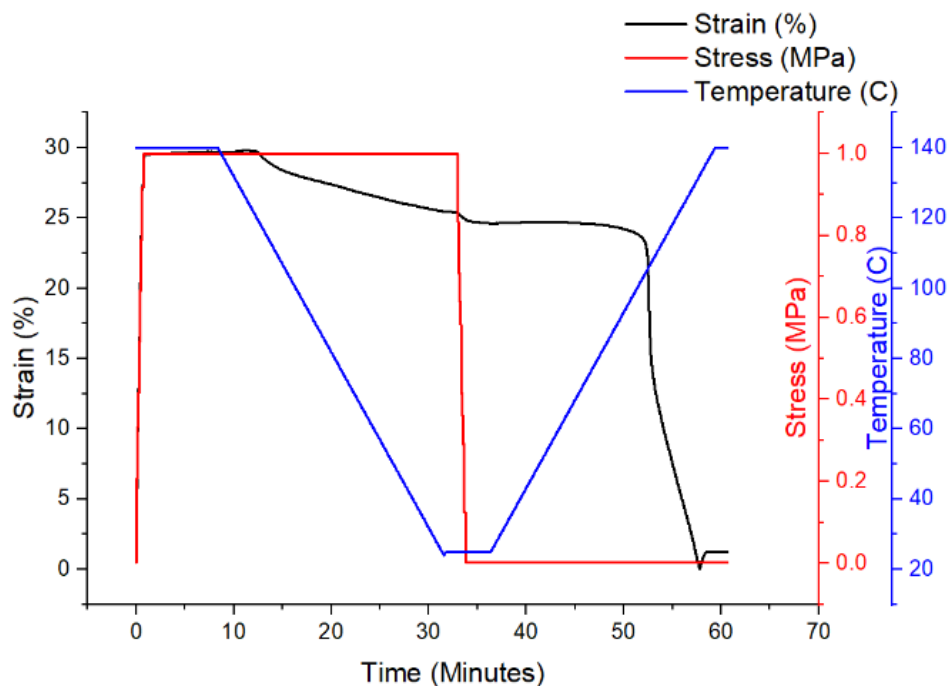


Fig. 5 Quantitative thermal mechanical cycle of the LMDPE/EVA nanocomposite with 3 wt.% MWCNTs.

4. Conclusions

This study has developed a LMDPE/EVA based shape memory nanocomposite with enhanced shape recovery performance by incorporating MWCNTs. The LMDPE/ EVA blend had distinct phase separation prior to chemical crosslinking, and co-continuous phases after crosslinking. The electrical conductivity of the composites relied on the distribution of MWCNTs and the phase morphology. A percolation threshold of the non-crosslinked LMDPE/EVA/MWCNTs composites was achieved at 3 wt.% MWCNTs. The chemical crosslinking of the LMDPE/EVA polymer blend reduced the AC conductivity of the nanocomposite by changing the phase morphology and altering the distribution of MWCNTs. Shape recovery > 98% was observed for the crosslinked composites. The introduction of MWCNTs further improved the **shape fixing** and the shape recovery of the composites. With 3 wt.% MWCNTs, the crosslinked LMDPE/EVA/MWCNT nanocomposite **showed a combination of high electrical conductivity and excellent shape memory properties without significantly compromising the mechanical properties.** The formulation optimization to achieve the balance of properties for manufacturing the LMDPE/EVA/MWCNT shape memory nanocomposites in an industry friendly process will benefit a range of applications from high power systems to smart devices.

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