

Electroactive shape memory performance of polyurethane composite having homogeneously dispersed and covalently crosslinked carbon nanotubes

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Abstract

The electroactive shape memory of carbon nanotube-filled polyurethane composites, prepared by conventional blending, *in-situ* and cross-linking polymerization, is studied in terms of the dispersion of the tubes. The covalently bonded tubes are homogeneously dispersed within the polyurethane by introducing carboxyl groups on the sidewall of the tubes and selecting a cross-linking polymerization method. The resultant composites, which have 92% shape retention and 95% shape recovery, are expected to be used as preferential materials in various actuators.

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1. Introduction

Carbon nanotubes have been considered as an ideal reinforcing agent for high-performance polymeric composites due to their excellent structural, mechanical and electrical properties [1, 2]. However, the homogeneous dispersion of the tubes within polymer matrices still presents a challenge. Various methods have been examined in efforts to overcome this problem, such as mechanical mixing [3], chemical functionalization of the tubes [4-6], and the utilization of organic [7, 8] and polymeric surfactants [9] via non-covalent interactions. An *in-situ* polymerization [10], where nanotubes are incorporated into the prepolymer during the polymerization process, has been utilized to provide carbon nanotubes-reinforced composites with enhanced mechanical properties. On the other hand, the functionalization of carbon nanotubes is also very effective in preparing soluble carbon nanotubes by generating structural defects in strong acid [11, 12], and inducing a chemical reaction between alkyl groups and azide moieties [13], and π - π interaction with electron-rich molecules [6, 14].

This work is focused on the effects of the controlled dispersion structure of the tubes on the mechanical and electroactive memory of conductive polymeric composites. Carbon nanotubes generally aggregate to form bundles, and their dispersion structure strongly depends on the physical and chemical interactions between the tubes and the surrounding solvents or polymers. In this study, we have attempted to control the dispersion structure of the tubes in polymer matrix via *in-situ* and cross-linking polymerization [15, 16]. A comparison of these two methods might be useful for finding an effective way of controlling the dispersion structures of the tubes within the

polymer matrix as well as the electroactive memory of electrically conductive polymeric composites. In order to achieve this goal, we chose a polyurethane block copolymer as the polymer matrix due to its excellent shape memory, which is caused by the phase separation between hard and soft segments and thermo-responsive transitions corresponding to soft segments [17], together with acid-treated multi-walled carbon nanotubes (MWCNTs) as the reinforcing filler rather than carbon black [18]. Subsequently, we prepared polyurethane composites reinforced with carbon nanotubes using three different polymerization methods (namely conventional blending, *in-situ*, and cross-linking polymerization), and performed a comparative study of the dispersion structure of the carbon nanotubes and their effects on the mechanical and electroactive shape memory of three types of polyurethane composites filled with nanotubes.

2. Experimental

MWCNTs (Iljin Nano Tech) with a diameter of 10-20 nm and an average length of 20 μm were used after being subjected to chemical modification in a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ (1:3 molar ratio) at 90°C for 10 min. Poly(ϵ -caprolactone)diol (PCL, Solvay Co., MW=3,000 g/mol), 4,4'-methylene bis(phenylisocyanate) (MDI, Junsei Chemical), and 1,4-butandiol (BD, Ducksan Chemical) were used for the synthesis of PU. For the *in-situ* polymerization, the specified weight fractions of the acid-treated MWCNTs were dispersed in PCL. After that, MDI was added to this mixture to obtain prepolymers by the reaction between the $-\text{OH}$ groups of the polyol and the $-\text{NCO}$ groups of MDI at 80°C for 90 min. In this case, most of the reaction between $-\text{OH}$ and

–NCO occurs since the carboxylic groups in acid-treated MWCNTs have relatively low reactivity in comparison to the reaction between PCL and MDI molecules. Finally, BD was added to the prepolymer in order to obtain nanotube-filled polyurethane composites by *in-situ* polymerization. Regarding the cross-linking polymerized composites, the prepolymer was prepared from a reaction between MDI and PCL under the same conditions as the *in-situ* polymerization, after which a calculated amount of tubes was added to the prepolymer at 110°C and the mixture was left for 150 min in order for covalent bonds to form between the –OH groups of the acid-treated MWCNTs and the –NCO groups of the prepolymer. As a comparative sample, we have prepared the conventional composites by blending carbon nanotubes with polyurethane using a mixed solvent consisting of tetrahydrofuran (THF) and dimethylformamide (DMF) (1/1 w/w). In all cases, the added amount of tubes with respect to polyurethane was fixed at 4 wt%. We have prepared composite films having a thickness of ca. 150 μm by casting nanotube/polyurethane emulsions on a clean, flat-base Petri dish and drying in an oven.

Raman spectroscopy (Kaiser, 633 nm) was used to measure the structural changes of the carbon nanotubes resulting from the acid treatment. X-ray photoelectron spectroscopy (XPS) (ESCA2000) was adopted in order to measure the surface composition of the nanotubes. Transmission electron microscopy (TEM) measurements were carried out in order to observe the morphology of the nanotubes by using TEM-2000FX2 (JEOL), while the surface topology and the current images of the spin-coated samples were obtained by contact-mode atomic force microscopy (AFM) (Seiko Instruments Inc., SPA-300HV + SPI-3800N). Finally, the shape memory test of the composite films was carried out within a controlled thermal chamber, as described

in our previous report [17]. The electroactive shape memory properties of shape recovery and shape retention were evaluated by applying constant electric voltage while monitoring the temperature and the length of the samples [16].

3. Results and Discussion

The dispersed state (or structure) of the nanotubes within the polymer matrix is influenced by the surface properties of the carbon nanotubes. In order to confirm the modification of the surface properties of the tubes resulting from the acid treatment, Raman, XPS, and TEM measurements were carried out for both the pristine and the acid-treated tubes (figure 1). The relatively increased R value (I_D/I_G , which is the intensity of the D band at 1325 cm^{-1} divided by the intensity of the G band at 1580 cm^{-1}) of the acid treated tubes (figure 1(a)) indicates the effective generation of structural defects on the sidewall of the nanotubes [19]. XPS clearly supports the introduction of chemical moieties on the sidewall of the tubes via acid treatment (figure 1(b)). In the case of the pristine tubes, there are peaks at 285.5eV , 286.5eV , and 287.5eV corresponding to C-C, -C-O-, and -C=O bonds, respectively. However, a newly observed peak at 288.9eV in the acid-treated tubes indicates the introduction of -COO- groups [20]. TEM observations also support the effectiveness of acid treatment for the introduction of defects and chemical moieties (figure 1(c)) since the relatively long straight fringes are easily transformed into short corrugated fringes by generating structural defects preferentially on the sidewall of the tubes.

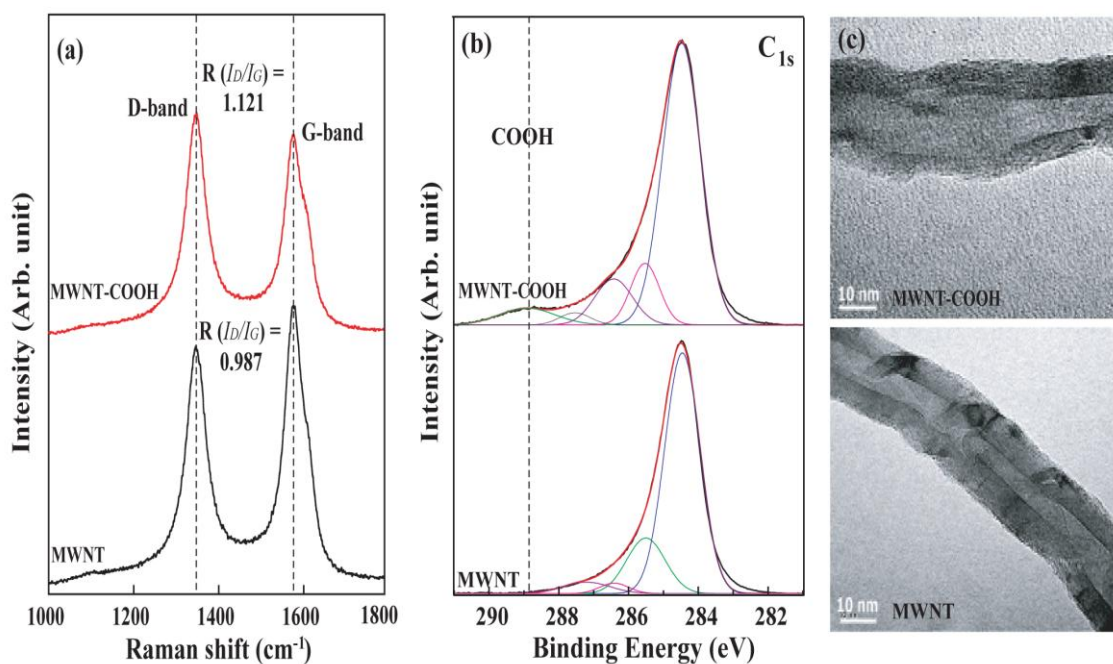


Fig.1. (a) Raman spectra, (b) C1 XPS spectra, and (c) TEM images of pristine and acid-treated multi-walled carbon nanotubes.

In order to compare the dispersion state of carbon nanotubes within the polyurethane, we performed detailed TEM and AFM observations on the spin-coated samples (figure 2). From the TEM images (figure 2(a)), *in-situ* and cross-linking polymerized composites have more black dots and lines, indicating the homogeneous dispersion of carbon nanotubes, while the conventionally blended composite has aggregated tubes due to poorly dispersed tubes. These results can be explained by the interaction between the nanotubes and the polyurethane molecules [16, 21]. We also confirmed the enhanced dispersion structure of the tubes in cross-linking polymerized composites, based on the presence of bright spots from the topographical AFM mapping images (figure 2(b)) and current AFM images (figure 2(c)) [22].

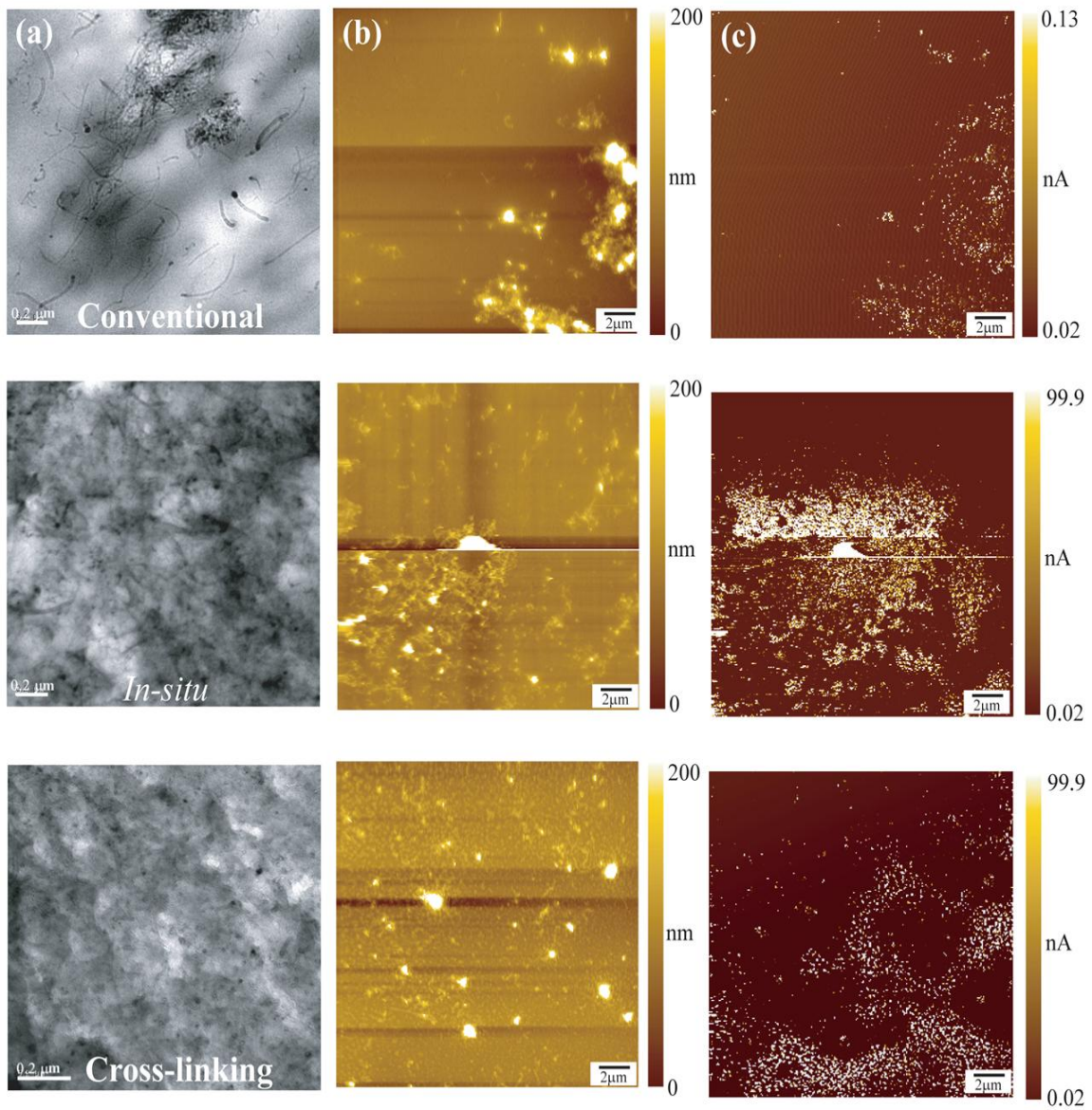


Fig.2. (a) TEM images, and (b) topographical and (c) current mapping AFM images for the polyurethane composites, prepared by conventional blending, *in-situ*, and cross-linking polymerization.

From the above results, it was concluded that cross-linking polymerization is the

optimal way to disperse the tubes homogeneously within the polyurethane matrix. Here we suggest a blocking effect of the cross-linked polymer chains with respect to the tubes, where the covalently bonded tubes/polymer chains effectively prevent the re-aggregation of the tubes, thus fixing the tubes within the polyurethane matrix in a homogeneous distribution. Regarding the polyurethane composites prepared with *in-situ* polymerization, it is possible for the nanotubes to reorganize themselves in an aggregated form since they are physically dispersed within the polyurethane matrix. Consequently, we achieved the homogeneous dispersion of covalently fixed carbon nanotubes within the polyurethane matrix through the judicious selection of cross-linking polymerization (figure 3(a)).

It is noteworthy that the differences in the dispersion structure of the tubes depending on the polymerization method lead to differences in the physical properties of the resultant composites. For example, carbon nanotubes have been utilized as highly conductive routes for the purpose of increasing the electrical conductivity of various composites. In the case of materials possessing conductive shape memory [16, 21], the variation of the surface temperature due to electric heating caused by the application of voltage is closely related to the dispersion structure of the tubes within the polymer matrix. In this regard, we compared the electroactive shape memory of composites prepared by conventional blending, *in-situ* and cross-linking polymerization (figure 3(b) and 3(c)). A twofold improvement of the thermomechanical properties of the samples prepared with *in-situ* and cross-linking polymerization which has an elongation of up to 200% was observed in comparison to that of the conventionally blended sample (figure 3(b)). When the samples were elongated up to 200%, they were unloaded after quenching to room temperature using liquid nitrogen. Finally, the

change in length of the samples due to the applied electric voltage of 40 V was measured in order to obtain shape recovery (figure 4). The highest shape retention (92%) and shape recovery (95%) were observed for the composite prepared with cross-linking polymerization (figure 3(c)), whereas a shape recovery of 92% and 83% was obtained for the composites prepared by *in-situ* polymerization and conventional blending, respectively.

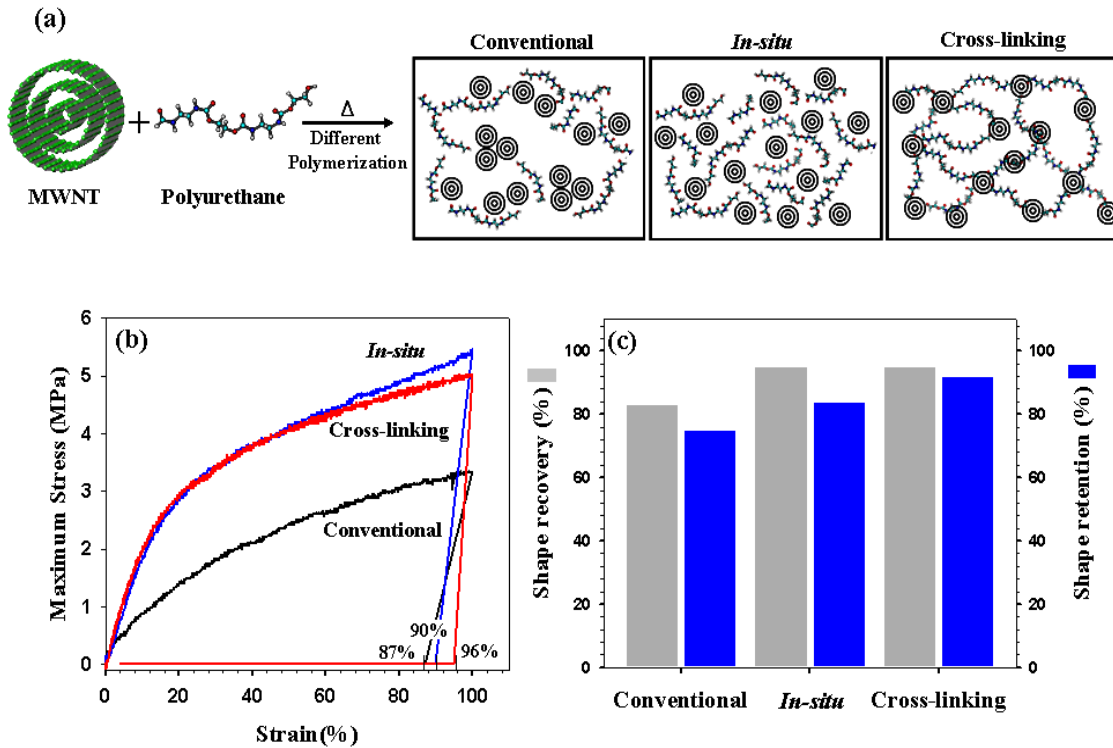


Fig.3. (a) A schematic representation of the controlled dispersed structures of the tubes within the polymer matrix, (b) thermomechanical properties curves (200% elongation at 50°C), and (c) shape recovery and shape retention (quenching/unloading and subsequently applying an electric voltage of 40 V) for the polyurethane composites prepared by conventional blending, *in-situ*, and cross-linking polymerization.

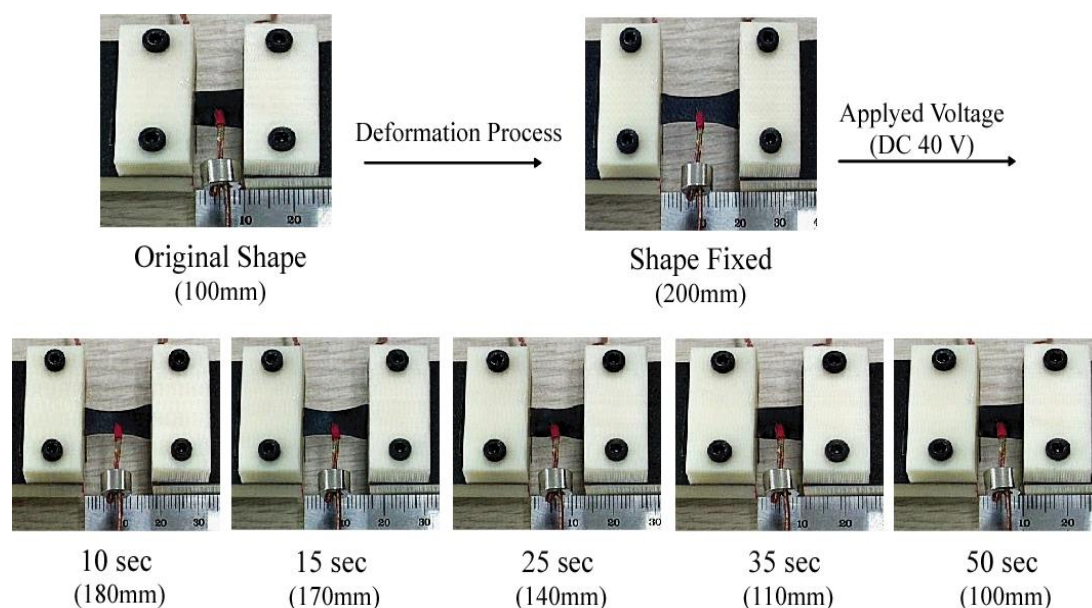


Fig.4. Pictures describing the electroactive shape recovery behavior of MWCNTs (4 wt%)-reinforced polyurethane-derived composite. The sample undergoes the transition from temporary shape (original length: 100mm) to permanent (deformation length: 200mm) within 60 seconds when a constant voltage of 40V was applied.

The variation of the surface temperature of the conductive polymer composites due to the application of electric power can be used as an effective indicator of the dispersion structure of the nanotubes (figure 5(a)). By applying an electric voltage of 40 V to the composites, we measured the temperature as a function of time. It is noteworthy that the surface temperature increased up to 100°C within 60 seconds in the composite prepared by cross-linking polymerization. However, the conventionally blended composite reached an equilibrium temperature of 38°C within 20 seconds. Interestingly, the patterns of the increasing surface temperature are very similar to those of the shape

recovery curves (figure 5(b)) for all samples. The sample prepared by cross-linking polymerization exhibits the highest increase rate for shape recovery with respect to time, and soon reaches an equilibrium shape recovery state. From these results, it is expected that the variations of the surface temperature can be utilized as an indirect indicator for evaluating the electroactive shape recovery behavior of our conductive polyurethane composites since both properties are strongly influenced by the dispersion structure of the tubes.

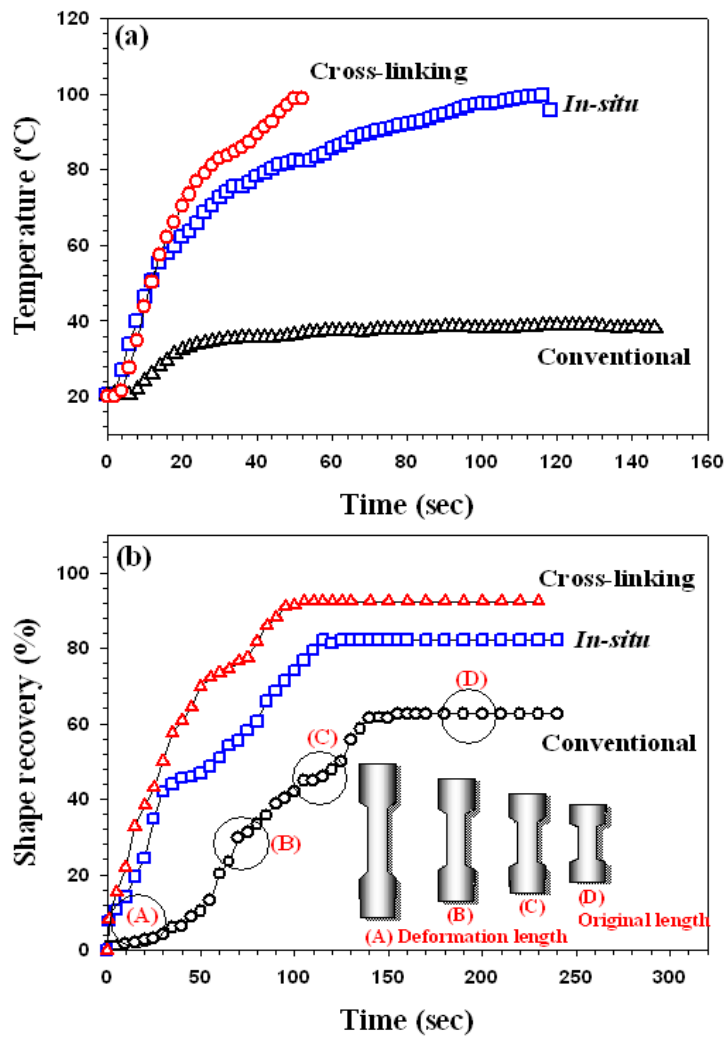


Fig.5. The fluctuations of the surface temperature and the shape recovery for the polyurethane composites prepared by conventional blending, *in-situ* and cross-linking polymerization for a voltage of 40V.

4. Conclusions

In conclusion, we succeeded in controlling the dispersion structure of the tubes in polyurethane composites filled with nanotubes by using conventional blending, *in-situ*, and cross-linking polymerization methods. We found that the optimal dispersion structure of the tubes within the polyurethane matrix is achieved by using chemically modified carbon nanotubes with carboxyl groups on their walls together with the cross-linking polymerization method. The covalently linked nanotubes/polyurethane hybrid structure effectively prevents the re-aggregation of the tubes within the polymer matrix. The composites prepared by cross-linking polymerization exhibited superior mechanical and shape memory properties in comparison to the ones prepared with *in-situ* polymerization and conventional blending. We found that both the surface temperature and the shape recovery with respect to the applied electric voltage were strongly influenced by the dispersed structure of the tubes in polyurethane composites filled with nanotubes. Both the homogeneous dispersion of carbon nanotubes within polyurethane and the covalent bonds between them are critical conditions for achieving high-performance shape memory.

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