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Shape memory effect of polymeric composite materials filled with NiMnSbB shape memory alloy for textile materials

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Abstract

The aim of the study was to obtain a smart textile material with shape memory alloys. NiMn-based shape memory alloy was produced by arc melting system for this purpose. Phase transition temperatures of the fabricated alloy were determined by using differential scanning calorimeter (DSC). The crystallographic structure of the fabricated alloy was characterized by x-ray diffractometer (XRD). The fabricated shape memory alloy was converted to the particle form and filled into polymer matrix to obtain shape memory effect of this polymeric composite material. Polymeric composites (PCs) were produced in film form and shape training of PCs were studied under different conditions. The shape memory behavior of samples was investigated into the water for fast response during applying heat. Damping capacity of composites was measured by using dynamic mechanical analyzer (DMA) according to temperature rising. The shape recovery was observed under certain stimuli on the SMA filled polymeric composites.

1. Introduction

Smart textiles have a crucial role in textile industry. Shape memory materials (SMMs) are one of the distinct smart materials due to their stimuli-responsive structure. SMMs are capable to change their properties by responding to external factors. These changes enable some new functions or adapt the materials to change in the shape by the effect of external factors such as temperature, stress, magnetic or electrical fields [1, 2]. Various alloys, polymers, ceramics, and gel structures are materials that have shape memory effect. In textile applications, shape memory polymers (SMPs) are used as filament, foam or coating/lamination materials and shape memory alloys (SMAs) are used as wires and fiber coating and also, can be used as fillers in reinforced composites to improve tensile properties [3–9]. While, SMAs are widely used in many industrial areas ranging from the automotive to medical products, they have limited usage in textile applications [10–12].

SMAs are stimuli-responsive materials and able to change their structure under the right stimulus. Shape change is based on phase transformations between austenite and martensite phase. During the deformation, phase transformation occurs and causes to change in the physical and mechanical properties of alloys. Austenite start temperature ($A_s$), austenite finish temperature ($A_f$), martensite start temperature ($M_s$) and martensite finish temperature ($M_f$) are the four characteristic temperatures of SMAs. Austenite, called parent phase, is stable phase at high temperature and the martensite is softer phase at lower temperatures. SMA transforms from martensite to austenite phase when it is heated. This transformation starts with $A_s$ and completes at $A_f$. When SMA heated above $A_s$, it recovers into its original shape. During the cooling, the martensitic transformation starts at $M_s$ and completes at $M_f$. For martensitic transformation of SMAs, the shape memory effect (SME) is a distinctive property. The reverse transformation temperature is the critical temperature for recovering the original shape upon heating after the alloy is deformed in low temperature [13, 14].

The motivation of the study is to achieve shape memory composites for textile materials by adding shape memory alloy particles into a polymer matrix. Thus, it is expected that the structures having shape memory effect can be transformed by stimulating with body temperature and this shows that it can be used in medical products such as corsets, medical products like bandages, or various textile products with functional structure.
As it is different from the NiTi shape memory alloy which have been widely studied, we used NiMn-based ferromagnetic alloys. This alloy was prepared in different atomic ratios and bulk material is produced by using arc-melting method. After determination the transformation temperatures of alloys, pieces were cut from bulk alloy materials and mechanically crushed in agate mortar. This SMA particles were filled into polyvinyl chloride (PVC) coating polymer in emulsion form to observe the shape recovering of composite materials after reaching the suitable transformation temperature. Fundamental of this study is to produce the SMA and fabricated the SMA filled polymeric composite with good shape memory effect (SME) and/or super elasticity (SE) properties.

2. Materials and methods

The NiMn-based alloys are produced as Ni$_{50}$Mn$_{36}$Sb$_{11}$B$_{3}$ (at%) in composition by using Nickel (Ni, 99.8%), Manganese (Mn, 99.6%), Antimony (Sb, 99.5%), and Boron (B, 99.9%) metal powders. Alloy was fabricated by the vacuum arc-melting method and the ingot was melted several times to provide homogenization and then annealed under argon atmosphere at 900 °C for 17 h [15]. NiMnSbB alloy was fabricated to use as filler in the polymer matrix. Thus, fabricated ingot alloy was cut into pieces and reduced to particles form as seen in figure 1 by applying mechanical force and crushing in agate mortar. The size of obtained SMA particles are varied between 150–250 μm range.

PVC coating polymer in emulsion form was used as polymer matrix to reinforce the alloy particles and be aimed to identify the shape memory effect of the NiMnSbB particles.

2.1. Preparation the shape memory composites

NiMnSbB SMA particles were reinforced into PVC polymer at 1, 2, 3 wt% and homogenously mixed and then the polymeric composites were applied onto a flat Teflon surface as a film form in about 0.26 mm thickness, and dried at 160 °C for 15 min. The strips (width: 5 mm, length 75 mm; thickness: 0.26 mm) were cut from these composite films as seen on figure 2 and then shape training studies were carried out for memorizing the temporary shape to samples. Shape training studies of samples were carried out in 75 °C for 5, 10, and 15 min. The temperature was selected as 75 °C that is above the austenite finish temperature. Spiral form was given as the temporary shape at room temperature and then samples were put into hot water at 75 °C for 5, 10, and 15 min, separately. After then samples were rapidly cooled into iced water to store the temporary shape.

The crystallographic structure of alloys was investigated by x-ray diffraction (XRD) using Philips X’Pert Pro diffractometer with a $2\theta$ step and Cu Kα radiation with a scanning speed of 0.08° s$^{-1}$. The transformation temperatures of the samples were determined by using Perkin Elmer differential scanning calorimeter (DSC) at a temperature range between −40 °C–150 °C in a nitrogen environment with a 10 °C min$^{-1}$ heating-cooling ratio. Damping capacity (tan δ) of composites was measured by using TA Instrument dynamic mechanical analyzer (DMA) in a temperature range from 30 °C to 100 °C. The test parameters used were frequency of 1 Hz, ramp rate 1 °C min$^{-1}$, and amplitude 15 μm. The typical dimensions (lengthxwidthxthickness) of the composite samples tested on the DMA were 6 mm × 3.5 mm × 0.26 mm.

Figure 1. (a) Metal powder mixture; (b) fabricated SMA; (c) SMA particles.

Figure 2. Strip form of polymeric composite.
3. Results and discussions

3.1. Structural properties of alloys
Crystallographic structure of fabricated NiMnSbB alloys were investigated and the XRD patterns of the NiMnSbB alloy are shown in figure 3. The intensity and sharpness of the peak at $2\theta = ~43^\circ$–$44^\circ$ (220) is signaling the crystallization of the L2₁ structure of NiMnSb and corresponding to a well crystallized structure [16, 17]. Also, a few weak peaks exhibit the presence of NiSb and MnSb phases.

3.2. Transformation temperatures of alloys
DSC curve of the NiMnSbB alloy is shown in figure 4 and it was observed that fabricated alloy showed reversible phase transformation. According to DSC result, martensite start ($M_s = 36.32^\circ$C) and martensite finish ($M_f = 27.70^\circ$C), and austenite start ($A_s = 45.15^\circ$C) and austenite finish ($A_f = 57.68^\circ$C) temperatures were determined.
The surface morphology of 3 wt% NiMnSbB particle filled PVC composite can be seen in figure 5 in different magnifications and indicates that the particles were homogeneously distributed in the PVC matrix. The bright ones belong to the NiMnSbB particles. Interlocking between the filler and polymer matrix can be seen in figure 5(b).

3.3. Shape memory effect of composites

According to transition temperatures of filler that was aimed to observe shape memory behavior of composite material. The samples were dipped into water to observe their rapid response against thermal stimulus. Shape memory effect of the PVC composite samples against temperature are shown in figures 6–8. In training process,
Figure 6. Images of thermally induced 1% NiMnSbB particle filled PVC polymeric composites.

Figure 7. Images of thermally induced 2% NiMnSbB particle filled PVC polymeric composites.

Figure 8. Images of thermally induced 3% NiMnSbB particle filled PVC polymeric composites.

Figure 9. Images of thermally induced pure PVC samples.
the spiral form was given to the samples as a temporary shape. It can be seen that all composites memorized its temporary shape between 24 °C and 38 °C and the sample exhibited recovery to the flat permanent shape above 48 °C. In these figures, a; the sample trained for 5 min, b is the sample trained for 10 min and c is the sample trained for 15 min.

As can be seen in figures 6 and 8, duration is important for shape training studies for samples waited for 5 min 10 and 15 min are efficient waiting times to memorize the temporary shape. When heat was increased, above the austenite start temperature, samples returned to their flat permanent shape. The pure PVC samples are seen in figure 9 and cannot be seen any response to temperature.

Tan δ for the SMA filled composite and pure PVC was measured during heating cycle to compare the damping values and the variation of Tan δ depending on temperature can be seen in figure 10. When the composites were heated, martensite state of alloy began the reverse transformation. Based on the damping values of samples, it can be seen in figure 10, 1 and 3 wt% composite showed damping capacities of the austenite and PVC polymer at 48 °C. But the composite filled with 1 wt% could not be measured above 60 °C. The composite filled with 2 wt% exhibited similar effect like pure PVC. The peak in tan δ at 100 °C was caused by a peak in damping capacity of the PVC.

4. Conclusions

The shape memory alloy was prepared with predefined metal elements and their combinations unlike the commercial and known products. Phase transformations between 45 °C and 50 °C were found to be effective transformation temperatures for Ni₅₀Mn₃₆Sb₁₁B₃ alloy particles. It was observed that the best shape memory effect was obtained at 3 wt% SMA particles filling to polymer according to the DMA results and shape memory effects.

Thus, composite materials can be produced by combining with the good shape memory characteristic of SMAs and a polymer material for textile applications. NiMnSbB SMA particles into a polymer in emulsion form was to produce shape memory materials which is adapted in textile structures. New compounds with different elements and compositions can be produced to provide a new phase transformation temperature around 35 °C. Therefore, new composite structures can be obtained in relatively lower temperatures.

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