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Shape Memory Performance in Composites with the addition of TiO_2

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Shape memory polymers (SMPs) are smart materials that can change their macroscopic properties such as shape and colour with the effect of external stimuli and return to their original state when the stimulating effect is removed. Factors such as heat, light, magnetic field, electric field, and pH are accepted as external stimuli. There are basically two requirements for obtaining the shape memory effect (SME). The first is that the polymer has a stable network structure. The other is that the polymer has key points that allow it to change shape under certain stimulating effect and to reinstatement when the effect is removed. Shape memory polymers are advantageous in that they are light, low density, easy to produce, have high biodegradability and easily adaptable glass transition temperature. However, there are some difficulties that prevent the use of these materials in practical applications. One of the main disadvantages of shape memory polymer applications is their relatively low mechanical properties, and particularly recovery stress. In order to overcome such disadvantages, significant advances have been made by incorporating various reinforcing materials into the shape memory polymer. Therefore, in this study different proportions of TiO_2 nanomaterial were added to the Poly (Vinyl Alcohol) (PVA) matrix in order to improve its shape memory property. Thermal, spectral, chemical, and structural characterizations of the obtained composites were made using DSC/TGA, FT-IR, SEM/EDS, and XRD analysis methods. In addition, shape memory performances were determined by the bending test.

Keywords: *Poly (vinyl alcohol), Shape memory composites, Bending test.*

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1. Introduction

The active action of polymers can be in two forms, shape fixity capacity and shape recovery capacity. The polymer's having these two properties depends on the presence of regions sensitive to external stimuli in its structure. One of them is that the polymer has fixed points of cross-linking and a network structure of polymer segments. Another is that the polymer has secondary cross-linking between polymer segments that allow the temporary shape to be fixed [1, 2]. According to these theories, the temporary shape is fixed by the formation of secondary cross-linking by providing appropriate programming conditions. The recall of the permanent shape is determined by the presence of primary cross-links and the entropic properties of the polymer segments between them [3].

Shape memory polymers (SMPs) and shape memory polymer composites (SMPCs) are expected to play a leading role in providing smart materials of the future for new and advanced applications. It is anticipated that there will be an increase in future research activities for these materials, which attract the attention of materials scientists and engineers. It is hoped that in future studies the current difficulties preventing the use of these materials in practical applications will be resolved. One of the main disadvantages of shape memory polymer applications is their relatively low

mechanical properties, and particularly recovery stress. Above the transition temperature required to initiate shape recovery, shape memory polymers exhibit mechanical properties that are not good enough. For this reason, various types of reinforcements are included in the shape memory polymer and studies on materials that have high shape memory property with minimum effect are focused on [4].

2. Materials Method

In this study, transparent, porous Tio_2 purchased from Arıteks Nanotek company was used. The surface area of this material, which is used as a filler in the produced shape memory polymer composites, is 90 m^2 and the average particle size is 14 nm. The PVA solution used as a matrix in composite materials was prepared as mentioned in our previous study [5]. PVA/TiO_2 nanocomposites are produced in three different compositions using the solvent method [6, 7]. For the production of PVA/TiO_2 nanocomposite material, 0.01 g TiO_2 nanomaterial was added to the prepared 50 mL PVA solution. Then the mixture was stirred in an ultrasonic mixer for 1 hour. Finally, the homogeneous mixture was left at room temperature for 48 hours to dry. After these processes, at the ratio of 50/0.01, PVA/TiO_2 nanocomposite material named 'SMPC-1' was obtained. The same steps have been carried out for the production of shape memory PVA/TiO_2 polymer composites named 'SMPC-2', at the ratio of 50/0.02, and 'SMPC-3', at the ratio of 50/0.03.

3. Results and Discussion

The DSC and TGA curves that allow the thermal properties of the shape memory polymer nanocomposites to be determined are given in Fig.1. The glass transition temperature (T_g) of the PVA polymer was determined as 81.10 °C in our previous study [8]. According to the DSC curves, as TiO_2 nanomaterial is included in the PVA matrix, it is determined that the T_g increases to 83.68, 95.23, and 100.63 °C for SMPC-1, 2, and 3 samples, respectively. Restriction of the mobility of PVA chains by TiO_2 layers is thought to cause this value to increase. Therefore, it can be said that a strong interfacial interaction occurs between the TiO_2 layers and the PVA matrix [9]. The melting temperatures (T_m) associated with decomposition are 204.86, 204.84, and 202.81 °C for SMPC-1, 2, and 3 samples respectively, and the enthalpy values corresponding to the T_m were calculated as 0.41, 7.78, and 11.30 J/g. As TiO_2 additive ratio increases, the decrease in T_m values is related to the irregular arrangement of the PVA chains damaged by the nanomaterial layers [10]. TGA thermograms were obtained by sampling 4-6 mg of synthesized materials. When these thermograms are examined, a three-stage degradation curve is observed. The loss of mass in the first region is due to the removal of moisture created by the water molecules in the polymer. The mass losses in this region are 7.808, 10.404, and 9.935% for the SMPC-1, 2, and 3 samples, respectively. The second and largest mass loss is related to the direct degradation of the PVA polymer and occurs as a result of the separation of the main and side chains in the PVA structure. For the SMPC-1 material, the mass loss in this region occurred after about 254 °C is 51.183%. For the SMPC-2 material, the loss of mass in this region occurs after about 262 °C, for the SMPC-3 material after 267 °C and they are 56.549 and 61.586% respectively. As the TiO_2 additive ratio increased, the decomposition starting temperature of the materials increased. Therefore, it can be concluded that the TiO_2 additive increases the thermal durability properties of the PVA structure. The third mass losses due to fragmentation of PVA main chains are 18.624, 26.703, and 23.974% for SMPC-1, 2, and 3 materials, respectively [11].

In Fig.2, FT-IR analysis results of the synthesized shape memory nanocomposites and the purchased TiO_2 nanomaterial are given. In the FT-IR spectrum of TiO_2, the absorption band at 3245 cm^{-1} is related to stretching and 1618 cm^{-1} to bending vibration of O–H, representing the water as moisture. The intense peak at 653 cm^{-1} wavenumber expresses the Ti–O stretching band which is the characteristic peak of TiO_2 [12]. The characteristic peaks obtained for PVA given in our previous study were determined in almost the same wavenumber for composites obtained by the addition of TiO_2 [5]. This shows that TiO_2 addition does not disrupt the PVA structure. It has been observed that the peaks, which associated with –OH stretching and observed at 3200-3300 cm^{-1} wavenumber for shape memory composites, are less severe than the peak observed at 3270 cm^{-1} for PVA. This indicates that hydrogen bonding between hydroxyl groups in PVA chains is reduced [13]. When the FT-IR spectra were examined, it was concluded that the obtained characteristic peaks were compatible with the literature.

The structural information of the materials was determined by XRD analysis and the results are given in Fig.4. It can be seen from the graph that a tetragonal crystal structure is formed in the anatase form of TiO_2 [15, 16]. Failure to observe a different phase peak indicates that the product is pure and well crystallized. In our previous study, the characteristic peak of the PVA polymer observed at $2\theta=19.601°$ according to the XRD spectrum of the PVA polymer corresponds to the (101) plane [5]. In the XRD spectrum of the nanocomposites (especially in the XRD patterns of SMPC-2 and SMPC-3) obtained by adding the TiO_2 nanomaterial to the PVA matrix, it is observed that the characteristic peaks of the TiO_2 nanomaterial completely disappear and a single peak is formed. This result shows that

TiO_2 is homogeneously distributed in the matrix without disturbing the PVA structure [17, 18].

Shape memory properties of shape memory polymer nanocomposites were examined by the bending test as detailed in our previous study [5]. The data obtained as a result of the bending test applied five times to determine

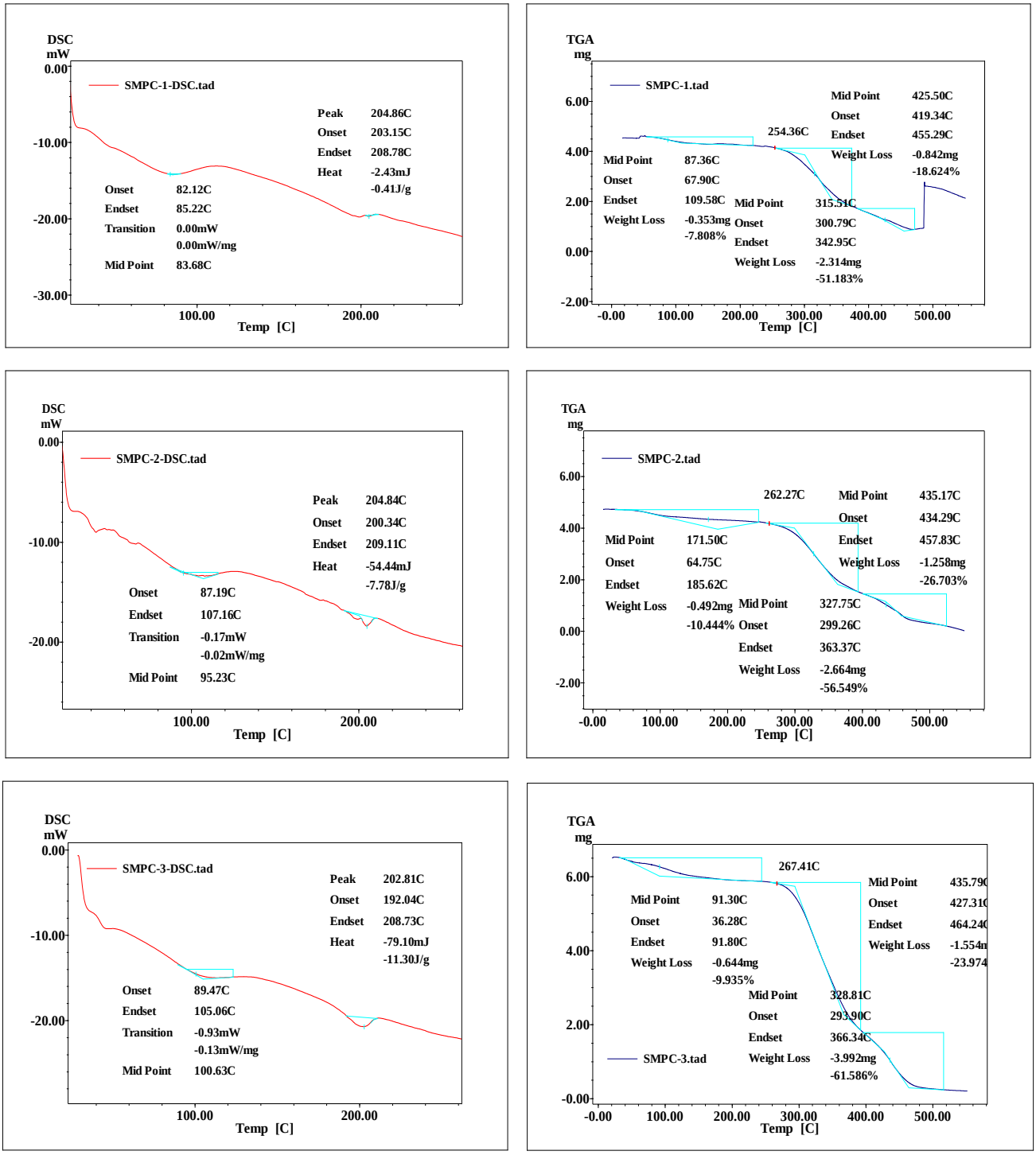

Fig.1. The DSC-TGA analysis of SMPC-1, SMPC-2, and SMPC-3

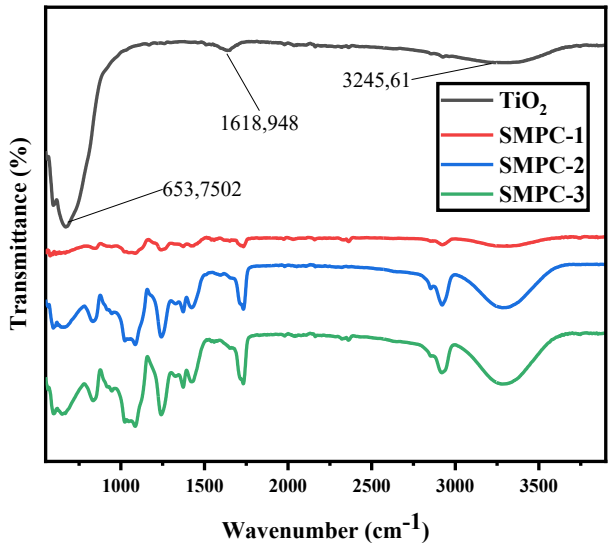

Fig.2. FT-IR analysis of the materials

Table 1. Shape memory property parameters of the samples.

Number of Cycles	θ_c (°)	θ_e (°)	R_f (%)	R_r (%)	
2	178	2	98.89	98.88	SMPC-1
3	178	3	98.89	98.31	
4	178	5	98.89	97.19	
5	178	5	98.89	97.19	
1	180	0	100	100	SMPC-2
2	179	1	99.44	99.44	
3	179	1	99.44	99.44	
4	178	1	98.89	99.44	
5	178	2	98.89	98.88	
1	180	0	100	100	SMPC-3
2	180	0	100	100	
3	179	1	99.44	99.44	
4	179	1	99.44	99.44	
5	179	2	99.44	98.88	

the shape memory properties of the synthesized shape memory composites are given in Table 1. As seen in the table, shape fixity (R_f) and shape recovery (R_r) ratios calculated for all materials show a decreasing trend with each passing cycle. This situation, which is compatible with the literature, is due to the deformation of the material with each passing cycle [19]. The average R_f and R_r ratios of the materials are given in Fig.5 with standard error. As the standard error decreases, the distribution narrows. Therefore, it is important to know these parameters in order to make predictions of shape memory performance more reliable [20]. It has been determined that the shape memory performance increases as the filling material ratio increases in the produced shape memory composites. Therefore, it can be concluded that TiO_2 positively affects the shape memory property of the PVA polymer.

4. Conclusion

Poly (vinyl alcohol) polymer is suitable for use as a surfactant in the production processes of some composite materials since it has both hydrophilic and hydrophobic functional groups [21]. In addition, this material is a synthetic polymer that is water-soluble, reacts easily with cross-linked chemicals, biocompatible, high chemical resistance, natural adhesive properties [22]. Due to its advantages, in this study PVA polymer was used as a matrix in nanocomposites produced by the solvent method. The measurement results obtained for shape memory PVA/TiO_2 nanocomposites doped with three different amounts of TiO_2 nanomaterials reveal that the synthesis of the materials has been achieved successfully.

According to the results of DSC analysis, it was observed that the T_g value increased as TiO_2 nanomaterial was added to the PVA matrix. This result, which is consistent with the literature, can be explained by the fact that the fillers make it difficult for the amorphous phase to relax. The mobility of the PVA chains was restricted by the filler material, and it was observed that as the amount of filler increased, the glass transition temperature also increased. This result, which proves that a strong interfacial interaction occurs between the fillers and the matrix, indicates that the nanomaterials are well dispersed in the matrix and have a wider interaction area. When the TGA results are examined, it is seen that degradation occurs in three steps in all materials. In shape memory PVA/TiO_2 nanocomposites, it was observed that as the amount of additives increased, degradation was delayed by the effect of heat. Therefore, it can be said that this nanomaterial improves the thermal resistance properties of the obtained nanocomposites. When the FT-IR spectra of the shape memory materials are examined, it was determined that the characteristic bands obtained for PVA are also seen in SMPC-2 and SMPC-3 samples. This means that in nanocomposites with high TiO_2 doping, a homogeneous structure is formed and an interface occurs between matrix and fillers. SEM images taken in order to determine the morphological properties of the materials are in accordance with the literature. When these images were examined, it was determined that as the additive was added, slight roughness, clumping, and wrinkled structures were formed on the surfaces. XRD analysis was used to determine the crystalline structure of the materials. Especially for SMPC-2 and SMPC-3 materials, the characteristic peaks obtained from XRD analysis are in line with the data in the literature. In these nanocomposites, it has been observed that the characteristic peaks of the nanomaterials disappear

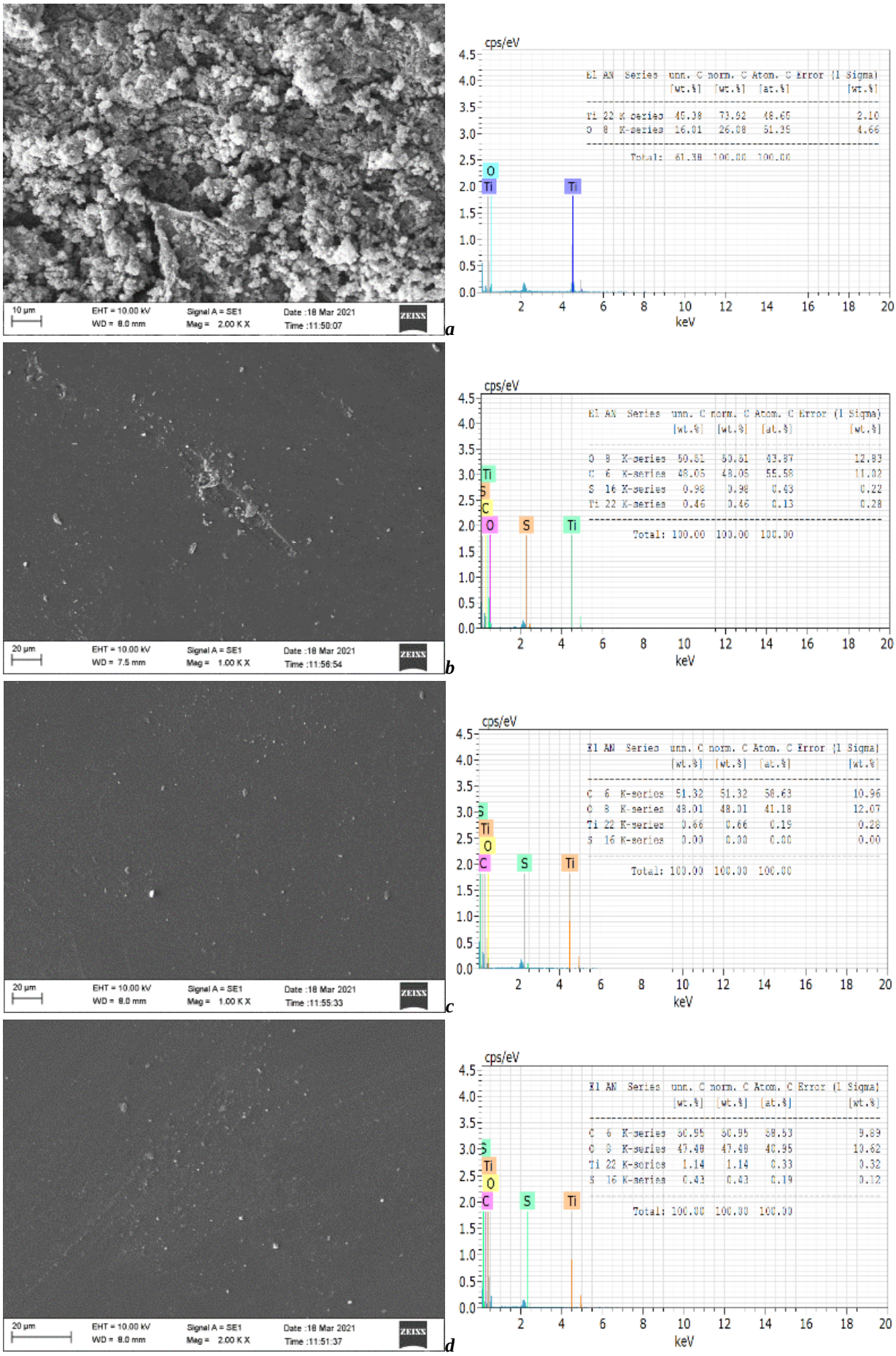

Fig.3. SEM/EDS analysis of TiO_2 (a), SMPC-1 (b), SMPC-2 and SMPC-3 (d)

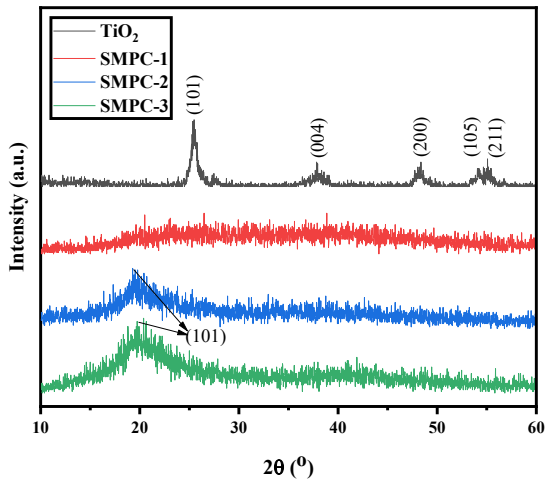

Fig.4. XRD analysis of the materials

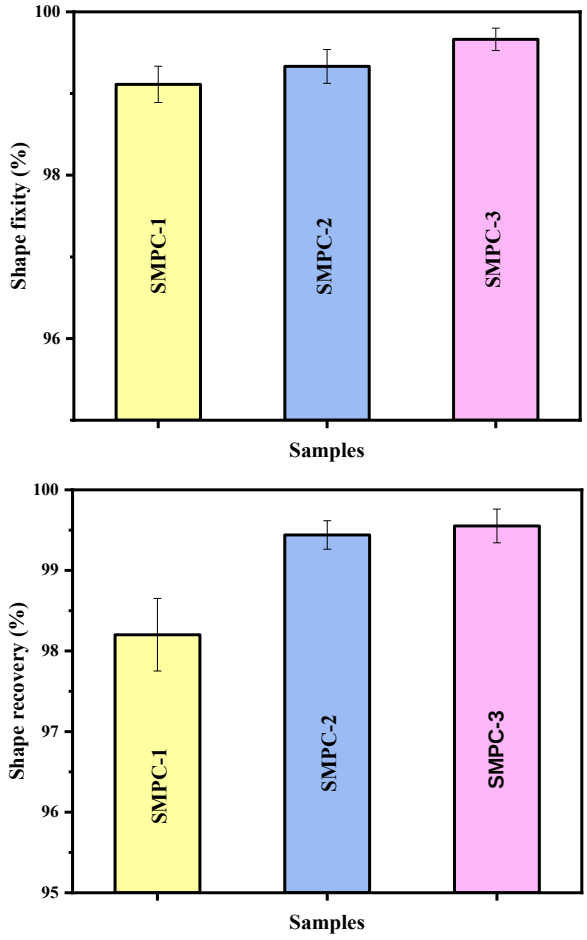

Fig.5. Shape memory performance of the samples

and the characteristic peak of PVA is formed. This result proves that the nanomaterial has a homogeneous distribution in the matrix without disturbing the PVA structure. The bending test applied to materials to determine their shape memory performances revealed that all produced materials have a significant shape memory effect with shape fixity and shape recovery rates. According to the shape memory test results, shape fixity (R_f) and shape recovery (R_r) rates and velocities for nanocomposite materials differed depending on the contribution rate. If the shape memory test is evaluated together with the calculated error bars, the shape memory performances increased as the contribution rate increased. As a result, it can be said that all materials with shape fixity and shape recovery rate above 95% are suitable for the production of shape memory featured materials and their use in the required fields.

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