UDK 678.84
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 46(3)243(2012)

SHAPE-MEMORY POLYMERS FILLED WITH SiO_2 NANOPARTICLES

POLIMERI Z OBLIKOVNIM SPOMINOM, POLNJENI S SiO_2 NANODELCI

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Prejem rokopisa – received: 2011-10-20; sprejem za objavo – accepted for publication: 2012-02-20

In this paper we discuss the mechanical and thermal properties of shape-memory polymer composites (SMPCs) filled with SiO_2 nanoparticles. A series of SMPC samples was prepared using a commercially provided shape-memory polymer (SMP) filled with different mass fractions of 600-nm and 130-nm SiO_2 particles. The mechanical properties of the SMPCs were determined by performing three-point bending (3PB) and Izod impact tests. The thermomechanical and thermal behaviors were investigated using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

Keywords: shape-memory polymer, SiO_2 nanoparticles, impact test, three-point bending, DMA, DSC

V članku obravnavamo mehanske in termične lastnosti polimernih kompozitov z oblikovnim spominom (SMPC), polnjenih s SiO_2-nanodelci. Serija SMPC-vzorcev je bila pripravljena z uporabo komercialnega polimera z oblikovnim spominom (SMPC), v katerega je bila dodana različna količina 600 nm in 130 nm SiO_2-delcev. Mehanske lastnosti SMPC so bile določene s tritočkovnim upogibnim preskusom in z žilavostnim preskusom Izod. Termomehansko in toplotno vedenje materiala je bilo preiskovano z uporabo diferenčne vrstične kalorimetrije (DSC) in z dinamično mehansko analizo (DMA).

Ključne besede: polimer z oblikovnim spominom, SiO_2-nanodelci, žilavostni preskus, tritočkovni upogibni preskus, DMA, DSC

1 INTRODUCTION

Shape-memory polymers (SMP) are stimuli-responsive materials, which have generated significant research interest in the past few years.

If an SMP is subject to deformation, large internal stress can be stored in the cross-linking structure by cooling the polymer below its switch transition temperature. By heating the polymer above the switch transition temperature, the SMP recovers its permanent shape as a result of releasing internal stress stored in the cross-linking structure[1]. For the thermoset SMPs the switching temperature is the glass transition temperature T_g.

Their capability to retain an imposed, temporary shape and to recover the initial, permanent shape upon exposure to an external stimulus depends on the "functional determinants" that, in simplistic terms, can be divided into structural/morphological and processing/environmental factors[2].

The major drawback of shape-memory polymers is the low recovery stress, limiting the size of commercial components to a few centimeters; the recovery stress of larger components is insufficient with regard to the initial shape because of the higher weight. The solution is the reinforcing of the SMP with particles or with fibers.

The properties of the final composite products are significantly affected by many factors such as processing techniques, filler distribution, interface, filler size, aspect ratio and matrix nature[1].

2 EXPERIMENTS

This research is based on the experimental work that involved the preparation of the SMPC and the mechanical and thermomechanical testing. A series of SMPC samples were prepared using a commercially provided SMP, filled with different mass fractions of 600-nm and 130-nm fumed silica. 130-nm silica nanoparticles were provided by Riedel-de Haën (Silica Cab-osil), while 600-nm silica particles were synthesized following the Stöber–Fink–Bohn method[3]. To prevent agglomeration, silica particles were initially treated with silane, IO7 T7(OH)3 (trisilanol isooctyl polyhedral oligomeric silsesquioxane, POSS) following the procedure as suggested by Wheeler et al.[4]

Four types of plates were prepared mixing the commercially available epoxy-based thermoset SMP Veriflex from Cornerstore Industries with a transformation temperature (T_g) of 45 °C and the SiO_2 nanoparticles.

The quantity of the SMP used is the same for all the plates. Veriflex is made of two components, A and B, as

marked by the manufacturer. For the mixing A and B are used in the ratio of 100/32,34. First, the nanoparticles were mixed with the component B and subjected to ultrasound in the ultrasonic device for 20 minutes to obtain homogeneous dispersion of the particles. Component A was then added and manually mixed with the component B-nanoparticle dispersion and finally poured into a closed vertical mould made of aluminum (Al) with the inner cavity thickness of 3 mm. The polymerization was realized in an oven following the manufacturer's instructions. Using this method the following four types of SiO_2-filled SMPCs were created:

1. a SMP with a 0.32 % volume fraction (vf) of 130-nm SiO_2 (recipe R1)
2. a SMP with a 0.32 % (vf) of 600-nm SiO_2 (recipe R2)
3. a SMP + SiO_2 with a 0.5% (vf) of 600-nm SiO_2 (recipe R3)
4. a SMP + SiO_2 with a 1% (vf) of 600-nm SiO_2 (recipe R4)

The mechanical behavior of the SMP + SiO_2 was investigated through the following series of tests: the Izod impact and three-point bending tests.

The thermomechanical behavior of the SMP + SiO_2 was determined by using the dynamic mechanical analysis (DMA) and the differential scanning calorimetry (DSC) methods and equipment. The scanning electron microscopy (SEM) images were used to provide information about the fractured surface structure of the SMP + SiO_2 designed samples.

Because of the high-volume fraction of the particles, the R3 and R4 plates were too soft and difficult to be extracted from the mould and it was not possible to obtain proper samples just for the DCS analysis.

For each group of the tests, specimen shapes and sizes have been chosen according to the relevant standards and also in such a way that they were compatible with the capabilities and requirements of the available testing devices.

The thermal properties are included in the key characteristics of the SMPs, especially T_g. To characterize the viscoelastic nature of the SMPCs, TA Instruments Q800 equipment was used for applying the DMA method. The SMP and SMP + SiO_2 samples were cut to 9 mm in width and 30 mm in length in order to fit the single cantilever beam. At a frequency of 1 Hz, after the chamber was cooled down to 0 °C, the temperature was ramped at 2 °C/min until it reached 80 °C. As a result, the storage modulus E', the loss modulus E'', and the loss factor tan $\delta = E''/E'$ were obtained.

To have a better understanding of different values for T_g, the DSC analysis on the TA Instruments Q 2000 equipment was applied because it provides rapid and precise determinations by using minimum amounts of samples.

To measure the resistance to failure of the V-notched samples according to the ASTM standard D256, the Izod impact strength tests were performed on the Zwick 053650 testing machine using a 1 J impactor. Samples were cut from the top of the plate and from the bottom part in order to see the difference in the strength of the material if an eventual non-homogenous dispersion of the SiO_2 nanoparticles were to occur. Because of the long polymerization time (12 h) of the SMPCs, the particles tend to move in the bottom part of the plate.

To determine and compare the modulus of elasticity of the pure SMP and the SMP + SiO_2 samples, the three-point bending tests were performed on the Instron 5985 testing machine according to ASTM D790-03. The test was performed at a load rate of 2 mm/min.

For the SEM imaging, the samples were frozen with liquid nitrogen and fractured. The fractured surface was then analyzed.

3 RESULTS AND DISCUSSION

3.1 The thermomechanical behavior

As shown in **Figure 1** and **Table 1**, different T_g values are essentially dependent on the vf of the SiO_2 filler. This result was achieved by other researchers too. The glass transition temperature decreases significantly with an increase in the weight percentage of aluminum-nitride filled shape-memory polymer composites. A similar phenomenon was reported about the SMP filled with other particles[5].

In **Table 1** different values for T_g determined from the DMA tests using the peak of the tan δ and E' curves and also from the DSC analysis are presented. Surprisingly, the DSC analysis shows an increase of around 4 °C for the composites, while the T_g values obtained with the DMA method show a drop of 4 °C for the 130-nm filled SMP + SIO_2 and 3 °C for the 600-nm filled SMP + SiO_2.

The T_g values are above the ambient temperature (25 °C) for all the SMPCs except for SMP + SiO_2 1 % 600 nm, which is 21.34 °C according to the DSC.

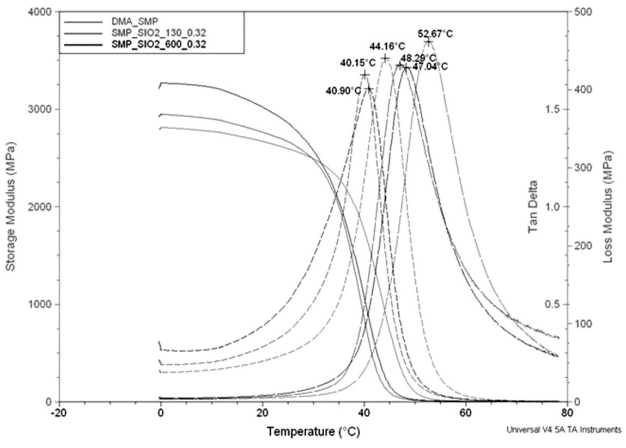

Figure 1: DMA curves overlay
Slika 1: Prekrivanje krivulj DMA

Table 1: T_g values
Tabela 1: Vrednosti T_g

Sample	SMP	R1	R2	R3	R4
DSC (°C)	33.56	38.41	39.53	30.43	21.34
Loss Modulus (°C)	44.16	40.15 ±0.30	41.40 ±0.30		
Tan δ (°C)	52.67	47.04 ±0.30	48.82 ±0.30		

Figure 1 presents the development of the storage modulus (solid lines), the loss modulus (long dashes) and tan δ (short dashes) as a function of temperature.

Figure 2 plots the DSC results of the pure resign and the composite samples during heating. The T_g temperature was taken at the median point in the glass transition temperature range.

The strain storage and the recovery behavior of a shape-memory polymer system must be well understood in order to design a device or a process that may use the polymer properties.[6]

The storage modulus (**Table 2**) is approximately the same at the temperatures lower than T_g and transforming above T_g significant differences can be observed because of the different T_g values of the SMPCs.

The storage modulus has a maximum value for the SMP + SiO_2 0.32 % 600 nm, indicating that the stiffness of this SMPC is the highest among all the tested samples.

Table 2: Storage-modulus values at different temperatures
Tabela 2: Modul shranjevanja pri različnih temperaturah

Sample name	SMP	R1	R2
E'(0 °C)	2875 ± 210	2575 ± 220	3241 ± 100
E'(25 °C)	2484 ± 390	2330 ± 300	2969 ± 50
E'(45 °C)	611,6 ± 90	87.78 ± 10	287.3 ± 30
E'(55 °C)	18 ± 2	6.29 ± 2	11.32 ± 1
E'(65 °C)	4,8 ± 1	2.82 ± 1	4.641± 0.2
E'(75 °C)	2,3 ± 0,4	1.89 ± 1	3.265 ± 0.1

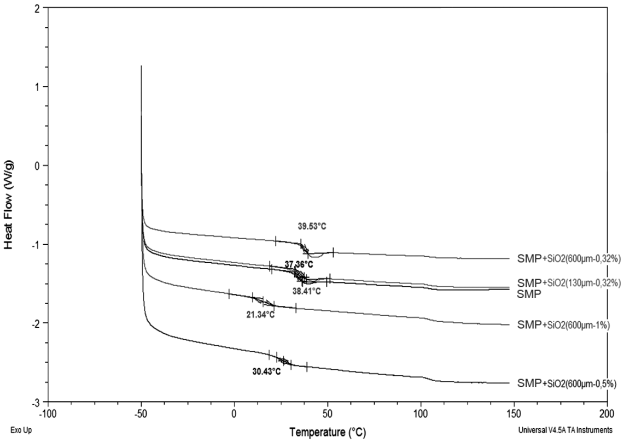

Figure 2: DSC analysis results
Slika 2: Rezultati DSC-analize

3.2 The mechanical behavior

Izod impact strength testing results are shown in **Table 3**. It is demonstrated that the SiO_2 filler contributes to the increase in the impact resistance of a SMP. The values for the pure SMP had also been determined and presented before by the authors. It is also important to note the difference between the results obtained from the top and the bottom of the part samples. As the particles agglomerate at the bottom, during the polymerization process, both 130-nm and 600-nm SiO_2-filled SMPC samples from the bottom show a higher impact resistance than the samples cut from the top part of the plates.

Table 3: Izod impact test results
Tabela 3: Rezultati udarnega preskusa Izod

Sample	Impact energy (J)	Impact energy/ Notch length (J/m)	Impact resistance (kJ/m^2)
SMP	0.09	7.39	2.54
R1 top	0.11	8.95	3.08
R1 botom	0.11	9.07	3.12
R2 top	0.11	9.27	3.36
R2 botom	0.15	12.07	4.37

Table 4: Three-point bending test results
Tabela 4: Rezultati tritočkovnega upogibnega preskusa

Sample	SMP	R1	R2
Modulus Load-Elongation (GPa)	2.44	1.94	2.14
Extension at Maximum Load (mm)	6.86	6.78	6.97
Maximum Load (N)	96.56	98.63	89.95

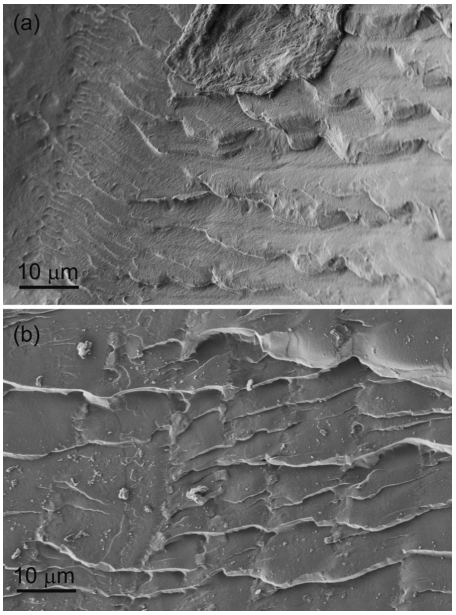

Figure 3: SEM images of the SMP fractured surfaces: a) SMP + 600 nm SiO_2, b) SMP + 130 nm SiO_2
Slika 3: SEM-posnetek površine preloma SMP: a) SMP + 600 nm SiO_2, b) SMP + 130 nm SiO_2

The three-point bending test results (**Table 4**) do not show any important change in the modulus of elasticity of the SiO_2-filled SMPCs.

3.3 SEM imaging

In **Figure 3** we can see the SEM images of the fractured samples, the SMPCs filled with 600-nm and 130-nm SiO_2 particles. Due to a small concentration of the SiO_2 particles, their arrangement in the SMPCs was not observed. There is, however, a clear difference in the formation of the steps on the fractured surfaces as the silica fillers serve as stress concentrators controlling the crack formation upon the fracture. In the 600-nm SiO_2 sample, the steps are higher, more pronounced and less sharp, whereas in the 130-nm SiO_2 sample the steps are sharper and lower.

4 CONCLUSION

This work describes the development of the new intelligent composite materials with better mechanical and thermomechanical properties than the pure SMP resign.

A controlled variation of the T_g, E'' and E' is fundamental in the use of the SMPs in industrial applications. The DMA analysis showed the improvement of the thermomechanical properties of the SMPCs and also the change in the T_g values by adding the SiO_2 nanofiller. This indicates a possibility of designing the SMPCs with different T_g even by adding a small amount such as a 0.32 % volume fraction of the filler.

However, the long polymerization time is an issue concerning the homogeneous dispersion of the particles, which tend to agglomerate at the bottom of the plate.

Although valuable information has been so far obtained during the mechanical testing, many tests are still needed in order to fully understand the material.

Acknowledgment

This paper was supported by the project "Doctoral studies in engineering sciences for developing the knowledge-based society – SIDOC", contract no. POSDRU/88/1.5/S/60078; the project was co-funded by the European Social Fund through the Sectorial Operational Program Human Resources 2007–2013 and the contract IDEI 205, nr.655/2009.

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