Applied Innovative Research
Vol. 1, March 2019, pp. 78-82

Development of Graphene Nanoplatelets Reinforced Shape Memory Polyurethane and Their DMA Studies

Ritesh Kumar Gupta[1], S A R Hashmi[1,2] , Krishan Kumar Patel[3], Avanish K Srivastava[1,2]

[1]Academy of Scientific and Innovative Research (AcSIR),
CSIR- Advanced Materials and Processes Research Institute, Bhopal 462 026, India
[2]CSIR-Advanced Materials and Processes Research Institute, Bhopal 462 026, India
[3]Maulana Azad National Institute of Technology, Bhopal 462 026, India

Received 9 September 2018; accepted 18 January 2019

Shape memory nanocomposites have been synthesized using ether type shape memory polyurethane (SMPU) and graphene nanoplatelets (GNPs). A twin screw co-rotating microcompounder with a back flow channel has been employed to ensure proper dispersion of GNPs in the polymer matrix. Four compositions of GNPs in SMPU have been prepared. Morphology of fractured nanocomposites reveals uniform dispersion of graphene in SMPU. The dynamic-thermo-mechanical properties of nanocomposites at 0.1 and 10 Hz have been studied. Addition of 1 phr GNPs increases storage modulus of SMPU from 2.8 to 3.73 GPa and the value of tan δ peak has been decreased from 0.81 to 0.53. The GNPs in SMPU matrix influence shape recovery which improves with the addition of GNPs with in experimental range.

Keywords: Shape memory polymer, Shape memory polyurethane, Graphene nanoplatelets, Dynamic mechanical analysis

Introduction

The shape memory polymers (SMPs) are one of the important category of smart material which have ability to undergo a large recoverable deformation[1] upon the application of external stimuli such as heat[2,3], light[4,5], moisture[6], electric field[7,8], magnetic field[9], and pH[10]. The SMPs have potential applications in biomedical, actuator, sensor, smart textile, self deployable structure and artificial muscles[11,12]. SMPs compared to shape memory alloy possess several advantage such as exceptional high recovery strain, easy process ability, low cost ,easy shape memory programming although their low recovery-force[13], low thermal and electrical conductivity results in limited applications. In thermoresponsive polymer, temperature acts as a transition switch thereby changing shape from temporary shape to permanent shape. SMPs change their stiffness from glassy state (high stiffness) to rubbery state (low stiffness) above glass transition temperature. The thermoplastic shape memory polyurethanes (SMPU) contain flexible (soft segment) and rigid(hard segment) alternative chains in the polymer back bone[14]. Hard segments are responsible for mechanical strength and toughness, and on the other hand, soft segments provide elasticity[15]. These hard and soft segments provide shape memory behavior in polyurethane. The limitation of low recovery stress in shape memory polymers is governed by the elastic energy stored within the hard segment of polymer chain[16]. Therefore one of the methods to improve recovery stress in polymer is reinforcement. In modern era nanomaterials are most recommended reinforcement for SMP due to their exceptional thermal, mechanical and electrical properties. Many studies reported improvement in shape memory properties on addition of nanofillers which includes reinforcement of SiC[17], nanoclay[18], carbon black[19], CNTs[1, 20] and cellulose nanowhiskers[21], etc.

Graphene nanoplatelets (GNPs) are recently developed short bulk form of graphene[22]. GNP has intermediate geometry with 12 nm thickness corresponding to 18 to 30 graphitic sheets. The key factor for transferring the GNP properties to composites are (i) homogeneous dispersion of grapheme in matrix ; and (ii) type of interaction between GNPs and the polymer matrix.

Dynamic mechanical analysis (DMA) is a very efficient technique for study of time, frequency, and temperature dependent mechanical properties of polymer composites. The study of shape memory properties is also carried out by using thermomechanical cycle, the detail is mentioned elsewhere[23]. Therefore DMA study is also useful to infer shape memory effects. Storage modulus indirectly

*Corresponding author (E-mail: sarhashmi@rediffmail.com)

shows the capacity to store strain energy elastically which results in higher shape recovery force. Damping factor peak gives the glass transition temperature of the composite. In present experimental study different fractions of GNPs were dispersed uniformly in shape memory polyurethane using micro-compounder. Dynamic mechanical properties were evaluated at two frequency 0.1 and 10 Hz. Shape recovery force, shape fixity and shape recovery were studied and reported here.

Experimental Details

Materials

The shape memory thermoplastic polyurethane (ether type) MM6520, in the form of pellets were obtained from SMP Technologies Inc. Japan. Graphene naoplatelets (GNP) 11-15 nm having specific surface area 50-80 m^2/gm obtained in the form of powder from io-li.tec nanomaterials GmbH Germany.

Sample preparation

The compositions of nanocomposites developed for present study are given in Table 1. Schematic presentation of sample prepared is given in Fig. 1. Weighted amount of ingredients were fed to microcompounder for melt blending at 210 ºC for 5 min. After mixing molten material was extruded in the form of strand through die and was allowed to cool down to room temperature. The process was repeated to obtain improved dispersion of GNPs in SMPU. The mixed molten mass was taken directly to barrel of micro injection molding machine and test specimen was molded.

Table 1 — Sample designation for composites.

Sample code	Composition of nanocomposites	
	SMPU (g)	GNP (g)
SMC1	100	0
SMC2	100	0.2
SMC3	100	0.6
SMC4	100	1

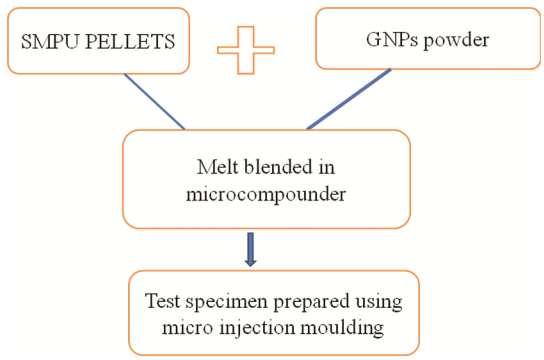

Fig. 1 — Schematic flow chart of sample preparation.

Characterization

Shape memory behavior evaluation

In this SM behavior involves following steps (i) heating the sample to a temperature T_h which is higher than the glass transition temperature T_g, (ii) deforming/stretching to a certain level, iii) bringing down the temperature below T_g without relaxing the deformation strain, (iv) removal of imposed strain (clamps etc.) and allowing the sample to relax and attain a fixed length (v) heating the sample in fixed position above glass transition temperature (vi) allowing recovery at this temperature by decreasing strain till zero recovery force achieved by decreasing strain 2 mm/min (vii)t hen loosing the clamp and allowing free recovery at same temperature.

Dynamical mechanical analysis (DMA) is a technique for measuring viscoelastic properties of material. It is known that shape memory properties are governed by modulus of material below and above the transition temperature. This experiment allows determination of the material's response by the application of temperature and dynamic load. Dynamic mechanical properties of the samples were determined using "Dynamic Mechanical Analyzer" DMs 6100 by hitachi Instruments. The samples were injection molded, with dimensions 40×10×1 mm^3.test conditions were as follows: measurement method was tensile mode, loading frequency 0.1 Hz AND 10 Hz, heating rate 2°C/min, for a temperature interval 30 – 85 ºC.

Morphological studies were conducted using FESEM of M/s Nova NanoSEM 430. The cryogenic fractured surfaces were observed after gold coating.

Result and Discussion

SEM studies were carried out to investigate the fracture morphology of the cryogenic fractured surface of the nanocomposites. SEM image of SMC1, SMC2, SMC3 and SMC4 are shown in Fig. 2. It can be seen in Fig. 2 (a), SMC1 (pure SMPU) is very smooth and homogeneous. However the surface of GNPs filled SMPU composite in Fig. 2 (b-d) become coarser and non uniform. SMPU contains fine domain having uniform structure. Coarse domain formation was observed due to incorporation of GNPs. Figure 2 (c) shows, the cracks grow on periphery of coarse domain.

Dynamic mechanical Analyzer was used to study behavior of material under dynamic loading at different temperature ranging from 30 ºC to 85 ºC.

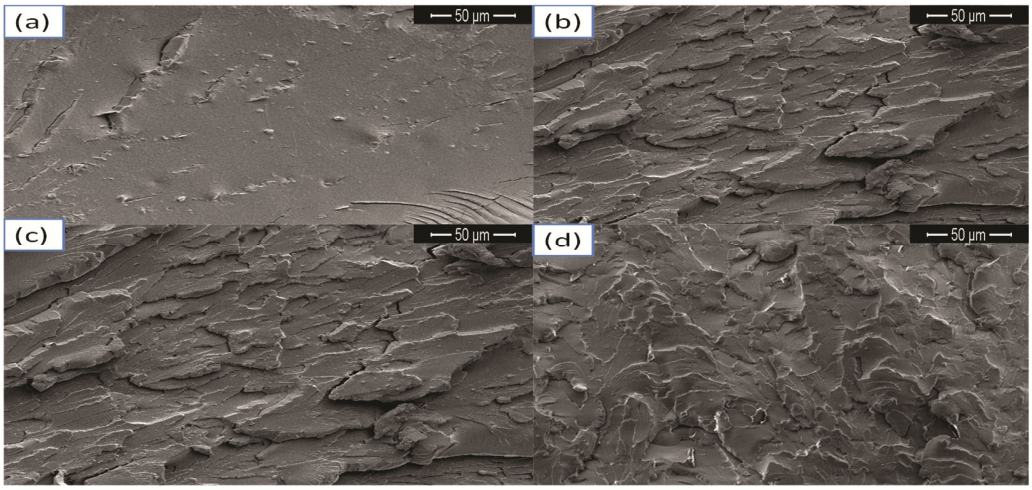

Fig. 2 — SEM micrograph of cryogenic fractured surfaces (a to d) of SMC1, SMC2, SMC3 & SMC4.

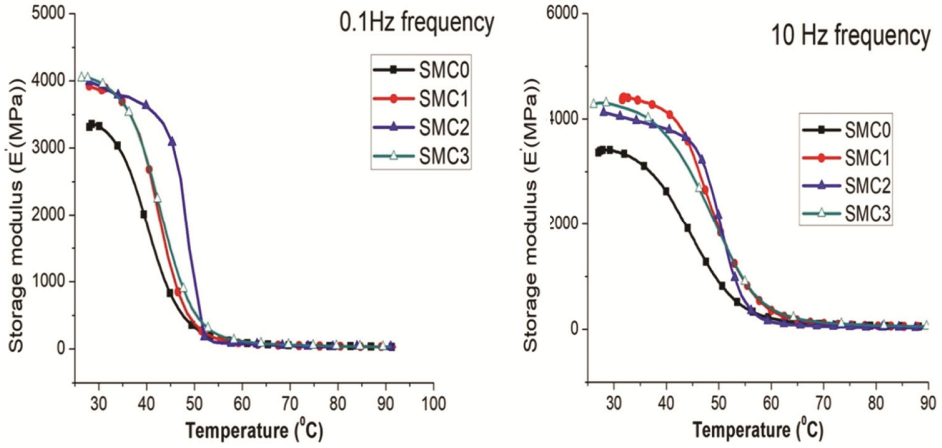

Fig. 3 — Variation of storage modulus with temperature for nanocomposites at two frequencies 0.1 Hz and 10 Hz.

Figure 3 shows the variation of storage modulus as a function of temperature for SMPU and SMPU-GNP composites at two frequencies 0.1 Hz and 10 Hz. The storage modulus (E') signifies the stiffness of polymer composite. This illustrate three different zones namely high modulus zone, transition zone and low modulus zone. In high modulus zone (glassy state), where mobility between chain segment is very limited, an increase in temperature follows a drop in storage modulus it switch over to transition zone and after transition there is low modulus zone(rubbery state) with very limited stiffness. The storage modulus is proportional to strain energy stored per cycle which governs shape recovery properties of shape memory polymer. Storage modulus decreased with increasing temperature and is attributed to increase in molecular mobility of polymer chains.

The value of E' was much higher for SMC4 as compared to SMC1 due to restriction provided by GNPs in molecular mobility of polymer chains. The value of storage modulus at 10 Hz was greater than at 0.1 Hz due to decrease in relaxation time as frequency increase.

Loss modulus (E") signifies the maximum heat dissipated per cycle under deformation. It is clear that the addition of GNPs in the SMPU matrix cause broadening of loss modulus peak. This may be attributed to the restriction in relaxation process as a result of increased chain segment with addition of GNPs[24]. The value of loss modulus increased with increase in loading of GNPs in SMPU matrix. The higher loss modulus may be attributed to increased frictional surfaces which enhanced the dissipation energy.

Damping properties of a material provides effectiveness of the viscous and elastic phase of polymer composites. Peak of tan δ curve gives the value of glass transition temperature. Figure 5 shows

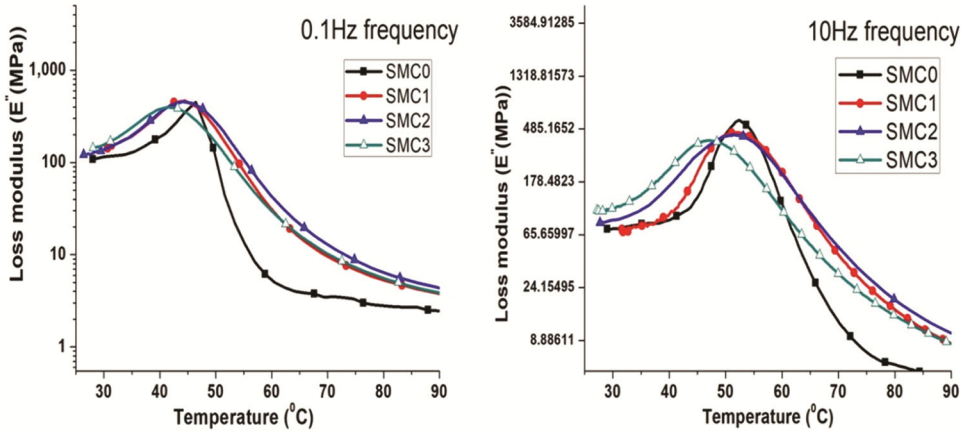

Fig. 4 — Shows the variation of the loss modulus for different composition of SMPU-GNPs nanocomposites with temperature at 0.1 Hz and 10 Hz frequency.

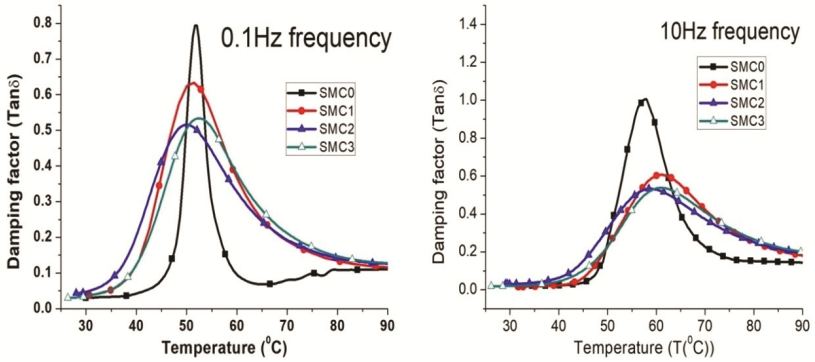

Fig. 5 — Variation in damping factor for different composition of nanocomposites with temperature at 0.1Hz and 10 Hz frequency.

that the value of tan δ for different wt% of GNPs-SMPU nanocomposites. The value of tan δ was lower than the pure SMPU. This suggests that increase in elastic modulus is more compared to loss modulus. Addition of GNPs greatly improves stiffness of nanocomposites. There was broadening of tan δ curve by loading of GNPs in SMPU matrix, that increase the transition range by suppressing relaxation time for chain segments. The value of tan δ was more at 10 Hz than that at 0.1 Hz for all nanocomposites. With increase in frequency dissipation energy increased as compared to energy stored so value of tan δ increased. Low value of damping factor for GNPs-SMPU nanocomposites suggest more thermal energy was required for translational and rotational motion of the chain segments.

Shape memory properties were evaluated using thermo-mechanical cycle as described elsewhere[23] and summarized in Table 2 . Shape fixity ratio shows ability to remember temporary shape on programming. Addition of GNPs resulted in increased shape fixity ratio. Shape recovery ratio shows the ability to regain its permanent shape on recovery. Addition of GNPs decreased shape recovery ratio. Higher Shape recovery force is needed to use SMP as an actuator. Addition of 1 phr GNPs improved recovery force of SMPU from 15.7 N to 32 N.

Table 2 — Shape memory properties for different nanocomposites.

Sample name	Maximum recovery force (N)	Shape fixity ratio	Shape recovery ratio
SMC1	15.7	95.2	96.5
SMC2	21.9	97.5	94
SMC3	25.8	98	93.2
SMC4	32	98.53	91

Conclusions

A positive influence of GNPs addition on shape recovery and dynamic mechanical properties was observed. Storage modulus of SMPU on addition of 1 phr GNPs increased from 2.8 to 3.73 GPa at 0.1 Hz frequency. Value of storage modulus of nanocomposite increased at 10 Hz frequency as compared to 0.1 Hz frequency. The value of tan δ peak decreased on addition of GNPs. The glass transition temperature range is increased by addition of GNPs. Addition of 1 phr

GNPs improved recovery force of SMPU by 103.8 % and shape fixity ratio increased from 95.2 to 98.53%.

Acknowledgement

The Authors are highly thankful to CSIR, New Delhi for granting Fellowship under which the present work was carried out.

References

1 Hashmi S A R, Prasad H C, Abishera R, Bhargaw H N & Naik A, *MaterDes*, 67 (2015) 492.
2 Wu Y, Hu J, Zhang C, Han J, Wang Y & Kumar B, *J Mater Chem A*, 3 (2015) 97.
3 Pieczyska E, Staszczak M, Maj M, Tobushi H & Hayashi S, *Meas Automat Monitor*, 61 (2015).
4 Eisenbach C D, *Polymer*, 21 (1980) 1175.
5 Finkelmann H, Nishikawa E, Pereira G & Warner M, *Phys Rev Lett,* 87 (2001) 015501.
6 Yang B, Huang W, Li C & Li L, *Polymer,* 47 (2006) 1348.
7 Wang W, Liu D, Liu Y, Leng J & Bhattacharyya D, *Compos Sci Technol,* 106 (2015) 20.
8 Liu X, Li H, Zeng Q, Zhang Y, Kang H & Duan H, *J Mater Chem A,* 3 (2015) 11641.
9 Schmidt A M, *Macromolecul Rapid Commun,* 27 (2006) 1168.
10 Han X J, Dong Z Q, Fan M M, Liu Y, Li J H & Wang Y F, *Rapid Commun*, 33 (2012) 1055.
11 Liu C, Qin H & Mather P, *J Mater Chem,* 17 (2007) 1543.
12 Hu J, Zhu Y, Huang H & Lu, *Progress Polym Sci*, 37 (2012) 1720.
13 Rousseau I A, *Polym Eng Sc*, 48 (2008) 2075.
14 Kim B K, Lee S Y & Xu M, *Polymer*, 37 (1996) 5781.
15 Meng Q, Hu J & Zhu Y, *J Biomater Sc*, 19 (2008) 1437.
16 Yoshihara N, Ishihara H & Yamada T, *Polym Eng Sc*, 43 (2003) 1740.
17 Liu Y, Gall K, Dunn M L & McCluskey P, *Mech Mater*, 36 (2004) 929.
18 Cao F & Jana SC, *Polymer,* 48 (2007) 3790.
19 Carlos A G R, Mario F G D, Hoejin K, Luis C, Deidra H & Paras M, *Mater Res Exp*, 5 (2018) 065704.
20 Du F P, Ye E Z, Yang W, Shen T H, Tang C Y & Xie X L, *Compos Part B: Eng*, 68 (2015) 170.
21 Olalla A S, *Multifunctional Polymeric Nanocomposites Based on Cellulosic Reinforcements*, Elsevier Inc, 2016.
22 Nieto A, Lahiri D & Agarwal A, *Carbon,* 50 (2012) 4068.
23 Prasad H C, Hashmi S A R, Naik A & Bhargaw H N, *J Appl Polym Sci,* 134 (2017) 7.
24 Hameed N, Sreekumar P A, Francis B & Yang W, Thomas S, *Compos Part A: Appl Sci Manuf*, 38 (2007) 2422.