Rheology of Shape-Memory Polymers, Polymer Blends, and Composites

Sanjay Mavinkere Rangappa, Suchart Siengchin and Jyotishkumar Parameswaranpillai

Abstract Shape-memory polymers (SMPs) have attracted considerable attention in recent decades due to the characteristics of switching from permanent shape to temporary shape and vice versa by the application of an external stimulus. The significance and diverse applications of SMPs in the scientific and commercial scope generate researchers to have keen knowledge in the manufacturing of new shape-memory polymers and their blends and composites with improved thermomechanical and other desired properties. This chapter will provide a generalized view on the rheology of SMPs and their blends and composites that would give a holistic picture of this promising area of research.

1 Introduction

Shape-memory polymers (SMPs) are smart polymeric materials capable of returning from a deformed state to their original shape and vice versa induced by an external stimulus such as temperature, electricity, magnetic field, UV light, change in pH, etc. [1–5]. SMPs are materials with great potential for the use in intelligent materials and structures [6–9]. The advantages of SMPs over shape-memory alloy and ceramics are excellent elastic deformation, greater recoverable strain, low cost, and lightweight [10, 11]. Polynorbornene, epoxy resin, polyurethane, poly(ε-caprolactone), etc. are the generally used SMPs [12–17]. Owing to this, SMPs have found promising applications in fields as diverse as medicine (e.g., vascular stents and surgical sutures) [18], flexible electronics, actuators, deployable space structures, and transport (e.g.,

S. M. Rangappa · S. Siengchin
Department of Mechanical and Process Engineering, The Sirindhorn International Thai-German Graduate School of Engineering (TGGS), King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

J. Parameswaranpillai (✉)
Center of Innovation in Design and Engineering for Manufacturing, King Mongkut's University of Technology North Bangkok, 1518 Pracharaj 1, Wongsawang Road, Bangsue, Bangkok 10800, Thailand
e-mail: jyotishkumarp@gmail.com

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automobiles fenders, wings morphing), aerospace applications [19–22], and new application areas such as repair of cracks and scratches in coatings [5, 23].

Polymers blends and composites are smart and economical materials for the development of new and improved polymeric materials that are difficult to obtain by direct polymerization process [24–27]. The advantages of manufacturing shape-memory polymer blends and composites are better shape recovery stress, simple technology, tuning of shape-memory transition temperature, and also SMPs sensitive to electricity, magnetic field, UV light, solvent, etc., could be developed [28, 29]. Several shape-memory polymer blends have been reported by several authors including polyethylene/nylon 6 [30], PVDF/PMMA [31], poly(D,L-lactide)/hydroxyapatite [32], etc. The SMP composites containing nanofillers, such as carbon black [33], carbon nanotube (CNTs) [34], carbon nanofiber (CNF)/SMP [35], etc., have been reported.

2 Rheology of Shape-Memory Polymers

Rheology studies of SMPs enable the understanding of the processing of the polymers. Since the rheological performance of polymers depends on a large extent on the molar mass, processing temperature, and shear rate [36], the parameters obtained from the rheological experiments are storage modulus, loss modulus, tan delta, complex viscosity, shear stress, etc. The variations of above-said parameters with respect to time, temperature, frequency, shear strain, etc., give an overview of the morphology, polymer structure, phase separation, progress in curing, gelation (crossover point), verification (the final plateau region in the rheological profile), etc. In thermosetting SMP's systems like epoxy, phenol formaldehyde, polyurethanes, etc., the rheology can be used to study the curing of thermosets (either by isothermal curing or by dynamic curing), the phase separation process, changes in phase morphology, extend of phase separation, etc. [37–41]. Figure 1 shows the rheological profile of neat epoxy and 10 wt% ABS-modified epoxy blends. For neat epoxy system, a typical rheological profile is observed (Fig. 1a). But for the 10 wt% ABS-modified epoxy blend system, the phase separation took place at ca 600 s, and this is confirmed by the drop in tan δ and the rise in G′ and G″ [37].

In thermoplastic SMPs, the rheology enables the understanding of polymer structure, molecular weight, branching in polymers, processing parameters, etc. [42]. In thermoplastic polymer blends, the phase separation, changes in phase morphology, extend of phase separation, etc. can be easily studied by rheological studies [43, 44]. For polymer composites, the filler dispersion, interactions between the filler and polymer, polymer–polymer interactions, and filler–filler interactions can be carefully analyzed using rheological studies [45–48].

The different stages of shape-memory cycles are the deformation of the permanent shape above T_g or T_m by the application of external stress, and this is followed by slow cooling to room temperature with the applied external stress for shape fixing. Once the stress is released, the temporary shape is fixed. Upon heating again, the

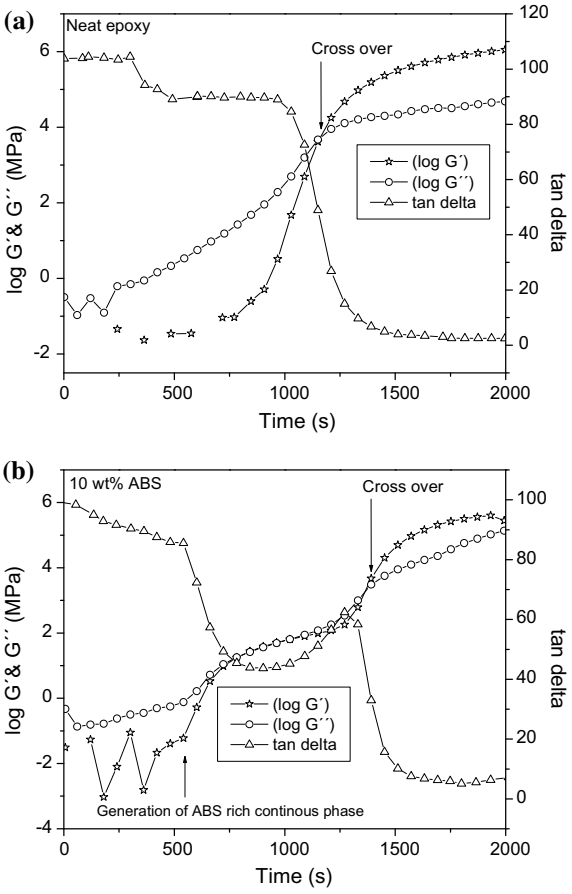

Fig. 1 Rheology of **a** neat epoxy, **b** 10 wt% ABS different ABS-modified epoxy blends at 180 °C [37]

SMPs regain its original permanent shape. The breaking of the cross-linking chains and their reforming during the shape-memory process are shown in Fig. 2 [10].

Different rheological models were introduced by the scientists for the study of the shape-memory process in SMPs. Some of the interesting works are mentioned as follows. Bhattacharyya et al. [49] derived the mechanical response of a four-element rheological model for shape-memory polyurethane under the conditions of constant stress (creep), constant strain (stress relaxation), constant stress rate, constant strain rate, and periodic strain for the better understanding of the performance of shape-memory polyurethane. They found that the shape-memory strain/damping could be considerably reduced by the application of frequency higher than the threshold frequency. The damping or shape-memory strain is maximum at the glass transition temperature. Recently, Hosseini et al. [50] introduced a rheological model for the understanding of the change in the size of the SMPs with respect to temperature. The developed nonlinear viscoelastic model allows the better understanding of the

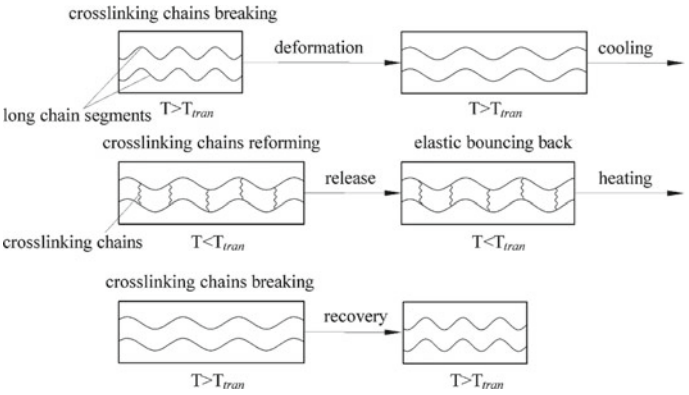

Fig. 2 Breaking of the cross-linking chains and reforming during the shape-memory process [10]. (Reproduced with permission from Elsevier, License Number-4502761431416)

production of heat-shrinkable SMPs. In another work, Liu et al. [51] developed a small-scale constitutive model for SMPs to study the strain and stress recovery at the molecular level during the shape-memory cycle. Inomata et al. [52] studied the shape-memory effect of poly (methyl methacrylate)-graft-poly (ethylene glycol) copolymers. Interestingly, the copolymer shows excellent shape-memory effect because of the physical cross-links formed due to the entanglements of the copolymer chains, confirmed by the stress relaxation studies of the SMPs.

3 Rheology of Polymer Blends and Composites

García-Huete et al. [5] studied the rheology of polycyclooctene (PCO)/poly(ethylene-co-methacrylic acid) (EMAA) zinc ionomer (Surlyn 9520) shape-memory blend for the study of self-healing. They observe a crossover for Surlyn 9520 in the range of 0.01–0.1 Hz, suitable for good healing, but PCO is a poor healing agent and shows a crossover at ca. 20 Hz. Three different blend systems were prepared 30/70, 50/50, and 70/30 with 3 wt% DCP. The authors claim that only 30/70 (PCO/Surlyn 9520) blend is suitable for self-healing, which shows a crossover at a lower frequency range. Ping et al. [53] prepared poly(ε-caprolactone)-segmented polyurethane-based shape-memory polymers. The phase separation of the hard segments in the PCL matrix was carefully analyzed by rheological measurements. The hard segments and the PCL crystals impart shape-memory properties for the PCL-segmented PU system. Sungsanit et al. [54] investigated the rheological properties of linear PLA (L-PLA) plasticized with varying content of poly(ethylene glycol) (PEG). The authors observed reduced viscosity and modulus with increasing PEG content. Feng et al. [55] successfully synthesized PLA/poly(ethylene glycol)-succinate copolymer (PES) and PLA/poly(ethylene glycol)-succinate-l-lactide copolymer (PESL) blends. They

observed a shear thinning behavior for both the blends and also the blends showed reduced viscosity and modulus with an increasing amount of PES and PESL. The rheological behaviors of PLA/PES and PLA/PESL are shown in Fig. 3.

Wei et al. [56] prepared hybrid composites containing both carbon black (CB) and carbon nanotubes (CNTs) in a 70/30 blend of polylactide (PLA)/thermoplastic poly(ether)urethane (TPU) for the making of an electrically actuated shape-memory polymer composites. The concentrations of the CB and CNTs used for making the composites are CB (3 phr, 5 phr) and CNTs (0, 0.25 phr, 0.5 phr, 0.75 phr, 1.0 phr, 2.0 phr). The rheology of the polymer composites was studied for the understanding of the filler–filler interaction and polymer–filler interaction. The authors observed a percolation threshold (filler network formation) for all the composites prepared. Similarly, the percolation threshold in multiwalled carbon nanotube/polycarbonate and multiwalled carbon nanotube/poly(methyl methacrylate) composites was reported by Pötschke et al. [57, 58].

In a more recent work, Chen et al. [59] studied the network formation of CNTs in thermoplastic polyurethane (TPU) by rheological measurements. From the rheological results, 2 wt% CNT provides a moderate level of network formation in the polymer matrix. On the other hand, a dense network of nanofillers is formed in the polymer composites at higher concentrations. The network formation by the CNTs affects the stress/strain curve (stress increases considerably at higher filler content). Similarly, storage modulus increases and the T_g shifted to higher temperatures due to the reduced mobility of the polymer chains because of the network formation with increasing filler content. The strain sensitivity and shape-memory performance of the composites can also be tuned with increasing filler content. In another work, Haghayegh et al. [60] studied the network formation in shape-memory polyurethane/clay nanocomposites using rheology. The best shape-memory properties were obtained for the composites containing 1 wt% clay.

Kim et al. [61] used rheology for the study of filler (Na-MMT intercalated with a PEG) dispersion and role of Na-MMT intercalated with a PEG as a physical cross-link in poly(ethyl methacrylate) (PEMA) nanocomposites. The authors observed a pseudo-solid behavior of the composites from the rheological results. This pseudo-solid behavior is due to the better dispersion of the Na-MMT fillers within the polymer matrix, also the nanofillers intercalated with a PEG acts as effective physical cross-links for the polymer composites even at 1.2 wt% filler content. In an interesting work, Meng et al. [62] developed shape-memory polyurethane/multiwalled carbon nanotube fibers. The fibers were spun by a single screw extruder. The authors observed that the spinnability is significantly reduced with increasing MWCNTs. In fact, at 8 wt% MWCNTs the spinnability of the composites is completely lost due to its poor rheological properties. Gelfer et al. [63] introduced organoclay in polystyrene (PS), poly(methyl methacrylate) (PMMA), and PS/PMMA blends by the melt blending process. The authors studied the rheology of the polymer composites for the understanding of the interactions of the filler with the polymer matrix. They found that the organoclay has no effect on the rheological properties of the polymers, which means the fillers have no interaction/weak interaction with the neat polymers or polymer blends.

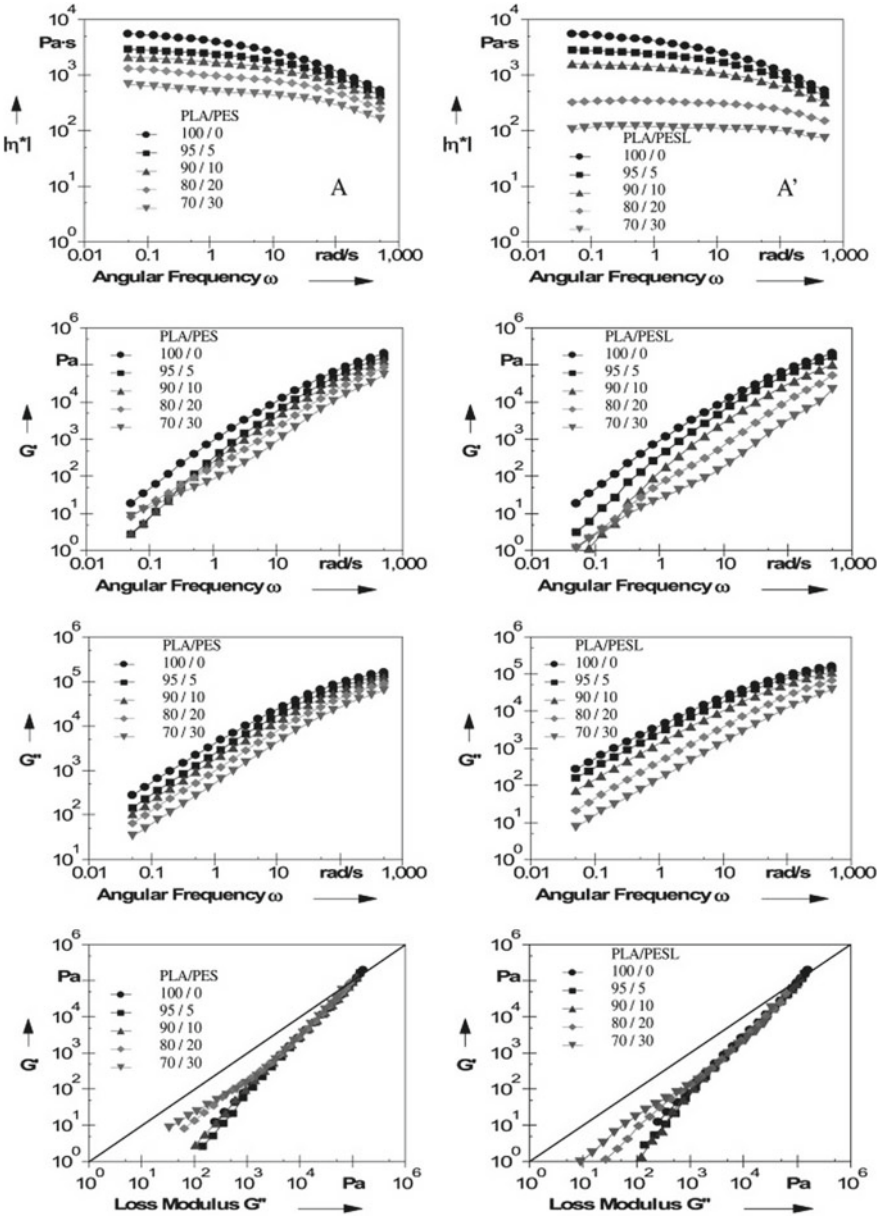

Fig. 3 The rheological behavior of PLA/PES and PLA/PESL blends [55]. (Reproduced with permission from Elsevier, License Number-4502771066270)

4 Conclusion

Rheological studies of polymers, polymer blends, and composites give an overview of polymer structure, phase morphology, phase separation, polymer–polymer interaction, polymer filler interactions, filler dispersion, etc. The processing and shape-memory performance of the polymer depends on all the above-said parameters, underlining the importance of rheological measurements of SMPs for advanced applications.

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