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Shape memory polymers (SMP) are being investigated for improving their recovery stresses to broaden the area of their application in engineering applications. The conventional shape memory creation procedure of SMP was modified, that shows significant improvements in recovery stresses. The conventional deformation steps were replaced by progressive stretch-relax–stretch scheme of deformation.

Keywords: Carbon nanotubes, polyurethane, recovery stress, recovery strain, shape memory polymers.

A modified procedure of creation of shape memory effects in polymers and their composites

Shape memory polymers (SMPs) have numerous advantages like high recoverable strain, low cost, easy formability and response to a wide range of stimuli, including heat, moisture, solvent or change in pH value, light, stress, etc. SMPs possess exceptional shape memory strain, but their low mechanical strength, particularly low recovery stress often results in limited applications. To overcome these difficulties various functional fillers, including carbon nanotubes (CNTs) have been added to the SMP matrix and are being studied[1–4].

Interestingly, shape memory effect (SME) is not an intrinsic performance of a polymer, but it results from the combination of molecular architecture, morphology and shape memory creation procedure (SMCP) of a polymer[5,6]. A modification in SMCP was introduced by researchers at CSIR-AMPRI (Advanced Materials and Processes Research Institute), Bhopal to improve energy stored during deformation at high temperature. The conventional deformation step which is required to fix a temporary shape of the SMP was replaced by progressive stretch–relax–stretch (PSRS) scheme of deformation, to obtain higher values of recovery-stress in the composites.

The conventional SMCP approach involves (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 and (iv) removal of imposed strain (clamps, etc.) and allowing the sample to relax and attain a fixed length l_f or a temporary shape. The sample is now ready to evaluate SMEs as shape memory has been created in the specimen. As mentioned in step (ii), the sample was stretched continuously to a maximum length l_s at temperature T_H in conventional SMCP, whereas under the modified SMCP the deformation step (ii) was replaced by the PSRS scheme of deformation. Accordingly, the maximum strain in step (ii) was attained in several steps with intermittent relaxation. In other words a small strain is followed by relaxation and stretching, and further followed by a second relaxation and stretching. The process continues until the maximum designed strain is achieved. Steps (iii) and (iv) remain the same as in conventional method for creating shape memory in the polymeric materials.

The steps involved in modified SMCP, PSRS scheme and SME determination are shown in Figure 1 by three-dimensional representative curves obtained experimentally for SMTPU. The processes involved in each step are: (a) stretching at 70°C, (b) cooling to room temperature by maintaining the deformed strain, (c) relaxing and fixing the temporary shape at room temperature, (d) heating to 70°C by maintaining the fixed strain and (e) constrained recovery at 70°C by decreasing the strain until the sample recovers completely. Suffixes 1–3 in the figure represent the first, second and third progressive thermomechanical cycle.

Experimentally, the multi-walled CNT (MWCNT) reinforced shape memory polyurethane (SMTPU) films were cast to observe this phenomenon for composites having different loadings of MWCNT. Figure 2 shows the stretching stresses as well as the recovery stresses for 0, 1, 2, 3 and 5 phr MWCNT reinforced SMTPU. Stretching curves show the stresses developed during stretching of samples at 70°C. The samples were brought to room temperature at 25°C under the same clamped conditions and thereafter were relaxed to attain a temporary deformed length that was slightly less than that of the stretched length. The samples were reclamped without applying any stress and the temperature of bath was brought to 70°C. Under this condition recovery stresses developed in the test specimen, which were determined using the test set-up developed for the purpose in CSIR-AMPRI[7].

The slope of the curves increased with the increase in MWCNT content (Figure 2), indicating an increased

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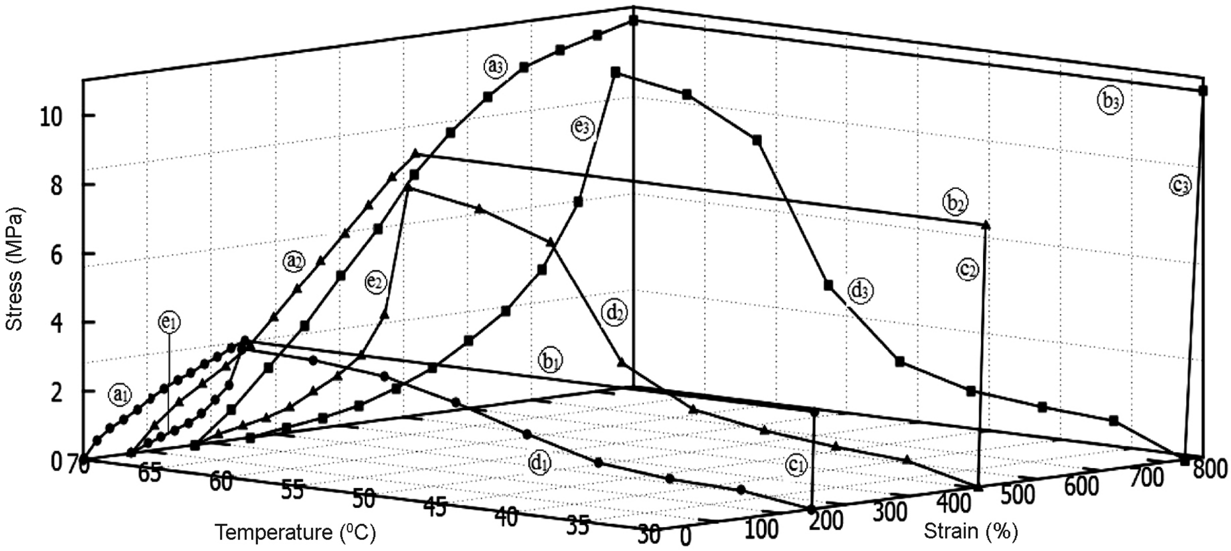

Figure 1. The steps involved in modified shape memory creation procedure, progressive stretch–relax–stretch (PSRS) scheme and shape memory effect determination illustrated by three-dimensional representative curves obtained experimentally for SMTPU.

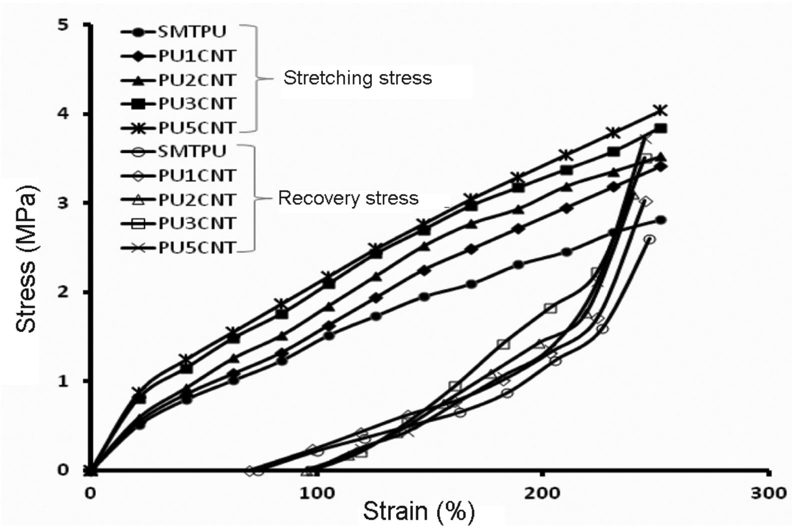

Figure 2. Stretching stresses as well as recovery stresses for 0, 1, 2, 3 and 5 phr MWCNT reinforced SMTPU.

modulus of MWCNT reinforced SMTPU with increased reinforcement. Recovery stresses also showed a rising trend with reinforcement. This can be attributed to the effective transfer of stress to the MWCNTs through the interfacial shear stress between MWCNTs and the polymer. Recovery stress of specimen shows two segments; highly sensitive to strain at higher strain and less sensitive to strain at lower strain values.

Figure 3 compares the recovery stresses at different strains for various deformed test samples using both conventional continuous stretching and PSRS scheme. The conventional stretching was done by continuously stretching the samples to the maximum strain at 70°C at constant strain rate. The stresses observed show significant difference between the two stretching schemes. For a fixed strain percentage, the corresponding recovery stress was significantly high in the PSRS scheme of deformation. The recovery stress of PU5CNT at 780% strain was found to be 6.95 MPa for PSRS and 3.68 MPa for conventional deformation schemes. At 620% strain the recovery stresses were 3.22 MPa for PSRS and 1.09 MPa for conventional deformation scheme. This comparison clearly demonstrates the effectiveness of PSRS over conventional method in improving the recovery stresses in SMPs and their composites.

A mechanism of improvement in recovery stress in PSRS deformation was proposed as follows. A cast film could be considered as made up of different domains of

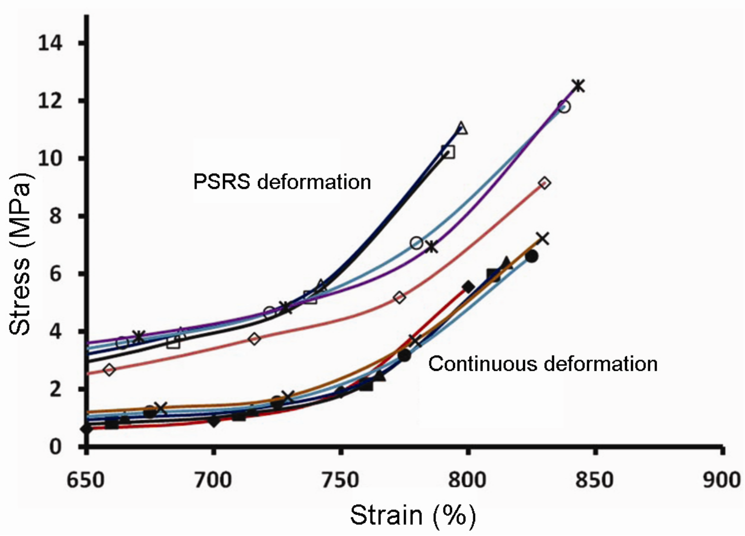

Figure 3. The recovery stresses at different strains for various deformed test samples using both conventional continuous stretching and PSRS scheme.

almost uniformly entangled polymeric chains. The domains can be formed with a slight variation in the polymer chain density due to the processing conditions. On stretching the sample in one step, the domains are deformed with respect to neighbouring domains. The boundaries of domains quickly reach plastic deformation and start dissociating partially, leading to low stress values during stretching and recovery. When the PSRS scheme was applied, the partially stretched samples were relaxed; this allowed rearranging molecular chains to a more stable system in the direction of stretching. On re-stretching, the new stable arrangement of molecules takes the load, which leads to an increase in the stresses developed. On relaxing again another, more stable rearrangement of molecules takes place. On further stretching, this stable configuration of molecules takes the load, showing still further increase in the stresses developed. This rearrangement of the molecular structure helps in distributing the load uniformly to the different constituents of the sample and exhibits improved stress as well as stress recovery. The PSRS scheme helps in rearranging molecular architecture with the smaller stretching and relaxing followed by the next progressive stretching of the sample. It also helps in homogenizing the material with repeated loading and unloading, finally yielding higher strength and stress recovery.

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