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Cyclic Thermomechanical Analysis of Polyethylene Glycol Based Shape Memory Polymers

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Abstract

Shape memory polymers (SMP's) are a type of smart material that possess the ability to remember its original shape. Shape memory polymer quickly recovers to its original or permanent shape. As a result of these properties, SMPs can be used as sensors, actuators, and transplants, as well as auxiliary materials in a variety of applications. It has been used in a variety of domains over the previous two decades because to its shape memory capability, and its applications are growing at a quicker rate. Due to its biocompatibility, wide range of tunable stiffness, large deformation, large recovery, high elastic property, water vapour permeability, and multi responsive shape memory effect, memory polymers, polyurethanes are the most adaptable polymeric material. They offer several advantages over other types of shape memory materials, such as shape memory alloys, such as easier manufacturing, lighter weight, lower cost, larger recoverable strain, and lesser toxicity. When compared to shape memory alloys (SMA's), SMPs have a few disadvantages, such as lower moduli, which results in lower recovery stresses, and longer response times. In some applications, a proper recovery stress derived from the elastic recovery stress created during the deformation process is crucial. There is no literature on how to synthesize SMP's in an efficient manner. SMP's and its classification in terms of their distinct qualities. This work focuses on the analysis of cyclic thermomechanical tests of linear SMP's in order to address some of these problems. Form memory polymers were made using a two-step polymerization process in this study, with the composition of PEG 6000-IPDI-PEG600-BDO as 58wt%-42wt%-1ml-1ml respectively and the shape memory effect was assessed using a bend test. Cyclic thermomechanical analysis method involves tensile test procedure in thermal chamber with intermediate temperatures. Mechanical properties such as cyclic thermomechanical test, dynamic mechanical analysis, and tensile test are used in the validation process. In the primary cycle can be determined as for the sample 10 when we applied the load of 0.8 Mpa the strain was found as 200% the shape fixity and shape recovery values are 98.95 and 97.0 respectively.

Keywords: *Shape Memory Polymers, Cyclic thermomechanical test, Dynamic mechanical analysis, Shape Fixity, Shape Recovery.*

1.0 Introduction

Shape memory polymers (SMP's) belong to the cluster of smart materials that have the ability to remember their original or permanent shape. SMP returns to its original or permanent shape as soon as it has been used in a variety of domains over the previous two decades because to its shape memory capability, and its applications are growing at a quicker rate. The ability of SMP to produce recovery force is one of its most outstanding qualities.

SMPs are a special sort of polymer with the ability

to regain their original shape after being exposed to an external stimulus.

1.1 Structure of the SMP

In terms of molecular structure, SMP's usually have phase segregation when it comes to linear block copolymers, which consists of essentially two things:

i. Glass Transition Temperature (iii) (T_g)

The Glass Transition is defined as the lowest set transformation temperature of the hard/crystalline fragment (T_{gh}) that is higher than the transition temperature of the amorphous fragment (T_{gs}).

ii. Melting Transition Temperature (T_m) in Crystalline Segment

T_g is the material's transition temperature. A certain percentage of the chains remain amorphous until the crystallization arrangement is constantly split. The number of crystallites framed predicts that the chains will revert to their distorted state as needed. Because of the number of crystallites framed, the chains will revert to their distorted state, and the temporary shape will be fixed. The SME qualities can be noticed when the polymer structure and morphology are combined, as well as specified processing with defined programming. It is also independent of a single polymer's individual material attribute [1]. The macroscopic properties of polymer are thought to be able to govern changes [2].

1.2. Parameters for Characterization

A set of parameters has been supplied to carry out the characterization process. The nature of the polymer can be expressed in its parameter while also distinguishing it from other material qualities [3]. The following is a brief overview of these parameters:

a. Shape fixity-RSF
b. Shape recovery-RSR

2.0 Material and Methods

2.1 Materials

Sigma-Aldrich provided the materials used in this study. Polyethylene glycol (Mw 6,000), commonly known as soft segment, is the polyol employed here. 4,42 -diphenylmethane diisocyanate (MDI), Isophorone diisocyanate (IPDI), also known as hard segments, were refrigerated before use, dimethylformamide (DMF) as a solvent was stored under molecular sieves, Polyethylene glycol (Mw200) as a crosslinking agent, 1, 4-butanediol (BDO) as a chain extender, and dibutyl dilaurate catalyst [4].

2.2 Methodology

A 500mL three-neck round bottom flask, a silicone oil bath with a temperature regulator, and a stirrer are used in the material synthesis set up. Dry nitrogen was used in conjunction with a rubber bladder to prevent oxidation, and a thermometer was used to monitor temperature. A weighed amount of Polyethylene Glycol-6000 (PEG-6000) and dimethylformamide (DMF) were put gently into the flask first, followed by Isophorone diisocyanate (IPDI) and two droplets of dibutyltin dilaurate (DBDT) catalyst. PEG-200 was dropped inside the flask after 2 hours of reaction at 90°C, and the process was proceeded with the addition of Methylene diisocyanate (MDI) [5]. The mixture of all of the foregoing was reacted for another hour with constant mixing. The mixture of all of the foregoing was reacted for another hour with constant mixing. The method is completed by gently adding the chain extender Butanediol (BDO) for the chemical reaction at 60°C for 60 minutes. The polymer resin is poured into the glass mold to complete the casting of SMP films. Finally, the polymer films were heat treated individually at 60°C for 12 hours, 80°C for 24 hours, and 100°C for 8 hours to obtain the molecular structure [6].The Pictorial view of synthesis of SMP's is shown in Figure 1.

3.0 Experimental Work

3.1 Cyclic Free Strain Recovery Tests

The dissimilarity between thermoplastic and cross-linked samples can be examined using the cyclic free strain recovery test in tension mode, which can be measured in percentage recoverable strain. The

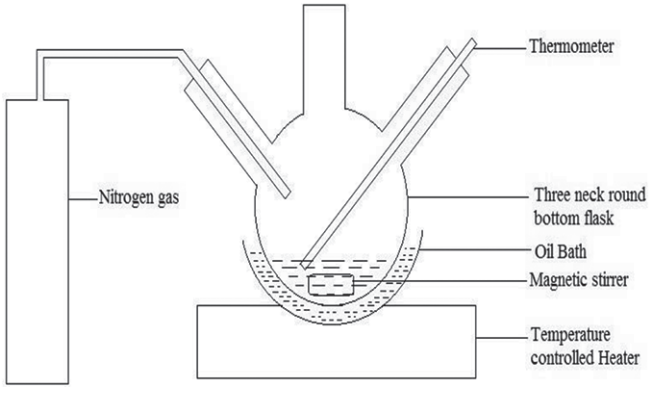


Figure 1: Pictorial view of synthesis of SMP's

temperature and time are recorded using the Q Series software. 2 and 3 cycle studies were carried out independently for cross-linked and thermoplastic samples [7, 8]. The Schematic representation of Cyclic Free Strain Recovery Test is shown in Figure.2.

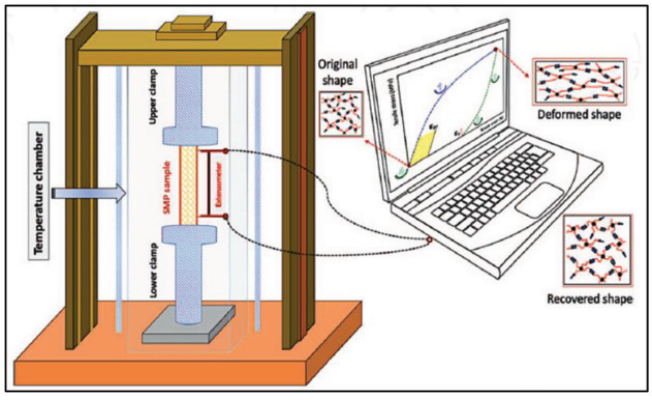


Figure 2: Schematic representation of Cyclic Free Strain Recovery Test

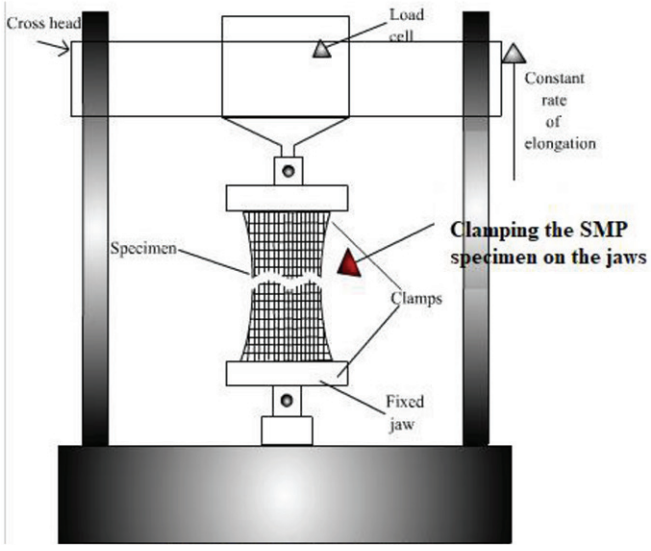


Figure 3: Schematic representation of constrained recovery test

At Step 1, SMP test is warmed to a high temperature, Thigh, over the exchanging temperature, Ttrans, and is stretched out to a planned strain (εm). At Step 2, the example is kept up with consistent strain εm, and is cooled to a low temperature, Tlow, beneath the exchanging temperature, Ttrans, to fix the impermanent shape. At Step 3, the cinches of the ductile analyzer return to their unique position. At the initiation of the emptying procedure, the versatile recuperation worry of the example is dense and transforms into zero at strain εu, and the example will twist with further emptying. At Step 4, the example is warmed to Thigh and after that recoups to the perpetual shape with a remaining strain εp. From that point forward, the cycle starts again.

3.2 Constrained Stress Recovery Tests

To see how cross-linking affects recovery stress and restricted stress recovery, sample 10 was chosen to see what the maximum recovery stress of the examples in the SMP's was. Sample 5 was chosen because at a rate of 5°C/min from 0 to 150°C. The temperature-dependent recovery stress is measured [9,10]. Schematic representation of constrained recovery test is shown in Figure 3.

Experimentation was carried out on samples to evaluate the toughness values, ultimate tensile strengths, and failure strains. As per the ASTM Standard D-638, I shape cross section shape samples were trimmed using a snipping tool. Figure 4 shows the dimensions for constrained recovery test.

4.0 Results and Discussions

4.1 Cyclic Thermomechanical Test

It can be seen that yielding occurs at a strain of 10%, and that the stress level climbs steadily until it reaches 60%, after which it inclines and the curve becomes

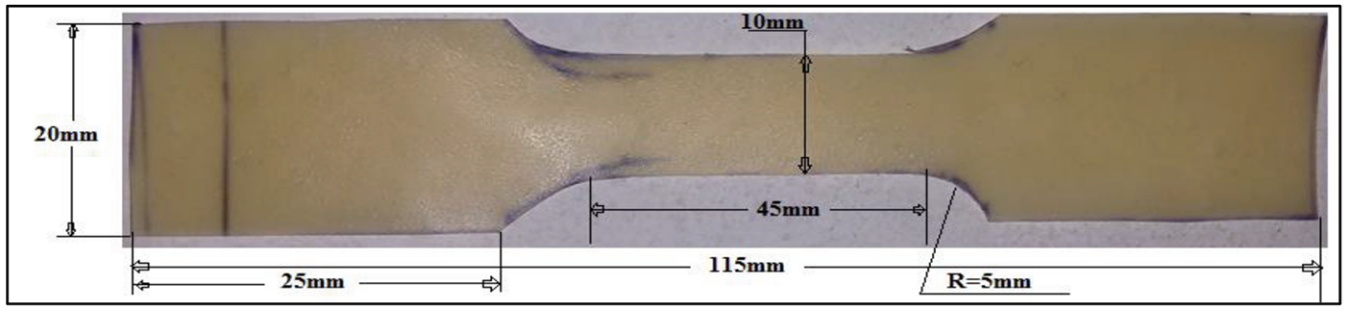
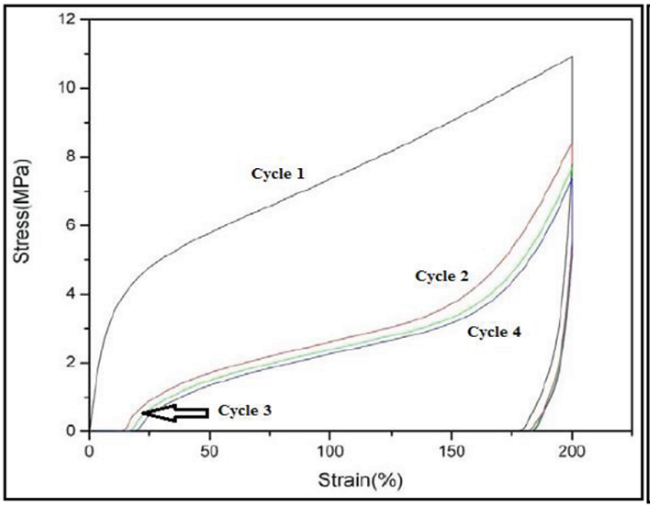
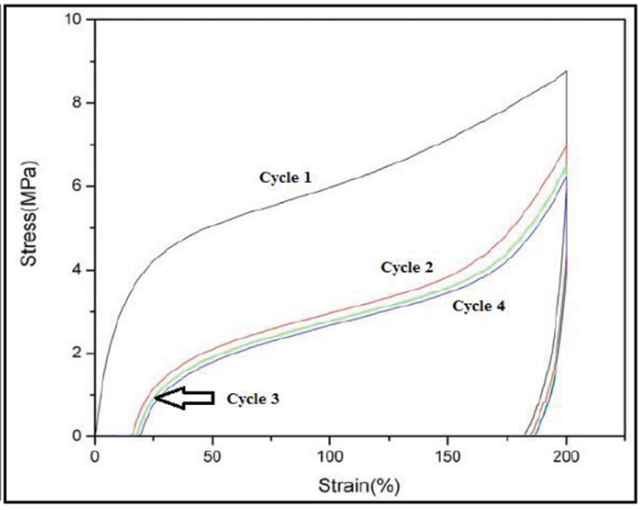


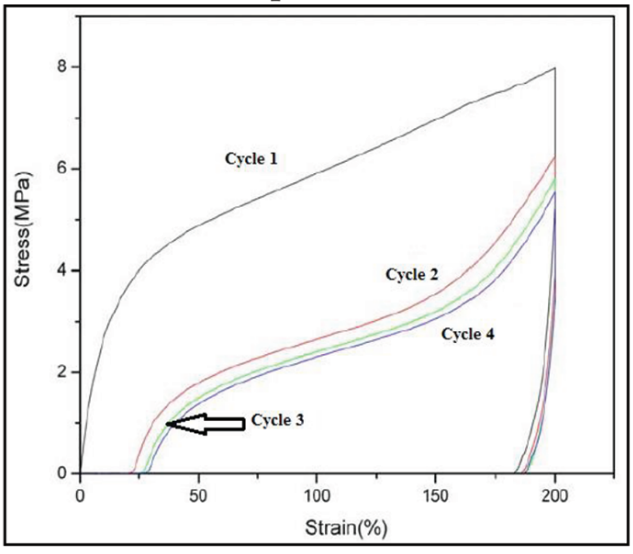
Figure 4: Sample showing the dimensions for constrained recovery test



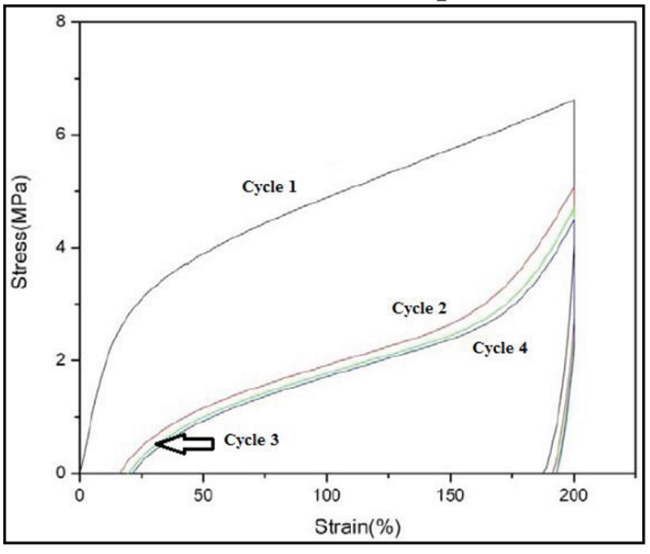
Sample 1



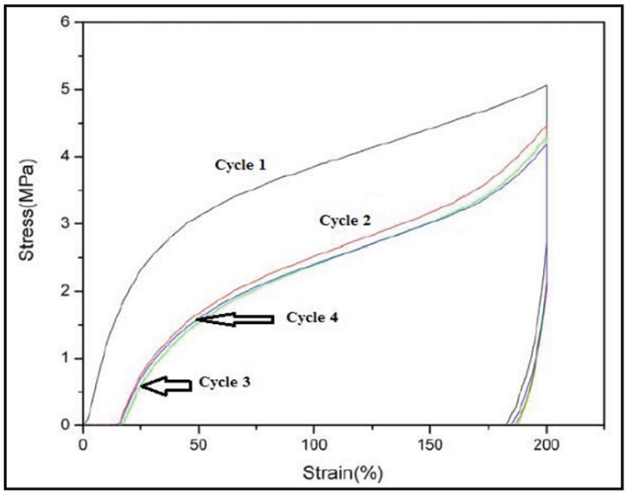
Sample 2



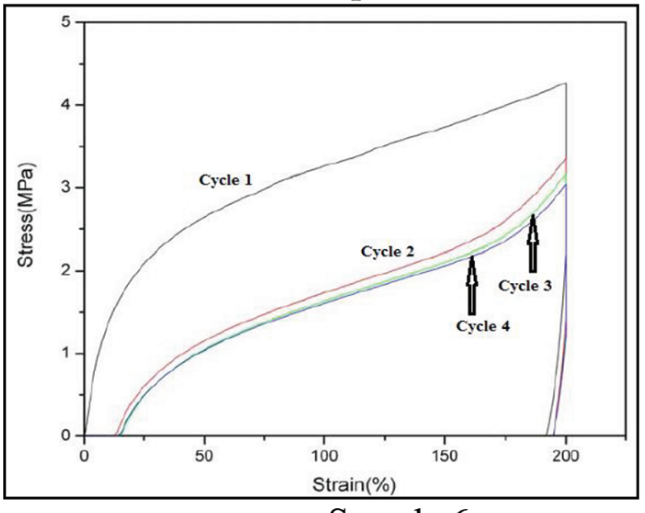
Sample 3



Sample 4



Sample 5



Sample 6

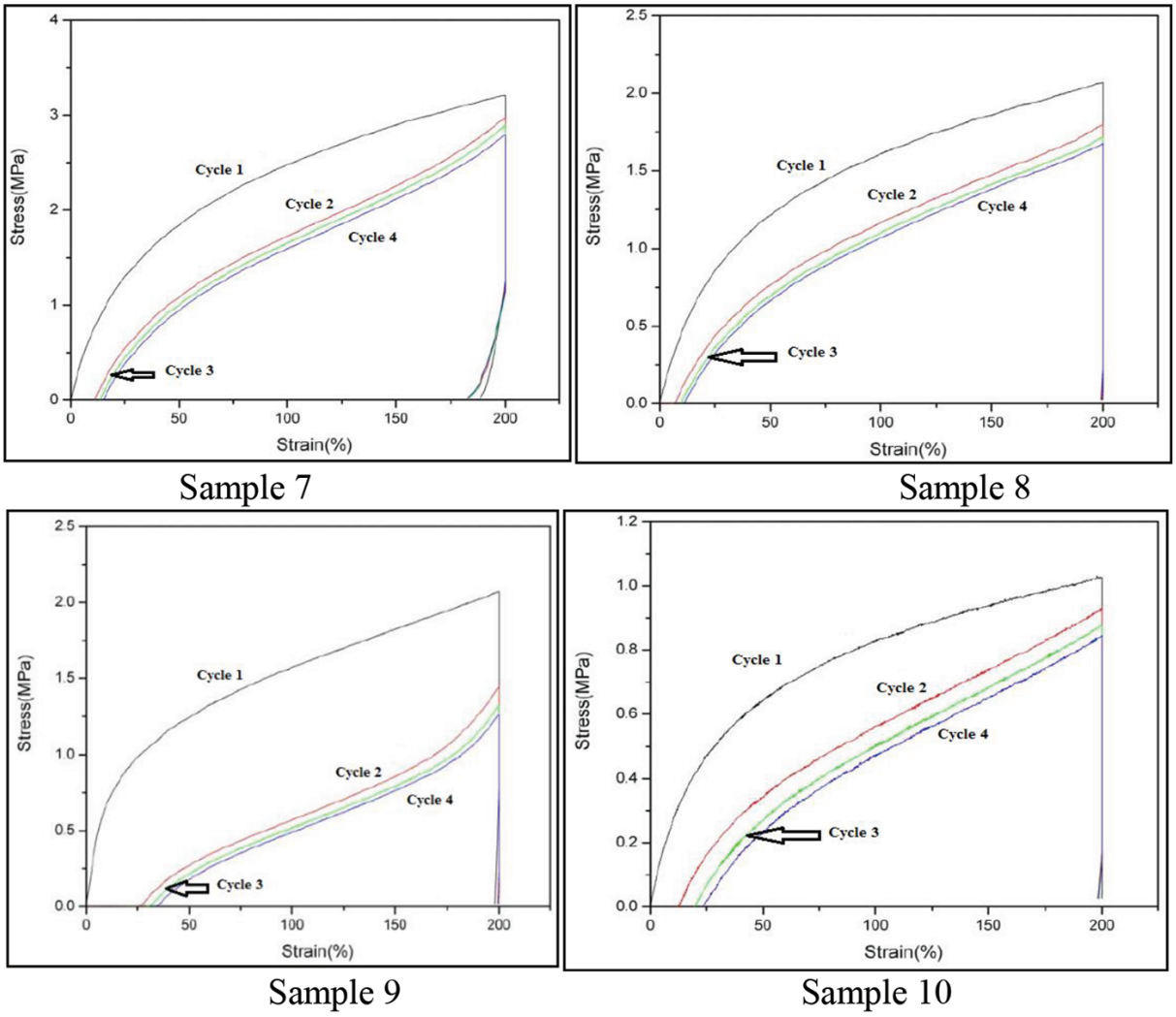


Figure 5: Showing the thermomechanical cycles from sample 1-10

steep. When the stress is in that range, dislocation of cells occurs in the axial direction of compression. The material is consistently compacted and deformation resistance increases in the ascending zone over a tension of 60%. Stress dissipates fully beneath Tg in the cooling approach. As a result, the most remarkable strain is maintained, resulting in a rate of shape fixity R_{sf} of 98.95 per cent.

In the main cycle, the shape recovery rate (R_{sr}) and shape fixity rate (R_{sf}) can be calculated as 95 per cent and 91 per cent, respectively, using the equations R_{sr} [(m-p)/m] 100 per cent and R_{sf} (u/m) 100 per cent. In the primary cycle, samples 5-10 had R_{sf} of 90-91 per cent, while samples 1-5 had R_{sf} of 81-84 per cent

The increase in Mw of the PEG component increased crystallisation and, in turn, increased R_{sf}. The increase of Mw and the crystallinity of PEG-diols, on the other hand, had only a minor effect on R_{sr}. With an increased number of test cycles, R_{sr} climbed somewhat, reaching 99 per cent in the third cycle, but R_{sf} was about proportional in each of the three cycles. The percentage of switching segments which change. In each example, the percentage of switching segments between 65 and 75 per cent had a minor impact on R_{sf} and R_{sr}.

As shown in Figure 5. The shape recovery and fixity of PEG/MDI//BDO SMPUUs were similar to the PEG/MDI//BDO copolymer system. Both properties for sample 1 and sample 2 PU-M-CL-8K-BDA- 20% were above 90% along with a small deviation which showed excellent shape memory properties after programming. This result indicates that the shape recovery and fixity were closely related to the crystallinity of the PCL phase of specimens cooled in the elongated state. Meanwhile, the change of chain extender from BDO to

BDA increased the recovery stress significantly, for example, PEG/MDI//BDO -20% had a 5 MPa stress at 200% strain which was almost double of that in the PEG/MDI//BDO -20% copolymer.

4.2 Shape fixity (R_{sf}) and Shape Recovery ratio (R_{sr})

Shape fixity and shape recovery are two important shape memory factors that are commonly employed as measures to quantify shape memory performance. Shape recovery refers to a material's ability to restore a permanent shape, whereas shape fixity refers to its ability to store a temporary shape. They are both dimensionless ratios of various crucial strain points in the thermomechanical cycle. Shape fixity (R_{sf}) describes the switching segment's capacity to maintain a transient deformation during the programming procedure.

$$R_{sf}(N)=(\varepsilon_U(N))/\varepsilon_m \times 100\% \quad \ldots (1)$$

The shape recovery ratio (R_{sr}) describes how well shape memory materials may return to their original shape.

m= maximum strain applied, u = relaxed strain after cooling down with applied force, and p = residual strain after thermal recovery are the notations used here. For cyclic testing using the aforementioned stress, strain, and temperature sequence, N and N-1= nth and nth-1 cycle.

Table 1 shows the details of cyclic thermomechanical behaviour for samples; here the load applied is 10.5Mpa and the strain obtained is 185 per cent; this is because the hard segment percentage rate was less and the cross-linking density was also less; thus the shape fixity and shape recovery values are 92.5 and 93.6; as we keep increasing the hard segment content at one point, the strain remains constant because the molecules inside the structure won't reach saturation point; thus the shape fixity and shape recovery values are 92.5 and 97.0 respectively.

SMP-PEG-6000 polyol has a transition (melting) temperature from 42 to 52°C with a narrow transition region of ~10°C. It is known that low heat of fusion is an indication of low crystallinity and high phase compatibility between the hard and the soft segments.

Avoiding side chains, which disrupted hydrogen bond formation, was the most critical element in raising recovery stress. The main chain's molecular weight and rigidity also contributed to the increased recovery stress, but not to the same extent as the presence of side chains.

Figure 6 depicts a graph of shape fixity vs. number of cycles; cyclic thermomechanical testing confirm how long the specimen can temporarily fix the deformation during the programming procedure. Regarding multiple cycles utilized in cyclic testing, this test yields the figures of maximum strain applied, relaxed strain, and cooling down the force applied. The obtained values are less due to hydrogen bonding is less, which will reduce the ability of the material to take more loads and thus the strains are less, whereas once the composition of hard segment, cross-linking agent, and chain extenders are added more, the hydrogen bonding and carbonyl groups increase, giving more. Carbonyl groups rise, giving the material more strength to withstand loads and higher values, as illustrated in Figure 2, where the values are 0.91 and 0.90, respectively, with a form fixity value of 98.95.

Table 1: Details of Rsf and Rsr ratio values with respect to strain values

	Sample ID	relaxed strain •εu%	maximum strain •εm%	residual strain εp%	Shape fixity R_{sf}%	Shape Recovery ratio Rsr%
1	SMP-1	0.42	0.45	0.10	92.45	93.6
2	SMP-2	0.45	0.49	0.13	92.65	94.3
3	SMP-3	0.49	0.51	0.15	93.92	94.9
4	SMP-4	0.52	0.54	0.17	94.85	95.3
5	SMP-5	0.54	0.56	0.19	95.45	95.8
6	SMP-6	0.57	0.59	0.21	96.55	96.1
7	SMP-7	0.65	0.68	0.23	96.65	96.3
8	SMP-8	0.74	0.76	0.25	97.75	96.5
9	SMP-9	0.82	0.85	0.27	97.85	96.7
10	SMP-10	0.90	0.91	0.34	98.95	97.0

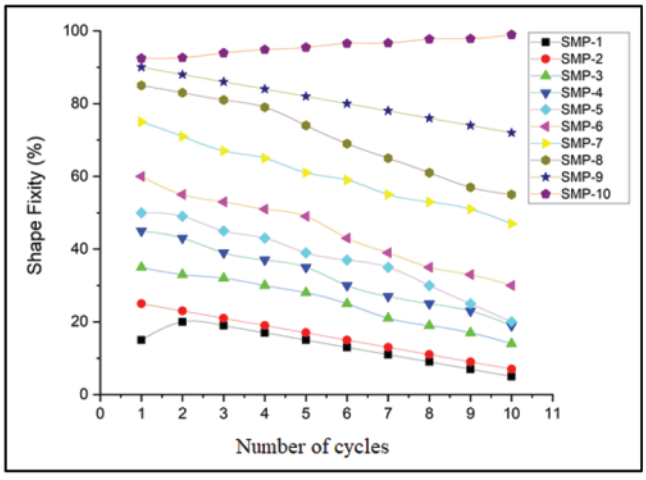


Figure 6: Showing the percentage of shape fixity with respect to number of cycles

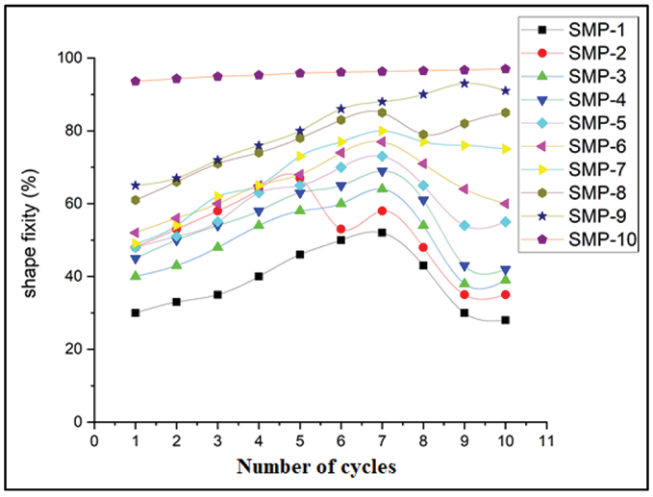


Figure 7: Showing the percentage of shape recovery ratio with respect to varying composition.

Strain is increased in the prescribed region of Tg in the heating operation under no load, according to thermomechanical tests with respect to strain-temperature curves. Strain is maintained because the miniature Brownian movement of fragile SMP segments is established in the smooth zone at temperatures below Tg. Brownian movement becomes dynamic and the strain is recovered when the material is heated to temperatures in the region of Tg due to the smaller scale Brownian movement. Reiteration has no effect on the strain-temperature curves. The amount of strain left in the wake of heating is minimal, regardless of the number of cycles, and the rate of form recovery Rr is 97.0 per cent.

Figure 7 illustrates the shape recovery ratio vs. the number of cycles; cyclic thermomechanical testing confirm the SMP's capacity to return their original shape. The residual strain after recovery is collected from different cycles for cyclic testing for the nth-1 cycle, together with the highest strain applied. As demonstrated in Figure 3, the strain applied is initially very low, therefore the residual strain obtained is also low, at 0.45 and 0.10, respectively. Because the HS are more diverse in composition, the specimen will be less stressed. Figure 3 shows that as the iterations go, additional segments are inserted, increasing the maximum strain applied and residual strain after recovery to 0.91 and 0.34 for nth and nth-1 cycles, respectively.

5.0 Conclusions

1. From the cyclic thermo-mechanic tests, the recovery stresses of PEG-MDI-IPDI was found to be 3.5 MPa and recovery strain is found to be 200%.
2. Using thermomechanical test with respect to strain-temperature curves it can be observed strain values are increased in the specified region of Tg in the heating procedure under without load.
3. Shape fixity and Shape Recovery Ratio which is obtained to be 98.95% and 97.0 respectively. This is because HS percentage rate is less and crosslinking density was also less.
4. For the sample 10 it was observed that the applied load of 0.8 Mpa the strain was found as 200% of the shape fixity and shape recovery values are 98.95 and 97.0 respectively.
5. Percentage of switching segments between the range of 65% and 75% are slightly affected with respect to Rsf and Rsr.
6. SMP-PEG-6000 polyol has a transition (melting) temperature from 42 to 52°C with a narrow transition region of ~10°C.

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