Synthesis and characterization of graphite based shape memory polymers

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Abstract. Shape memory polymers are the class of materials which regains its shape up on external stimulus like heat, magnetic field, light etc. these polymers have got wide range of applications in biomedical and automobile industries. There are many researches going on about the shape memory polymers and it is better than other smart materials in some characteristics. This paper covers about the strength of the polymer after adding graphite to the polymer. The addition of graphite would gradually increase the characteristics of the polymer. These polymers are flexible and have less strength. The primary idea of improving the characteristics was to increase the strength of the polymer. We have added graphite to peg based polymer which has increased the hardness significantly. Many tests were conducted on the graphite-based shape memory polymer like tensile test, hardness test and dynamic mechanical analysis, it was observed that the characteristics were enhanced by adding graphite to the polymer.

Keywords: Shape memory polymer, Cross-linking, Shape memory effect, thermomechanical,

1. Introduction

The materials which regains its original shape when an external stimulus is applied on it is known as shape memory polymers, the external stimulus might be heat, light, magnetic field etc. these smart materials are classified into shape memory alloys, shape memory ceramics and shape memory polymers [19]. SMPs have lower density, better strain recovery rate, and lightweight and most importantly it is cost effective. These polymers can replace other smart materials in many of the applications. It is mainly used in actuators, textile industries and in aerospace applications. Even though, shape memory alloys are better, there are some obvious reasons for going for SMPs like poor corrosion resistance, high mass density, low strain etc. The polymers which react to the temperature is called thermoresponsive polymers [19].

Literature studies shows that the addition of certain additives or fillers would enhance the properties of the polymer. Sometimes the addition of certain cross-linking agents would increase the stability of the polymer, these cross-linking agents might be functional groups such as alcohol, here in or experiment butane-diol (BDO) is used as the chain extender [18]. The addition of certain materials would increase the bond strength which in turn increases the hardness of the shape memory polymer [1]. The addition of hard segment would decrease the shape recovery speed of the polymer. The glass transition of the polymer will increase by adding more of hard segment [2]. The addition of the graphite in the polymer increases the cross-linking ability of the polymer which in turn increases the hardness of it. Graphite also increases the melting point and electrical conductivity of the polymer which makes the polymer suitable for electrical applications.
Researches are to be carried out on adding different additives to the shape memory polymer as it has got many advantages over other smart materials. Materials like graphene, CNT and other allotrope forms of carbon can also be added to the polymer by checking its solubility to enhance the properties of the polymer.

2. Materials and Methods

2.1. Materials

The chemicals of the soft and the hard segment is reported [3]. PEG-6000 is used as the soft segment. It is required to add 58% of soft segment and 42% of hard segment in order to get optimal result. Graphite was added to this concentration and the polymer was obtained. The hard segment used are 4,4’-diphenylmethane diisocyanate (MDI), isophorone diisocyanate (IPDI), PEG-200 and 1, 4-butaneediol (BDO). The concentration of PEG-200 is 10 wt% and the concentration of BDO used is 4.2 wt%.

2.2. Methodology

The set-up consisted of 2-neck round bottom flask of 500 mL, hot water bath along with a magnetic stirrer, temperature controller and a thermometer. The flask was continuously purged with dry nitrogen to prevent the reaction from contaminants. A measured amount of PEG-6000 was added to round bottom flask along with 25mL of DMF up on continuous stirring and purging of nitrogen gas till it reaches 90 degrees. Required amount of graphite was added to the solution and is dissolved completely, then we add suitable molar concentration of IPDI and 2 drops of DBTDI, the reaction is kept for 2 hours. After 2 hours, suitable amount of MDI and PEG-200 with 10mL of DMF solvent was added to the solution and the reaction was continued for 1 hour. Then, the temperature was reduced to 60 degrees and 10 drops of BDO with 5mL of DMF was added and the reaction is continued for another hour. The solution was poured into the glass mould and cured in 3 stages inside a hot air oven. Firstly, the solution is cured at 60 degrees for 12 hours. Then, it is cured at 80 degrees for 24 hours. Lastly, the solution was cured at 100 degrees for 8 hours. Finally, the polymer is taken out from the oven and removed from the glass mould.

3. RESULTS AND DISCUSSION

Tensile test, hardness test and dynamic mechanical analysis was carried out on graphite-based shape memory polymers, and it was found that the addition of graphite increased the hardness of the polymer. With respect to above test the shape memory test was also performed which shows 100% recovery with a span of 20seconds at 30°C. It can be found that the addition of graphite to PEG matrix nowhere affected the shape memory properties.

3.1. Tensile test

Tensile test is carried out to find out the tensile characteristics of the specimen like peak load, breakage points and other parameters to know the strength of the specimen. Graphite based specimen was cut into dumbbell shape and it was fed into the UTM. Uniform load was applied on the polymer
and the stress-strain relationship was found out. At one point, the specimen fails to take further load, the brittle materials will have less toughness whereas flexible materials will have more toughness.

Table 1: Tensile test results for varying graphite composition of different samples:

| Graphite (g) Wt% | Ultimate tensile strength (MPa) | Young’s modulus (MPa) | Percent elongation to break |
|------------------|--------------------------------|-----------------------|---------------------------|
| 0                | 36.5 (62)                      | 1957                  | 2.6 (3.5)                 |
| 0.05             | 13.4                           | 600                   | 40                        |
| 0.1              | 17.3                           | 170                   | 226                       |
| 0.15             | 41.8                           | 55                    | 628                       |

Figure 1. Tensile test graph for various wt% of graphite

It was found that the addition of graphite reduces the tensile strength of the specimen. In other words, the specimen becomes more flexible by reducing the graphite content but in contrast, it is very important to note that the flexibility of the polymer after adding graphite was not reduced to a greater extent. The reason behind reduction of strength is the SMP becomes brittle with the addition of more graphite content, hence and optimum wt% of graphite is added to PEG matrix to obtain good ultimate strength without compromising the shape memory effect. Table 1 shows the tensile test values with respect to graphite composition, the strength is 41.8MPa for the sample having 0.015wt% of graphite and the elongation is found to be 628, this shows the addition of graphite in higher percentage has not affected the elongation.

3.2. Hardness test

The hardness of the specimen is defined as the resistance to permanent indentation. The hardness of the natural rubber and rubber could be found out through Rockwell hardness test and Shore hardness test. Shore hardness test was carried out on the specimen in which the spring-loaded needle was placed against the sample and different pressures were applied on the sample at different intervals of time.
The indentation caused on the sample gives the respective pressure applied on the specimen. Hardness of the specimen is defined through the hardness number.

Table 2: Hardness test results for different samples:

| Graphite wt% | Durometer | Indenting foot | Time (s) | Load (Kgf) | Hardness |
|-------------|-----------|----------------|----------|------------|----------|
| 0           | Shore D   | 1.1 mm – 1.4 mm diameter | 20       | 60         | 56.2     |
| 0.1         | Shore D   | 1.1 mm – 1.4 mm diameter | 20       | 60         | 59.4     |
| 0.05        | Shore D   | 1.1 mm – 1.4 mm diameter | 20       | 60         | 65.3     |
| 0.15        | Shore D   | 1.1 mm – 1.4 mm diameter | 20       | 60         | 71.5     |

Figure 2. Hardness values with respect to load.

By increasing the graphite content of the polymer, we can increase the hardness of the specimen but, there will even be experimental anomalies which are to be taken into consideration for example, 0.05g of graphite specimen has got more strength than 0.1g of graphite specimen. As shown in figure 2 it is very important to follow every step of the methodology properly to get the desired properties of the polymer. As a whole, we can conclude that the addition of graphite will significantly increase the hardness of the polymer by compromising very less flexibility.

3.3 Dynamic mechanical analysis

DMA is an analysis in which a small stress is applied on a cyclic manner which allows the material to respond to frequency, temperature, stress and other factors. The basic objective of performing DMA on a specimen is to find stiffness and damping which is expressed in terms of tan delta and modulus. The storage modulus is represented as E’ and the loss modulus is represented as E”. The ratio of loss modulus to storage modulus is tan delta which is nothing but damping. The value of glass transition could be found out by DMA, glass transition temperature is a temperature at which the polymer becomes pliable. It is very important to know the glass transition temperature of the specimens in order to perform shape memory test. This temperature can be found out by plotting a graph between log scale of E’ and temperature. The graph plotted in figure 3 shows a peak, the corresponding value of the temperature gives the glass transition temperature of the specimen.
Figure 3. DMA graph for 0.1g of graphite

Figure 4. DMA graph for 0.05g of graphite

Figure 5. DMA graph for 0.15g of graphite
The graph plotted in figure 4 and figure 5 drawn taking log scale of $E'$ against temperature to find the glass transition temperature of the specimens and it was found that the glass transition temperature gradually increased up on the addition of graphite.

Table 3: DMA analysis results for different composition.

| Freq. (Hz) | Temp. (Cel) | $E'(G')$ (Pa) | $E''(G'')$ (Pa) | dL (um) | tanD | Ft (mN) | Time (min) |
|------------|-------------|---------------|-----------------|--------|------|--------|-----------|
| 5          | 36.94734    | 8.22E+08      | 1.6E+08         | 126.3881 | 0.194992 | 1248.163 | 0.15      |
| 2          | 36.94016    | 7.35E+08      | 1.48E+08        | 127.0825 | 0.201341 | 1248.163 | 0.283333 |
| 1          | 36.93109    | 6.73E+08      | 1.39E+08        | 129.8603 | 0.206434 | 1248.163 | 0.466667 |
| 0.5        | 36.92641    | 6.16E+08      | 1.31E+08        | 131.9436 | 0.211851 | 1248.163 | 0.683333 |

Table 3 gives the information of storage modulus, loss modulus, and tan delta. In figure 5, the storage shear modulus $G'$ and the loss shear modulus $G''$ are drawn against the temperature from -5°C to 150°C. Until accomplishing the region of the $T_g$ there is a drop away modulus $G'$ dynamically with increasing temperature. Changes in $G'$ with temperature are incredibly divergent for low and high frequencies starting from that area. For frequencies higher than 2Hz, there is an event of a fast decrease in estimations of the capacity modulus.

3.4. Shape Memory Effect

The SMP sample, in the beginning, rolled/bend to 100% on 60°C (> $T_g$), and by cooling it to ambient temperature the distorted shape was fixed (~20°C). After adjusting the hot plate to 60°C the sample was placed on top and the changes in shape were recorded after some time.

![Figure 6. Shape memory effect of graphite based SMPs at 30°C.](image)

Figure 6 shows the SME of blank SMP’s and 4.2 demonstrates the SME of SMP’s filled with graphite as a filler along with transition temperature and time, in figure 6 (a) the flat rectangular sample appears before deformation, figure 6 (b) demonstrates the sample after deformation (bent to u shape) which has been deformed in cold state, figure 6 (c) demonstrates the sample which has been recovered to flat rectangular i.e. earlier permanent shape upon heating to 30°C for a time of 20 second.
4. CONCLUSION

The addition of graphite significantly increases the hardness of the polymer by compromising minimum flexibility. Graphite is much cheaper than many other allotropic forms of carbon, it could be clearly seen that the research on this work is still in progress. All the three test results give the following inference:

1. Graphite based SMP’s have better hardness when compared to SMP’s but not so flexible after seeing the characterization result. It could be used where hardness is of greater significance.
2. The tensile strength of the graphite-based polymer is not much lesser than SMP’s.
3. The glass transition temperature of the polymer increases with the addition of graphite.
4. DMA results shows the graphite based SMP’s are good for damping related applications which shows good tan δ values.
5. Shape memory test reveals that graphite based SMP’s shows 100% shape memory effect.

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