INVESTIGATIONS ON ELECTRO-ACTIVE SHAPE MEMORY POLYMER NANOCOMPOSITES: POLYURETHANE – CARBON BLACK / CARBON NANOTUBE SYSTEMS

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Abstract

Materials those possess the ability to sense, process and respond to any external stimuli are termed as smart materials. Mimicking nature, human efforts towards smart systems have led to discovery of materials that are capable of sensing and responding to the environmental conditions. Such materials can be used in various applications such as medical, robotics, aerospace technologies, etc. The phenomenon exhibited by few smart materials to regain the original shape while exposing them to certain stimuli such as moisture, heat, light or chemicals etc., is termed as shape memory effect (SME) and such materials are called Shape Memory Materials (SMM). Polymeric shape memory materials with organic / inorganic nano scale fillers distributed homogeneously across the matrix, synthesized by physical blending or chemical polymerization methods are termed as Shape memory polymer nanocomposites (SMPC). The presence of nano fillers influences the mechanical, thermal and electrical property of such polymer nanocomposites. Material properties are also influenced by the synergistic combination of one or more kind of nanofillers in a polymer matrix.

To appreciate the current conduction phenomenon in polymer nanocomposites, correlation between experimental and theoretical model needs to be established. As the outcome of many of the models developed so far could not precisely match with the experimental results, a comprehensive model, which can predict percolation threshold and conductivity for specific fillers, is required to be worked on. Such a model can be used as a generalized prediction tool for any resin-filler system with their corresponding properties as input, and the same can avoid laborious experiments in the chosen system. This can take into account, the statistical and quantum tunneling approaches for current conduction in the polymer matrix filled with conducting nanofillers. Another grey area in the research of shape memory nanocomposite is about the synergy of multiple fillers in nanocomposites. Requirement of different orders of recovery speed and efficiency for specific applications demands the development of materials with variable sensitivity.

PU, being shape memory active and possessing tunable properties (based on careful selection of diisocyanates and polyols), was chosen as the matrix resin for synthesis of nanocomposites in current work. A two-stage pre-polymer route was followed for the PU synthesis, where the macroglycols were end capped with excess of diisocyanates, followed by chain extension of the diols. CB (Carbon Black, three-dimensional geometry) and MWCNT (Multi-Wall Carbon

Nano Tube, one-dimensional filler material) were used as filler materials with an aim to synthesize electrically conducting nanocomposites. The conduction phenomenon in these nanocomposites is either by contact between the fillers or by electron tunneling.

The synthesized PU has exhibited T_g of 85°C which is high compared to the reported values in published literature. The polymer resin and the CB filled nanocomposites were characterized for its chemical, electrical, thermal, mechanical and shape memory properties. The presence of 'aliphatic' diisocyanate (IPDI) and the CB in PU CB nanocomposite makes them stable against UV radiations thus making them an eligible candidate for space applications. The electrical, thermal and mechanical properties were observed to improve with increased carbon loading. The CB PU nanocomposite system has shown a percolation threshold of 6% by weight of resin experimentally which was simulated in the model considering the spherical particle dispersion in a Representative Cubical Volume Element (RCVE). For modeling the nanocomposite, a one micrometer size RCVE was considered and the filler particles were randomly placed in it. Varying the filler content, the process was repeated using Monte Carlo simulations to arrive at a converged percolation threshold. Beyond percolation threshold, the particles can have multiple networks thus increasing the conductivity of the material / system. Same approach was followed for CB and MWCNT as fillers whereas the model was tuned for the difference in parameters such as geometry, size, tunneling distance, contact possibility for each case. Visual C language platform was used for the development of the program and was optimised using multiple algorithms. On simulating the system, the first conductive network appeared at 6.2% weight fraction as per the model (statistically evaluated as the filler content corresponding to percolation probability of 50%).

A systematic modeling approach underlining the parameters specific to CNT-PU system was developed from the understanding of the CB-PU model. The RCVE filled with randomly oriented CNT with varying aspect ratio is simulated based on optimization algorithms. The percolation threshold in PU-CNT system based on the model and simulation arrives to 0.19% by weight of CNT. Compared to the CB model, the lower value of percolation threshold value is attributed to the high aspect ratio and geometry of the nanotubes. For evaluating the model, PU resin based nanocomposite was synthesized with MWCNT added in 0.1% - 10% by weight. The synthesized PU-MWCNT system was characterised for chemical, microstructural, thermal and mechanical properties and it was observed that the PU-MWCNT nanocomposite was superior to PU-CB system in mechanical and electrical properties. The large aspect ratio of MWCNT contributed towards network formation at lower filler content and caused percolation experimentally at 0.21% by weight of MWCNT, which closely matches with the theoretical results. Thus, a reliable generalised structural model for understanding and predicting percolation in nanocomposite systems was developed and established the reliability.

A multi-filler system was also experimented to understand the synergy between the CB and MWCNT in PU to form nanocomposites. The combinations showed a trend of increasing conductivity with increased MWCNT content per CB weight fraction. The conductivities varied from the order of 10^{-12} to 10^{-5} S/m, with 5% CB – 0.15% MWCNT combination showing percolation threshold. The observed electrical conductivity was found higher than the individual filler contents in binary single filler systems.

The relationships between the various parameters (T_g, Voltage, time of exposure) that influence the shape memory effect were also studied for all three systems. This can be used as a reference for designers to select filler content based on the required time and power availability. The thermal and electrical stimulation of shape memory effect was evaluated for all the three developed systems, and the highest efficiency and fastest recovery for PU based shape memory systems reported so far were observed.

The knowledge from this exploration can help the researchers to look outside the conventional actuation systems employed to less complex and lighter systems from shape memory polymer nanocomposites. A comprehensive understanding of the conductivity phenomenon in such nanocomposites helps to deduce different combinations of the fillers and to arrive at the optimal composition theoretically prior to synthesis. The established models can predict the electrical percolation threshold of nanocomposite systems, which can help reduce the number of time taking experiments. The possibility of combining the advantages of individual nanofillers to create novel materials with superior properties can be opened to the scientific world by the synergistic approach.