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Mechanical and thermal properties of MoS_2 reinforced epoxy nanocomposites

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Abstract. The effects of molybdenum disulfide (MoS_2) on thermal expansion and mechanical properties of epoxy composites were investigated. MoS_2 nanosheets were exfoliated by ultrasonication and reinforced into epoxy as nanofiller by mechanical stirring. Transmission electron microscopy observations demonstrated that MoS_2 exhibited better dispersion in epoxy matrix. Thermal expansion measured by dilatometer has revealed that increasing MoS_2 fraction in epoxy matrix significantly reduced the coefficient of thermal expansion (CTE). The 0.5wt% MoS_2 incorporated epoxy composites shows 35.8% reduction in CTE as compared to neat epoxy. The addition of small fraction of MoS_2(0.1wt%) in the composites increased the tensile and flexural strength 39.2% and 9.0% respectively. The glass transition temperature (T_g) of 0.1wt% MoS_2 incorporated epoxy composites shows 7.39% increase in T_g.

1. Introduction

Polymer nanocomposites is one of the emerging fields in materials research because of their novel applications ranging from electrochemical energy storage, light weight structures in aerospace and automotive, and flexible substrate in electronics. Among various fillers, carbon based nanofillers such as carbon nanotubes and graphene exhibit excellent electrical, mechanical and thermal properties, which make them as potential reinforcing filler for polymer composites [1–7]. However, carbon nanotubes are expensive and limits its industrial applications. On the other hand, graphene is electrically conducting, which often restricts its application in power electronics, electric motors, packing etc. [8]. Recently, two-dimensional (2D) transition metal dichalcogenides such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) have emerged as an ideal material to replace carbon nanotubes and graphene because for their unique functional properties and wide range of applications including lubricants, electro catalyst, hydrogen storage etc. [9–13].

The detailed investigation of thermal and mechanical behavior of epoxy nanocomposites fabricated by using MoS_2 as filler is limited. Therefore, the present work has been focused to fabricate epoxy nanocomposites with varying addition of MoS_2 and subsequently investigated

for thermal and mechanical properties. The fabrication of MoS_2 reinforced epoxy composites was made by combination of ultra-sonication and mechanical shear mixing techniques.

2. Experimental studies

2.1. Materials

MoS_2 was procured from Loba Chemie Pvt. Ltd., Mumbai, India. N, N'-dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Merck Life Sciences Pvt. Ltd., Mumbai, India. Diglycidyl ether of bisphenol A (DGEBA Araldite LY556) based epoxy resin was obtained from Huntsman, India. All the chemicals were used without further purification.

2.2. Synthesis of Exfoliated MoS_2 (ex-MoS_2) and Fabrication of epoxy-MoS_2 nanocomposites

First, 400 mg of MoS_2 powder was sonicated in 80 ml of DMF using a horn-type sonicator for 12 hours. Then, DMF was removed by filtration and the resultant exfoliated MoS_2 (ex-MoS_2) powder was dried in oven at 60°C for 12 hours. The as-obtained ex-MoS_2 powder was redispersed in a small amount of THF with a bath-type sonicator for 30 minutes. The resultant ex-MoS_2/THF dispersion was added to diluted epoxy resin and mechanically stirred using shear mixer for 4 hours at 700 rpm. Finally, calculated amount of curing agent (triethylenetetramine) was added and the reaction mixture was further stirred for 5 minutes. The resultant homogenous solution was poured in a silicone mold and cured at room temperature for 24 hours to obtain epoxy-MoS_2 nanocomposites. Finally, the samples were post cured at 60°C for 3 hours. The loadings of ex-MoS_2 in epoxy composites were varied (0.05wt%, 0.1wt%, 0.25wt% and 0.5wt%), and the resulting composites were named as Epoxy-MoS_2(0.05%), Epoxy-MoS_2(0.1%), Epoxy-MoS_2(0.25%), and Epoxy-MoS_2(0.5%) respectively.

2.3. Microstructural, Thermal, and Mechanical Characterization

Transmission electron microscopy (TEM) images of the ex-MoS_2 and epoxy-MoS_2 composites were obtained using a (JEOL JEM 2100 instrument). A small amount of ex-MoS_2 powder sample was dispersed in THF by bath sonication and then dropped on 200 mesh copper grids with supporting carbon films. For epoxy-Mos_2 composites, the TEM samples were prepared by ultramicrotoming technique. Scanning electron microscopy (SEM) images of bulk MoS_2 and ex-MoS_2 powder were obtained by using M/s FEI Quanta 3D FEG. Thermal expansion studies of nanocomposites were carried out using a Push-Rod Dilatometer, M/s VB ceramic consultants, India. Differential Scanning Calorimetry (DSC) measurements were performed using an M/s Netzsch DSC 200 F3 Maia instruments. The tensile properties of epoxy and EP-MoS_2 nanocomposites were using a UTM M/s Kalpak Instruments and Controls, Pune India. The flexural strength of the prepared nanocomposites was measured using UTM Instron 3365.

3. Results and discussion

The morphology of bulk MoS_2 powder and exfoliated MoS_2 (ex-MoS_2) was observed by SEM microscopy and the images are shown in figure 1. The figure 1 *a* and 1 *b* shows that bulk MoS_2 powder exhibits stacked layer-like morphology with thickness of several micrometers. However, ultra-sonication in DMF results in drastic exfoliation of layer structure, as evident from figure 1 *c* and 1 *d*.

To further understand the exfoliation state and morphology of ex-MoS_2 sheets, TEM analysis was carried out and the results are shown in figure 2. The ex-MoS_2 exhibits thin nano sheets morphology with several layers, suggesting that MoS_2 underwent effective exfoliation during ultrasonication process.

Flexural strength of epoxy and epoxy-MoS_2 nanocomposites were measured using a three point bend testing method and results are displayed in figure 3. As compared to neat

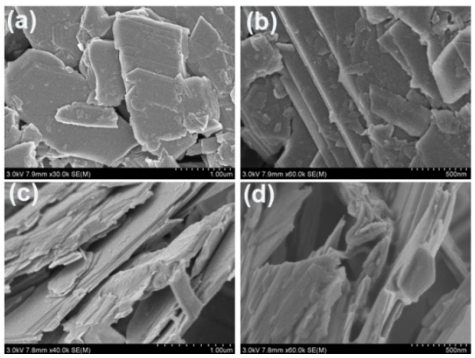

Figure 1. SEM images of (*a*, *b*) bulk MoS_2 and (*c*, *d*) ex-MoS_2.

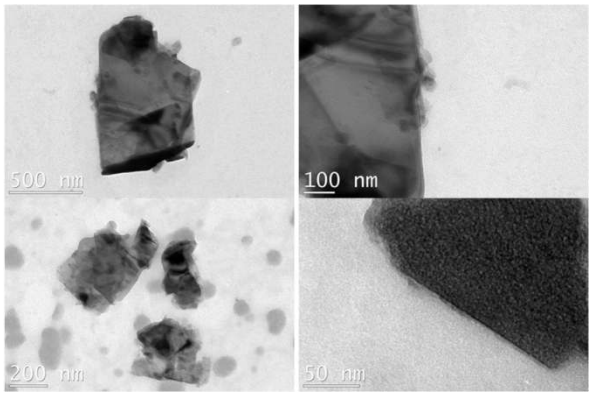

Figure 2. TEM image of ex-MoS_2.

epoxy (89.46 MPa), flexural strength of composites with 0.05wt% (113.49 MPa) and 0.1wt% (97.58 MPa) ex-MoS_2 content have increased 26.86% and 9.07%, respectively. However, the composites with 0.25wt% (64.90 MPa) and 0.5wt% (72.55 MPa) weight fractions of ex-MoS_2, the flexural strength has decreased to 27.45% and 18.90% with respect to neat epoxy (fig 3 *b*). The results indicate that the flexural strength increases for composites with lower nanofiller content ($\sim$ 0.1wt%), which can be attributed to good interfacial interaction between ex-MoS_2 and epoxy chains, as evidenced by TEM characterization (figure 2). However, flexural strength decreases for composites with higher nanofiller loadings (beyond 0.1wt%) which could be due to agglomeration of ex-MoS_2 results in lesser interfacial interaction between epoxy and nanofiller. Figure 3 *c* displays the flexural modulus values of neat epoxy and epoxy-MoS_2 composites. It has increased from 2.43 to 3.39, 3.46, 2.54, and 2.98 GPa when ex-MoS_2 content is increased from 0 to 0.05wt%, 0.1wt%, 0.25wt% and 0.5wt%, respectively. The reduction in flexural modulus beyond 0.1wt% nanofiller content in the composites was attributed to the agglomeration of MoS_2. The flexural strain at break values of neat epoxy and epoxy-MoS_2 composites is shown in figure 3 *d*.

Figure 4 *a* shows the tensile stress-strain plots for the neat epoxy and epoxy-MoS_2 composites with different weight fractions of ex-MoS_2 (0.05wt% to 0.5wt%). The test results demonstrate that tensile strength increases with increasing filler content (ex-MoS_2) up to 0.1wt%. However, beyond 0.1wt%, reducing trend is observed. The tensile strength of neat epoxy, epoxy-MoS_2(0.05wt%), epoxy-MoS_2(0.1wt%), epoxy-MoS_2(0.25%), and epoxy-MoS_2(0.5wt%) nanocomposites was found to be 51.03, 60.80, 71.04, 65.62, and 59.76 MPa respectively. The test results revealed that the tensile strength increased 19.15%, 39.21%,

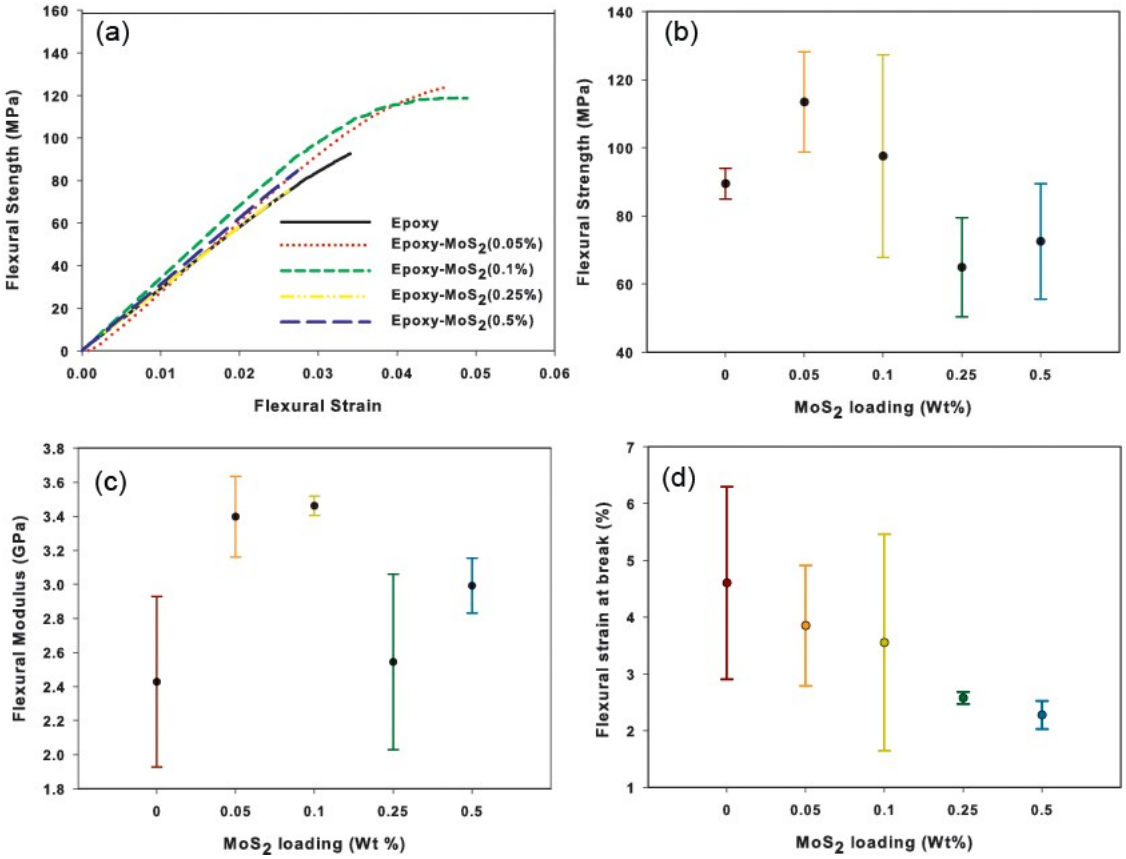

Figure 3. Flexural properties of epoxy-MoS_2 nanocomposites. (*a*) Flexural stress-strain curves, (*b*) Flexural strength with MoS_2 loading, (*c*) Flexural modulus with MoS_2 loading, (*d*) Flexural strain at break with MoS_2 loading.

28.59%, and 12.09%, respectively as compared to neat epoxy. The increase in tensile strength of the composites at ultralow nanofiller content (0.1wt%) was attributed to the good dispersion of MoS_2 and high interfacial interaction between nanofiller and polymer molecules, which is also evident from the TEM images (figure 2). However, at higher nanofiller content (beyond 0.1wt%), the ex-MoS_2 nanosheets are extremely close, as a result, the nanosheets tend to agglomerate and restack together due to their van der Waals forces. The Young's modulus of neat epoxy and epoxy-MoS_2 composites with different weight fractions of ex-MoS_2 ranging from 0.05wt%, 0.1wt%, 0.25wt%, and 0.5wt% to 0.5wt% was found to be 1.10, 1.15, 1.17, 1.10, and 1.0 GPa, respectively. The mechanical test results clearly indicate the effective reinforcement effect of ex-MoS_2 at ultralow filler content ($\sim$ 0.1wt%).

The thermal expansion studies of neat epoxy and its composites were carried out and coefficient of thermal expansion (CTEs) results are displayed in figure 5 *b*. The neat epoxy in this study exhibits CTE value of $6.7 \times 10^{-5}/°C$, whereas, epoxy-MoS_2(0.05wt%), epoxy-MoS_2(0.1wt%), epoxy-MoS_2(0.25wt%), and epoxy-MoS_2(0.5wt%) composites exhibits CTEs value of $6.0 \times 10^{-5}/°C$, $5.6 \times 10^{-5}/°C$, $4.8 \times 10^{-5}/°C$, and $4.3 \times 10^{-5}/°C$, respectively. The test results revealed that the CTEs decreased with increase in MoS_2 content in the composites. A similar trend was observed for the graphene based epoxy composites as reported in the literature. In order to understand the glass-transition temperature (T_g) of neat epoxy and its composites, differential scanning calorimetric studies were carried out (figure 5 *a*). The T_g of neat epoxy was found to be 67.6°C, however, incorporation of 0.05wt%, 0.1wt%, 0.25wt%, and 0.5wt% of

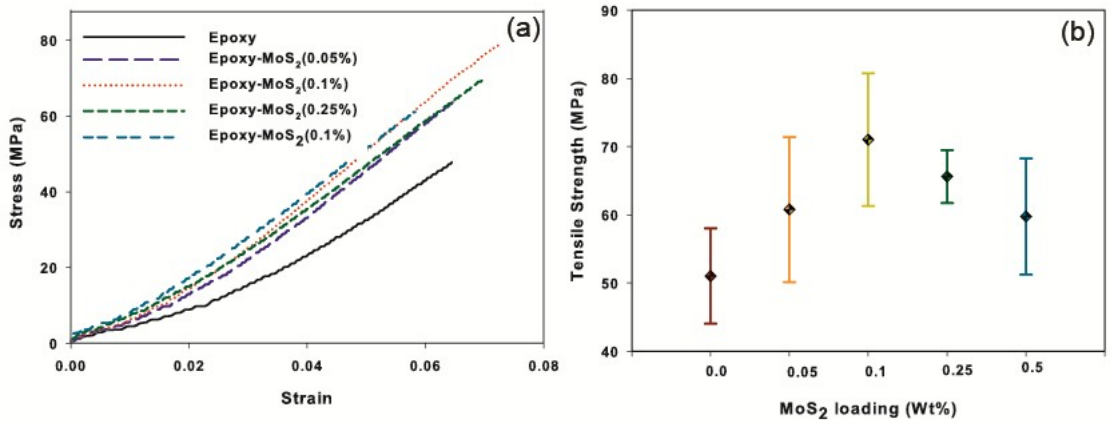

Figure 4. (a) Tensile stress-strain curves of epoxy and epoxy-MoS_2 nanocomposites, (b) Young's modulus of composites.

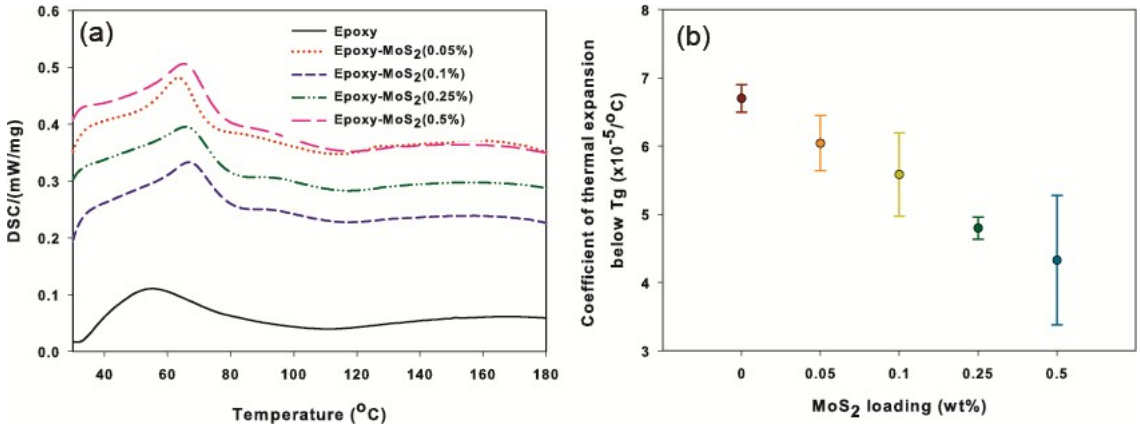

Figure 5. (a) DSC thermo grams of epoxy and epoxy-MoS_2 nanocomposites, (b) Coefficient of thermal expansion of epoxy-MoS_2 nanocomposites.

ex-MoS_2 in the composites increased the T_g to 68.0°C, 72.6°C, 72.3°C, and 71.1°C, respectively, which can be attributed to the restricted polymer chain mobility due to addition of nanofiller. The T_g result clearly indicates the good dispersion and interfacial interaction between nanofiller and polymer matrix.

Conclusions

MoS_2 reinforced epoxy nanocomposites were prepared by simple ultra-sonication and shear mixing techniques. The SEM observations revealed that the MoS_2 nanosheets were exfoliated after ultrasonication process. The TEM observations confirmed the significant interfacial interaction between MoS_2 and epoxy. The CTE of composites significantly reduced with addition of ex-MoS_2 in the composites. The incorporation of ultralow content (0.1% by weight) of ex-MoS_2 in the epoxy matrix has significantly increased the flexural (9.0%) and tensile strength (39.2%) properties of composites. The improvement in mechanical properties of epoxy nanocomposites can be attributed to the significant interfacial interaction between epoxy and MoS_2.

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References

[1] Punetha V D, Rana S, Yoo H J, et al. 2017 Functionalization of carbon nanomaterials for advanced polymer nanocomposites: A comparison study between CNT and graphene *Prog. Polym. Sci.* **67** 1–47
[2] Kuilla T, Bhadra S, Yao D, et al. 2010 Recent advances in graphene based polymer composites *Prog. Polym. Sci.* **35** (11) 1350–75
[3] Sahoo N G, Rana S, Cho J W, et al. 2010 Polymer nanocomposites based on functionalized carbon nanotubes *Prog. Polym. Sci.* **35** (7) 837–67
[4] Kim H, Abdala A A, and Macosko C W 2010 Graphene/Polymer Nanocomposites *Macromolecules* **43** (16) 6515–30
[5] Stankovich S, Dikin D A, Dommett G H B, et al. 2006 Graphene-based composite materials *Nature* **442** 282–6
[6] Bak J M, Lee T, Seo E, et al. 2012 Thermoresponsive graphene nanosheets by functionalization with polymer brushes *Polymer* **53** (2) 316–23
[7] Ramasamy M S, Mahapatra S S, and Cho J W 2015 Functionalization of graphene with self-doped conducting polypyrrole by click coupling *J. Colloid Interface Sci.* **455** 63–70
[8] Eksik O, Gao J, Shojaee S A, et al. 2014 Epoxy nanocomposites with two-dimensional transition metal dichalcogenide additives *ACS Nano* **8** (5) 5282–9
[9] Li Y, Wang H, Xie L, et al. 2011 MoS_2 nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction *J. Am. Chem. Soc.* **133** (19) 7296–9
[10] Han S, Ai Y, Tang Y, J. Jiang, D. Wu 2015 Carbonized polyaniline coupled molybdenum disulfide/graphene nanosheets for high performance lithium ion battery anodes *RSC Adv.* **5** 96660–4
[11] Meng F, Li J, Cushing S K, et al. 2013 Solar hydrogen generation by nanoscale p-n junction of p-type molybdenum disulfide/n-type nitrogen-doped reduced graphene oxide *J. Am. Chem. Soc.* **135** (28) 10286–9
[12] Xiao J, Choi D, Cosimbescu L, et al. 2010 Exfoliated MoS_2 nanocomposite as an anode material for lithium ion batteries *Chem. Mater.* **22** (16) 4522–4
[13] Tsai M-L, Su S-H, Chang J-K, et al. 2014 Monolayer MoS_2 heterojunction solar cells *ACS Nano* **8** (8) 8317–22