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Studies on Thermal Behaviour of DOPO-functionalized Mullite Reinforced Epoxy Nanocomposites

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Abstract: The present work describes the development of epoxy composites reinforced with varying weight percentages of DOPO functionalized mullite fibre and DGEBA (diglycidyl ether of bisphenol-A) epoxy resin cured with diamino diphenyl methane (DDM). The synthesised mullite fibre was surface modified with 9,10-dihydro-9-oxa-10 phosphaphenanthrene-10-oxide (DOPO).The introduction of DOPO functionality into mullite fibre has been confirmed by FT-IR and TGA analysis. The data obtained from the thermal studies, states that theDOPO modified mullite(DM) had a significant impact on the resultant epoxy nanocomposites when compared to that of neat epoxy matrix.
Keywords: DOPO functionalized mullite, epoxy nanocomposites, and thermal stability.

Introduction and Experimental:

As an important industrial material, epoxy resin present attractive characteristics of low shrinkage on cure, high adhesion to substrate, good chemical and corrosion resistance. However, thermal stability is one of the major disadvantages of epoxy resins, which restrict their high performance applications [1].Hence it's mandatory to improve thermal stability of epoxy resins. The most common approach is by incorporating the halogen based compounds into epoxy resin; due to the environmental concerns they have been prohibited. The organo-phosphorus compound 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has received a notable attention because of its additional merits such as environment-friendly, good thermal stability, and outstanding oxidation stability [2].On the other hand, incorporation of inorganic metal oxides into the polymer backbone gave an additional strength to the thermal properties of the resulting materials. One such is Mullite; a ceramic material consists of inorganic metal oxides of alumina and silica [3].

To enhance the thermal stability of the composites, an attempt has been made in the present work, to develop DOPO functionalized mullite fibre reinforced epoxy nanocomposites and its thermal stability has been investigated.

Preparation of DOPO functionalized Mullitenanoparticles:

Synthesis of surface functionalised mullite is as per the reported procedure [3, 4].0.5g of DOPO was introduced into the suspension of1gfunctionalisedmullite in toluene 35ml. Anhydrous triethylamine (0.5 g) was

added drop wise, and the mixture was kept under reflux for 24 h at 110^{0}C. Then the product was filtered and washed with toluene (50ml). The DOPO functionalized mullite was dried in a vacuum oven overnight at 110°C.

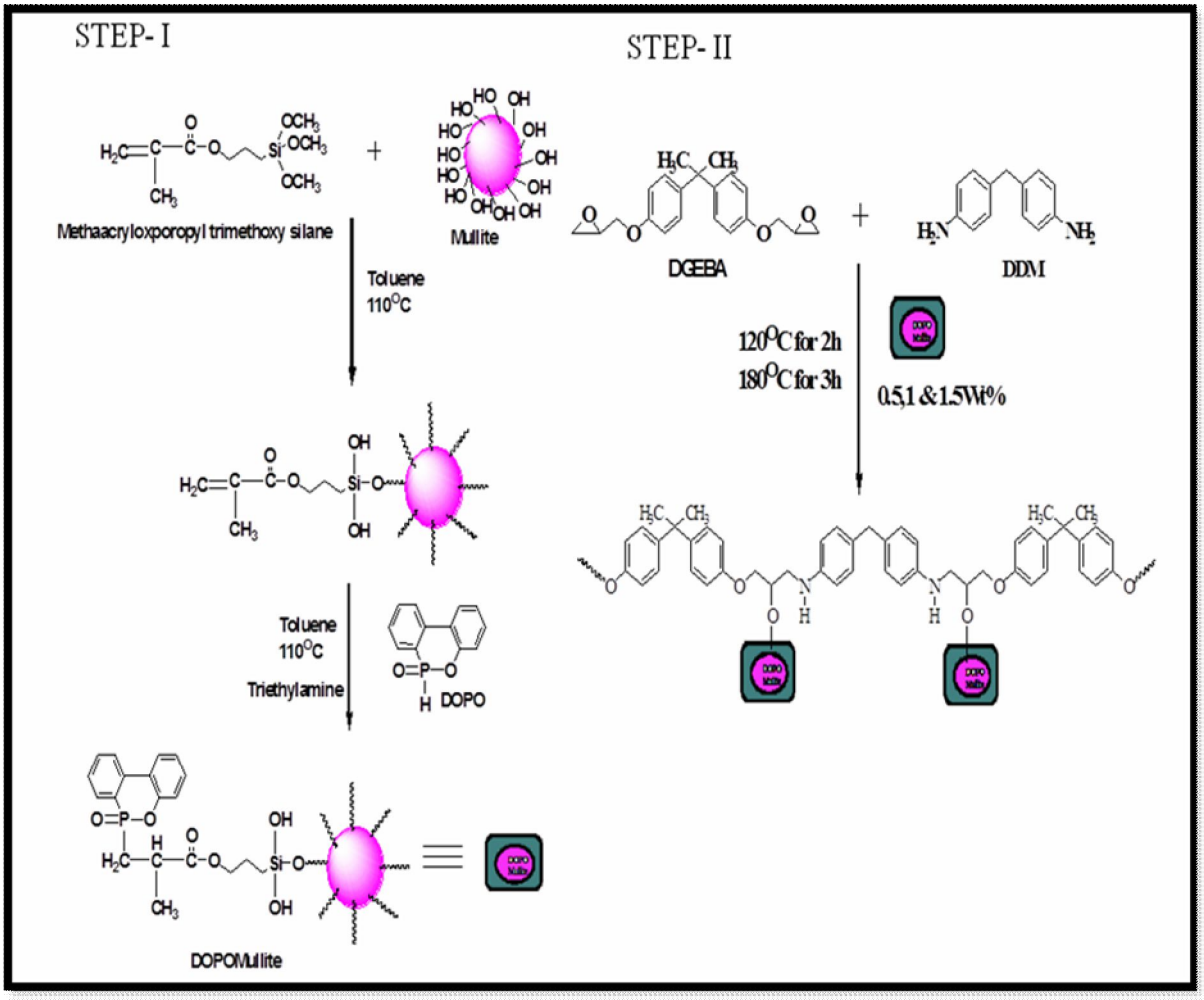

Figure 1: DOPO functionalized mullite fibre reinforced epoxy nanocomposites

Preparation of surface modified mullite fibre reinforced epoxy nanocomposites: The DGEBA epoxy resins and the desired amount of DOPO functionalised mullite (DM) (0.5, 1.0&1.5wt %) were mechanically stirred at 50˚C for 24 h. A stoichiometric amount of DDM corresponding to epoxy equivalents was also added.

Results and Discussion:

FT-IR spectral: Figure 2 represents the FT-IR spectra of neat, 0.5, 1.0, 1.5 wt % DOPO functionalised mullite reinforced epoxy composites. The peaks at 1237 cm^{-1},2946 cm^{-1} and 1612 cm^{-1} are assigned to (–P=O); aromatic (-CH_2-) and (-C=O) respectively and the disappearance of peak at 2434 cm^{-1} corresponds to (-P-H) in DOPO functionality. The band that appears 3395 and 1514 cm^{-1} corresponds to the -OH and -NH group. The disappearance of peak at 937 cm^{-1} indicates the epoxy underwent a complete curing reaction with DDM.

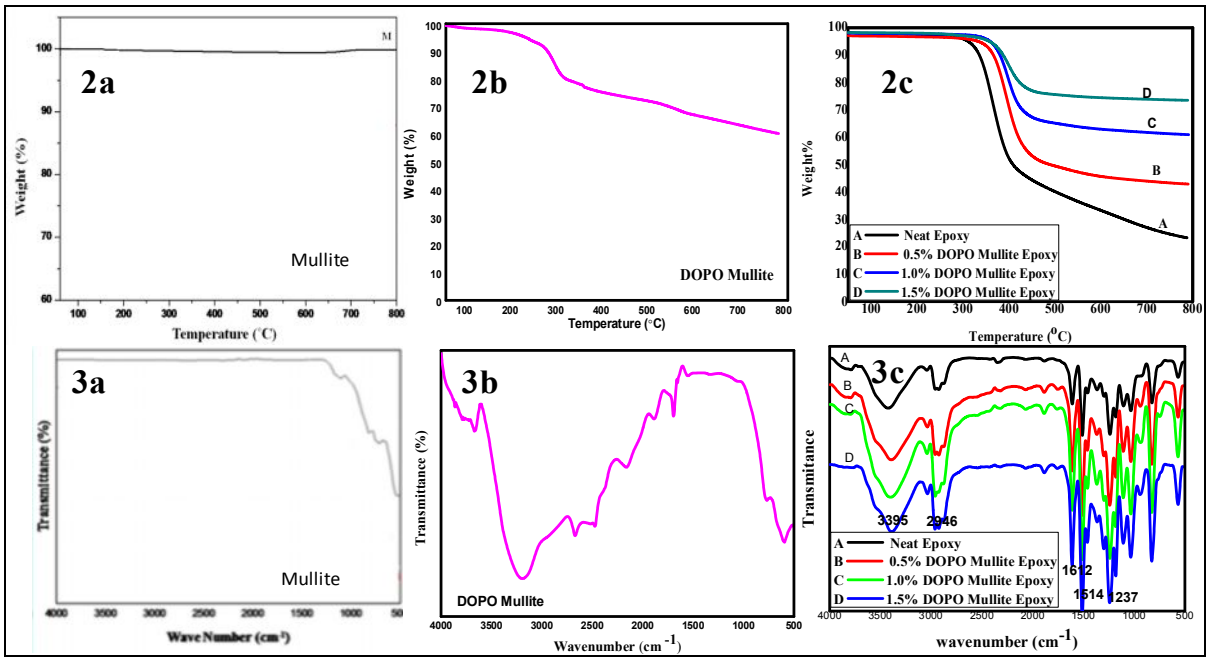

Figure 2: TGA of (2a) Mullite (2b) DOPO Mullite (2c)Neat, 0.5, 1.0, 1.5 wt %DOPO Mullitereinforced epoxy nanocomposites.Figure 3: FT-IR of (3a) Mullite (3b) DOPO Mullite (3c)Neat, 0.5, 1.0, 1.5 wt %DOPOMullitereinforced epoxy nanocomposites.

Thermo gravimetric analysis (TGA): The thermal degradation behaviour of neat DGEBA, and DOPO-mullite(DM) reinforced epoxy composites was analysed using the TGA (Figure3). The initial degradation temperature of the mullite modified epoxy system is lower than that of the neat epoxy system, due to the presence of inorganic components in the system. The char yield of neat epoxy, 0.5, 1.0, 1.5 wt % DOPO-mullite (DM) reinforced epoxy composites are 23.07, 42.80, 61.00 and 73.40 at 800˚C respectively. The above results indicate that the incorporation of the DOPO-mullite(DM) into the epoxy network could improve the thermal stability, resulting in strengthening of composites.

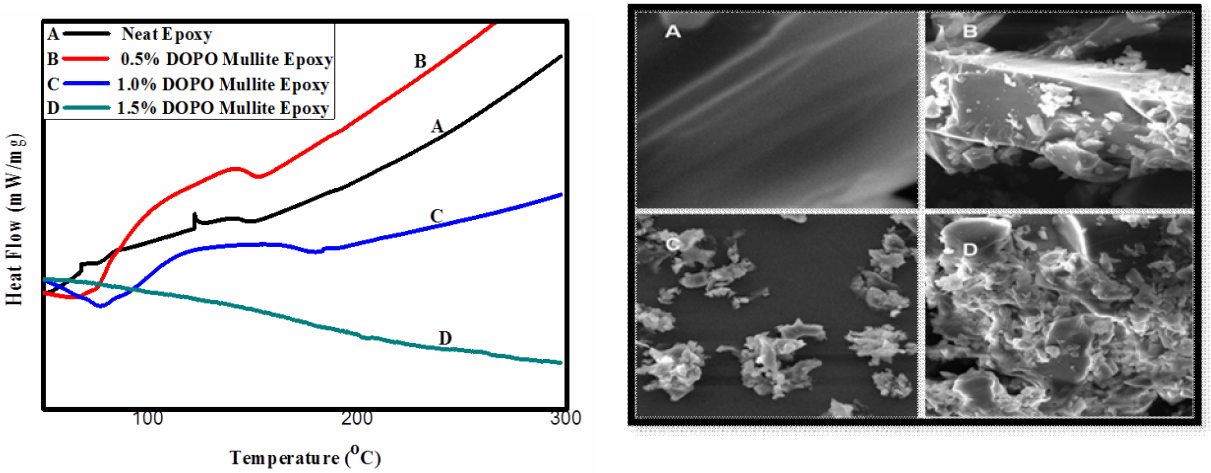

Figure 4 and 5: DSC &SEM image of (a) neat epoxy (b)0.5wt % DOPO-Mullite(c) 1.0wt%DOPO-Mullite and (d)1.5wt% DOPO-Mullitereinforced epoxy nanocomposites

Differential scanning calorimetry (DSC):

The values of the glass transition temperature (T_g) of neat DGEBA, and DOPO-mullite (DM) reinforced epoxy composites were obtained from DSC analysis (Figure 4). The neat epoxy matrix hasaTg value of 161˚C, whereas 1.5 wt%DOPO-mullite (DM) incorporated epoxy exhibited a T_g value of 204˚C. This is due

to the incorporation of DOPO-mullite (DM) in the DGEBA epoxy, which reduces the segmental motion and tightly holds the epoxy matrix in a cross linked structure and consequently enhances the values of T_g.

Scanning electron microscopy (SEM)

The morphology of the neat epoxy and DOPO-mullite (DM) reinforced epoxy composites were analysed using the SEM micrograph, as shown in Figure 5.The SEM images of neat epoxy clearly indicate a smooth surface, whereas the DOPO-mullite (DM) reinforced composite exhibits the uniform distribution of mullite particles into epoxy matrix due to the formation covalent bonding between the DOPO functionalised mullite and DGEBA.

Conclusion:

In the present work DOPO was successfully functionalized onto the surface of mullite through covalent bonding, which increases the thermal properties.DSC and TGA results indicated that DOPO functionalised mullite nanoparticles have significantly improved the thermal stability of epoxy composites according to their percentage incorporation.

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