

Curing and Thermal Properties of Epoxy Resin Containing Nanosilica Particles

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This paper describes the synthesis and curing behaviour of nanosilica particles and to study the modification in flammable properties of epoxy resin. Nanosilica particles were synthesized by using tetraethoxysilane (TEOS). Surface morphology was studied by SEM technique and particle size analysis was done by TEM studies. The size of nanosilica particles was in the range of 100 nm. The effect of nanosilica particles on the curing kinetics of epoxy resin along with 4,4'-diphenyldiamino sulphone (DDS) was studied by differential scanning calorimetry. Differential scanning calorimetry scans were recorded using TA 2100 thermal analyzer having 910 DSC module. The curing of diglycidyl ether of bisphenol-A (DGEBA) was initiated at higher temperature with DDS alone as compared to that with a mixture of nanosilica and DDS. The curing temperature were increased with increasing wt. % of nanosilica. Thermal studies were done using thermal gravimetric analyzer. Rheometric thermal analyser having TG1500 module was used for recording TG/DTG traces. These cured epoxy nanosamples have shown the significant improvement in the thermal properties.

Key Words: Nanosilica particle, Epoxy resin, Curing, Thermal stability.

INTRODUCTION

Nanotechnologies are now poised to revolutionize the electronic, chemical, biotechnology industries and biomedical fields. There are many interesting areas in nanotechnology^{1,2}. One of the most important aspects of this field is preparation and use of nanoparticles in the preparation of polymers. The nanoparticle-polymer composites have created strong interest, because of the combination of both the properties of inorganic nanoparticles (optical, electronic or mechanical) and those of polymer (solubility, film formation and chemical activity)³⁻⁶. The nanoparticles are prepared by using different techniques⁷⁻¹¹.

Organic materials cannot be used alone for high performance applications because they have limited properties. Therefore organic/inorganic composites are frequently employed in order to overcome the limitation. One of the widely used organic/inorganic composites is an epoxy/silica system. Since, epoxy resins as organic matrix

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have excellent heat, moisture and chemical resistance and good adhesion to many substrates, they are mostly applied in the field of coatings, adhesives, composites, laminates and encapsulation of semiconductor devices^{12,13}.

In the last two decades, a prompt development of epoxy resins in electronic applications has been achieved, which includes encapsulations for semiconductors, packaging for integrated circuit chip and ball grid access (BGA), insulating materials for electric devices such as copper clad laminates and solder mask resist ink for printed circuit board, *etc.* In most cases, these electronic applications absolutely require good flame retardancy for epoxy resins¹⁴⁻¹⁶.

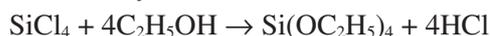
Several techniques have been incorporated to improve flame retardancy of epoxy resins. The most common approach is to incorporate the halogen atoms into the epoxy resins, however these resins on combustions give products which are harmful to environment, so it led to search of ecofriendly flame retardent epoxy resins^{17,18}. Mechanical properties of polymers can be improved by incorporating nanoparticles. However, epoxy resins due to their low mechanical properties and high coefficients of thermal expansion (CTE) value compared with inorganic materials cannot meet the requirements-especially for the applications of electrical and structural such as epoxy moulding compounds (EMC). Thus silica particles are commonly employed for the reinforcement of epoxy matrix to lower shrinkage on curing, to decrease thermal expansion coefficients, to improve thermal conductivity and to meet the mechanical requirements. The structure of cured resin depends on the epoxy monomer and curing agent used.

This paper describes the synthesis of nanosilica particles. Curing behaviour of diglycidyl ether of bisphenol-A (DGEBA) in the presence of stoichiometric amount of nanosilica particles and diamino diphenyl sulphone (DDS) was investigated by differential scanning calorimetry. Thermal behaviour of isothermally cured resin was evaluated using dynamic thermogravimetric analysis in nitrogen atmosphere.

EXPERIMENTAL

Diglycidyl ether of bisphenol-A (DGEBA, having an epoxy equivalent 186) was procured from NanYA Plastics Corporation and 4,4'-diamino diphenyl sulphone DDS (Aldrich) were used as received. Silicon tetrachloride, methyl ethyl ketone (Merck), ammonia and sodium acetate (qualigens) were used as such. Ethanol and acetic anhydride (qualigens) were distilled before.

Synthesis of silica nanoparticles was carried out by using tetraethoxysilane (TEOS), which was primarily synthesized by the reaction of silicon tetrachloride with ethanol:



The tetraethoxysilane (100 μL), so obtained was mixed with 5 mL of ethanol in a conical flask. The flask was then cooled to 0 °C and placed floating in an ice-cooled ultrasonicated bath. 5 mL of ammonium hydroxide (NH_4OH , 28-30 wt %) was added to the ethanolic solution of TEOS while ultrasonicated. After 1 h sonication, nanoparticles were centrifuged out of solution and were washed five times with both water and acetone and finally air dried.

Structural characterization of nanosilica particles: Structural characterization of nanosilica particles was done by using scanning electron microscopy (SEM) and transmission electron microscopic (TEM) techniques. Scanning electron microscopy was performed by using Jeol JSM 840 instrument. The transmission electron microscopy observation was performed with a Jeol JEM 2000 EX TEM instrument.

Curing studies: For curing studies, freshly prepared samples obtained by mixing stoichiometric amounts of DGEBA and DDS containing various weight percentage of nanosilica particles were used. For this purpose known amount of amine and nano silica particle were dissolved in a minimum amount of methylethylketone and then mixed with DGEBA. Differential scanning calorimetry scans were recorded using TA 2100 thermal analyzer having 910 DSC module. A heating rate of 10 °C/min and a sample size of 5 ± 1 mg was used in each experiment. Differential scanning calorimetry scans of isothermally cured samples were also recorded to determine effect of network structure on the glass transition temperature. The samples containing 0, 0.5, 1.0, 1.5, 2.0 % nanosilica particle are designated as DN0, DN1, DN2, DN3, DN4. The solvent was evaporated under vacuum and the freshly prepared samples were used for recording DSC traces in the static air atmosphere.

Thermal stability: Thermal stability of DGEBA cured isothermally by heating in an air oven at 200 ± 20 °C for 3 h in the presence of amine and nanosilica particle was investigated by recording TG/DTG traces in nitrogen atmosphere (flow rate 60 mL/min). Rheometric thermal analyser having TG1500 module was used for recording TG/DTG traces. A heating rate of 20 °C/min and sample size of 10 ± 2 mg was used in each experiment.

RESULTS AND DISCUSSION

Surface morphological studies: For surface morphological studies of prepared nanosilica particles scanning electron microscopy (SEM) was used at an accelerating voltage of 20 KV. Samples were notched by razor blade. The fractured surfaces were coated with a 100 Å of gold coating. This coating was carried out by using JEOL JFC 1100 ion sputter coater. Scanning electron microscopy was performed by using JEOL JSM 840 instrument. Fig. 1 shows the SEM micrograph of prepared silica particles.

Particle size analysis: Particle size analysis of prepared nanosilica particles was done by transmission electron microscopy (TEM). The material was dispersed in spectroscopic grade methanol by using ultrasonic waves. A drop of the dispersed liquid was dried on a formvar coated 200 mesh copper grid. The transmission electron microscopy observation was performed with a JEOL JEM 2000 EX TEM instrument. Transmission electron microscopy image of the nanoparticles shows that the particles are 100 nm and less in size and their size distribution is non-uniform with a standard deviation. Fig. 2 shows the TEM micograph of nanosilica particles.

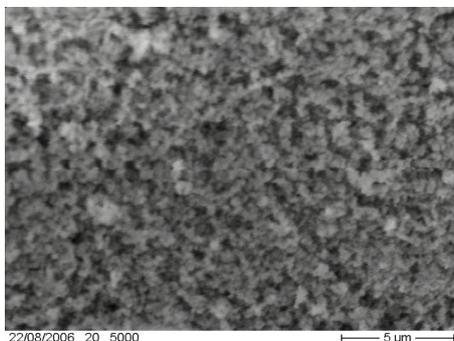


Fig. 1. SEM micrograph of prepared nanosilica particles

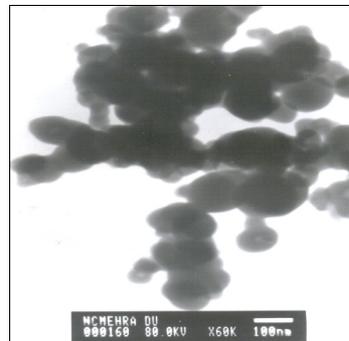


Fig. 2. TEM micrograph of prepared nanosilica particles

Curing studies: Fig. 3 shows the DSC scan of diglycidyl ether of bisphenol-A (DGEBA) in the presence of stoichiometric amount of 4,4'-diamino diphenyl sulphone (DDS). Figs. 4 and 5 shows DSC scans of DGEBA in presence of DDS and different weight proportions of nanosilica particles. Differential scanning calorimetry exotherms were characterized by noting the following temperature.

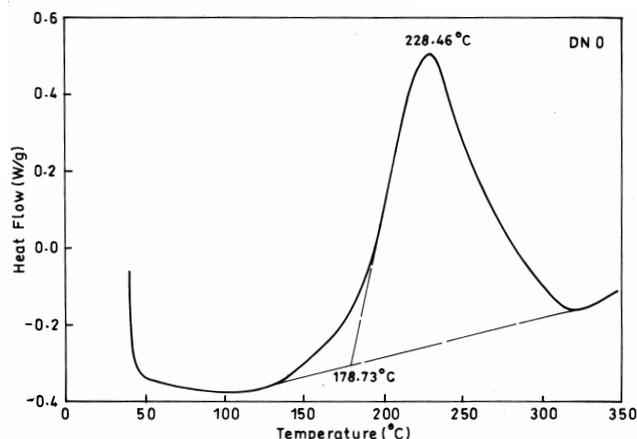


Fig. 3. DSC scan of DGEBA in the presence of stoichiometric amount of DDS

T_i = Kick-off temperature, where the curing starts. T_{onset} = temperature where the first detectable heat is released. It was obtained by extrapolation of steepest portion of curve. T_p = temperature of peak position of exotherm. T_f = temperature of end of curing exotherm obtained by extrapolation of the end set of the exothermic transition. ΔH = heat of curing calculated by measuring area under the exothermic transition.

The curing of the epoxy resins in presence of amines of varying structure is well reported in the literature^{19,20}. A broad exothermic transition was observed in the temperature range of 180-230 °C, which was dependent on the nature of curing

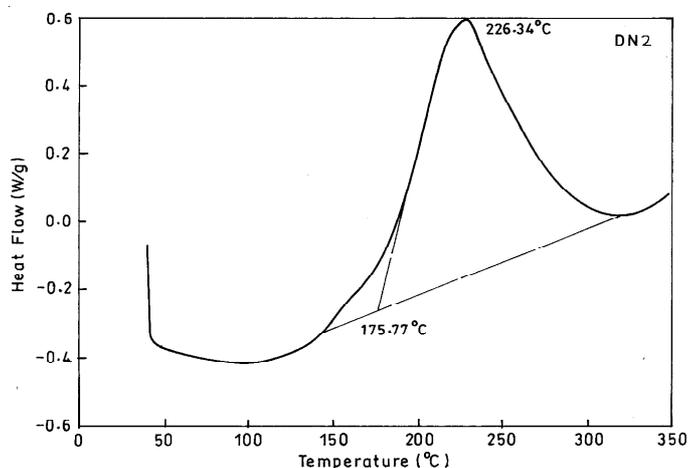


Fig. 4. DSC scan of DGEBA and DDS with 1 % nanosilica

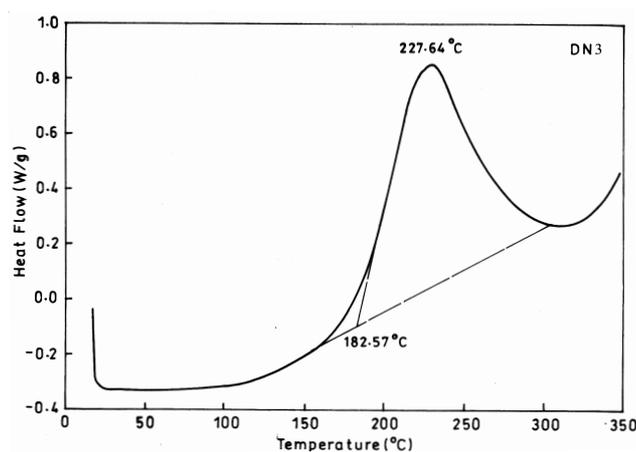


Fig. 5. DSC scan of DGEBA and DDS with 1.5 % nanosilica

agent and the weight percentage of nano silica particle. For samples cured with a mixture of amine and nanosilica particle, a single exotherm was observed, which thus indicated that they acted as cocuring agent and did not show separate curing exotherms. T_p of DGEBA mixed with amine and nanosilica particles increased with addition of more wt % of nanosilica particle. The curing of DGEBA was initiated at higher temperature with DDS alone as compared to that with a mixture of nanosilica and DDS. The curing temperature were increased with increasing wt. % of nanosilica (Table-1).

The DSC scans of samples cured isothermally (at 200 ± 10 °C in hot air oven for 2 h) showed no residual exotherm. These studies clearly indicated that the curing of epoxy resins can be tailored and controlled by using different weight percentage of nano silica particle with diamine.

TABLE-1
DSC DATA OF DGEBA IN PRESENCE OF DDS AND NANOSILICA PARTICLES

| Sample designation | T _i °C | T _{onset} °C | T _p °C | T _f °C | ΔH (J/g) |
|--------------------|-------------------|-----------------------|-------------------|-------------------|----------|
| DN0 | 116.00 | 178.70 | 228.50 | 322.60 | 326.8 |
| DN1 | 122.80 | 188.58 | 224.77 | 270.00 | 217.6 |
| DN2 | 130.00 | 175.77 | 226.34 | 319.70 | 292.1 |
| DN3 | 144.70 | 182.57 | 227.64 | 303.90 | 328.3 |
| DN4 | 152.08 | 189.71 | 229.32 | 312.80 | 352.7 |

Thermal studies: Thermogravimetric analysis was performed to assess the relative thermal stability of the cured epoxy resins. The TG traces were obtained by plotting the percentage residual weight against temperature. Percentage char yield at 700 °C and following temperatures were noted from TG/DTG traces: IDT: Initial decomposition temperature, FDT: Final decomposition temperature, T_{max}: Temperature of maximum rate of weight loss.

Figs. 6-9 shows the TGA scan of diglycidyl ether of bisphenol-A (DGEBA) in the presence of DDS and different weight proportions of nanosilica particles. A single step decomposition was observed in all of the samples. Major weight loss in all the samples were observed in the temperature range 380-450 °C. The results are summarized in Table-2. The T_{max} increases with increase in weight percentage of nano silica particle added to DGEBA and DDS. Also char yield increases thus showing that nanosilica particle contribute to thermal stability. As nanosilica particle contain silicon atom and nitrogen is present in diamine so silicon and nitrogen are showing synergistic effect.

Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resins in accordance with Van Krevelen and Hoftyzer equation²¹.

$$\text{LOI} = 17.5 + 0.4\text{CR}$$

where CR = char yield.

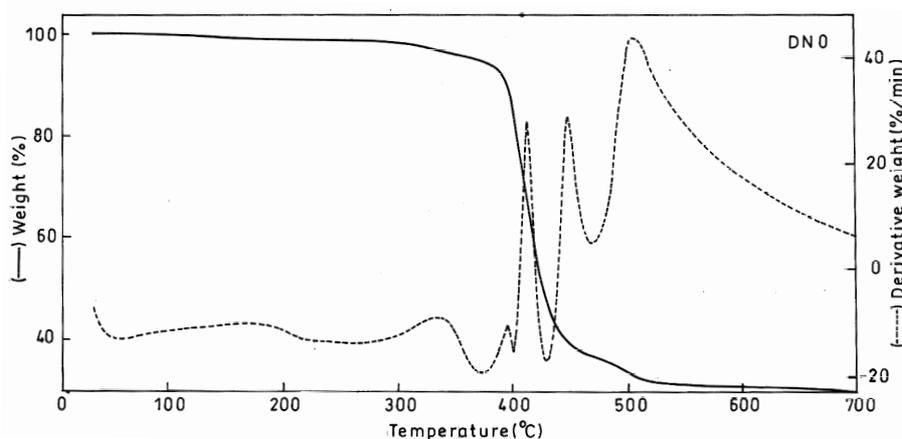


Fig. 6. TGA scan of DGEBA in the Presence of Stoichiometric amount of DDS

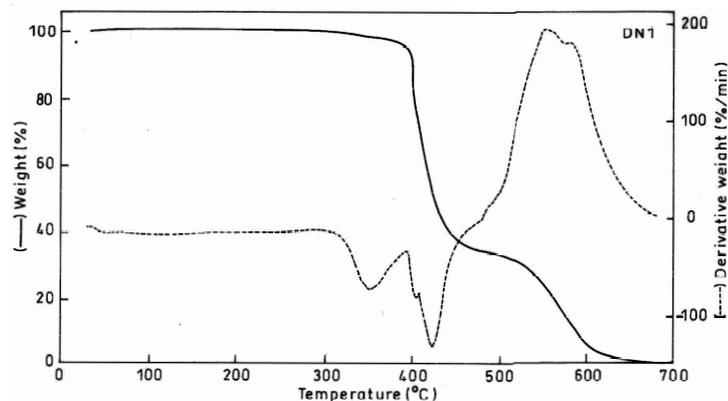


Fig. 7. TGA scan of DGEBA and DDS with 0.5 % nanosilica

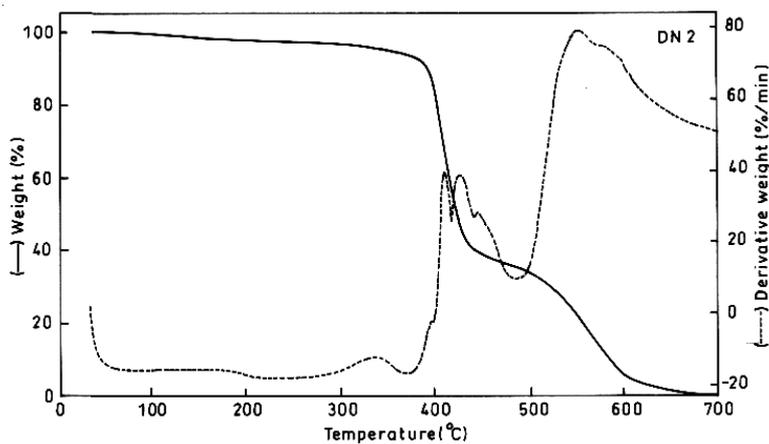


Fig. 8. TGA scan of DGEBA and DDS with 1 % nanosilica

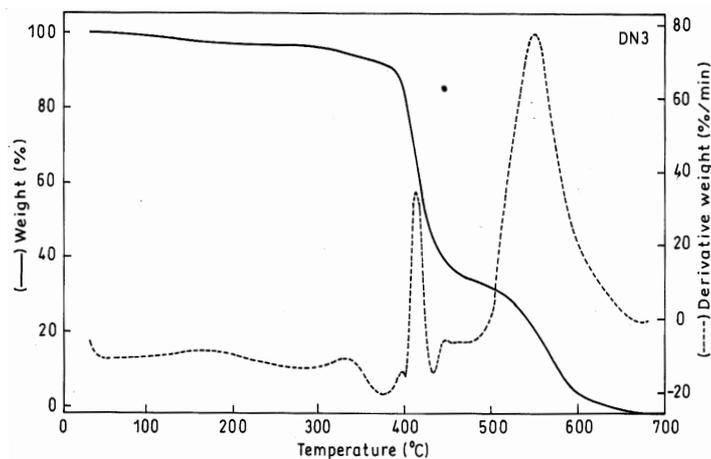


Fig. 9. TGA scan of DGEBA and DDS with 1.5 % nanosilica

TABLE-2
TGA DATA OF DGEBA IN PRESENCE OF DDS AND NANOSILICA PARTICLES

| Sample designation | IDT °C | T _{max} °C | FDT °C | Char yield (%) at 700 °C | LOI |
|--------------------|--------|---------------------|--------|--------------------------|-------|
| DN0 | 345 | 380 | 400 | 6.9 | 20.26 |
| | 400 | 419 | 430 | | |
| DN1 | 350 | 385 | 420 | 7.2 | 20.38 |
| | | 418 | 498 | | |
| DN2 | 362 | 478 | 498 | 8.8 | 21.02 |
| | | 421 | | | |
| DN3 | 400 | 421 | 435 | 8.1 | 20.74 |
| DN4 | 412 | 441 | 456 | 9.1 | 21.14 |

Conclusion

From these results, it can be calculated that the curing behaviour of epoxy resins can be altered by changing the molar ratio of curing agents and nature of curing agents. Thermal stability of cured material was found to be dependent on the structure of network. Composition of the mixture has a large effect on the curing of thermal behaviour. Nitrogen and silicon both are present in cured samples thus enhancing the flammability resistance.

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