Studies on Epoxy/Calcium Carbonate Nanocomposites

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ABSTRACT: The article describes the preparation of epoxy-calcium carbonate nanocomposites using diaminodiphenyl sulfone (DDS) as a curing agent. The curing behavior of diglycidyl ether of bisphenol-A (DGEBA) (1 mol) in the presence of varying amounts of nanocalcium carbonate was investigated by differential scanning calorimetry (DSC) using stoichiometric amounts of diaminodiphenyl sulphone (0.5 mol) as curing agent. The amount of calcium carbonate ($\sim$ 44 nm) was varied from 2% to 10% (w/w). In the DSC scans of these samples, a broad exothermic transition due to curing was observed in the temperature range of 110–335°C. As expected, heat of curing decreased with increasing amount of nanocalcium carbonate; however it did not affect the curing characteristics, thereby indicating that the filler did not hinder the curing reaction. Thermal stability of DGEBA in the presence of varying amounts of nano-CaCO$_3$ after isothermal curing [(i.e., by heating in an air oven at 80°C (1 h), 100°C (1 h), 120°C (1.5 h), and 180°C (4 h)] was evaluated by thermogravimetry. All the samples were stable upto 350°C, and char yield at 800°C increased with increasing amount of nanocalcium carbonate. Rectangular bars were prepared by mixing DGEBA, DDS, and varying amounts of CaCO$_3$ using silicone mold. The nanocomposites were characterized by X-ray, scanning electron microscopy (morphological characterization), and dynamic mechanical analysis. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2161–2168, 2009

Key words: epoxy nanocomposites; DGEBA; diaminodiphenyl sulphone (DDS); curing behavior; DSC; TGA

INTRODUCTION

The reinforcement of polymer using filler is very common and important in the production of modern plastics. The use of inorganic fillers has been a common practice in the plastic industry to improve the mechanical properties of thermoplastics and thermosetting resins, such as heat distortion temperature, hardness, toughness, stiffness, and mold shrinkage. The effects of filler on the mechanical and other properties of composites depend strongly on its shape, particle size, aggregate size, surface characteristics, and degree of dispersion. In general, the mechanical properties of the composites filled with micron-size filler particles are inferior to those filled with nanoparticles of the same filler.[1,2] There are several ways to define nanocomposites. First of all, many different nanofillers can be found, including zero-dimensional nanoparticles, one-dimensional linear chain structure nanomaterials (e.g., nanofibers), two-dimensional layered structures [e.g., exfoliated layer-structure montmorillonite (MMT) clay] and three-dimensional network structures with nanometer-scale channels (e.g., zeolites). In general, these nanofillers have sizes in the range of 1–100 nm, and they are well dispersed in matrix materials to create nanocomposites. When polymeric materials are used as matrix, the composites are named polymer nanocomposites. Two main applications of polymer nanocomposites are engineering applications and packaging materials. Because of the increase in modulus, tensile strength, heat distortion temperature, and retention of impact strength, polymer nanocomposites have many possibilities for engineering applications, e.g., automobile parts (especially, under-the-hood applications). Polymer nanocomposites with matrices based on epoxy,[3–8] polyamide-6,[9–11] polypropylene (PP),[12] polystyrene,[13] and nanofillers based on MMT clay, TiO$_2$, CaCO$_3$, SiO$_2$[14–16] have been extensively studied. Significant efforts have been paid to achieve maximum dispersion of nanofillers in polymer matrices. However, aggregation of nanofillers, to various degrees, is unavoidable.

In addition, the physical properties, such as surface smoothness and barrier properties, cannot be achieved by using conventional micron-sized particles. In the recent years, intensive research efforts have been devoted to the development of nanocomposites.[17–19] The improvement in properties at a

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loading of <5% nanofiller is comparable to high volume fraction loading (~50%) in traditional composites.

Polymers are often mixed with various particulate additives and fillers to produce a new class of materials termed polymeric composites.[20] The combination of materials brings about new desirable properties. Of the various mineral fillers used, calcium carbonate ($CaCO_3$) is one of the most common, mainly because of its easy availability and low cost.[15]

The use of $CaCO_3$ has been extensively investigated as a filler using thermoplastic matrices; however, to the best of our knowledge no reports are available with epoxy resin.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol-A (DGEBA; Grade LY 556; epoxy equivalent 177, procured from Hindustan Ciba Geigy Ltd.), nanocalcium carbonate ($CaCO_3$; particle size 44 nm, KPS Consultants & Impex Pvt. Ltd.), diaminodiphenyl sulphone (DDS Aldrich), and acetone (Merck) were used as received.

Curing studies

For curing studies, freshly prepared samples obtained by mixing DGEBA (1 mole) with stoichiometric amounts of DDS (0.5 mole) was used for recording differential scanning calorimetry (DSC) traces. In order to investigate the effect of nano-$CaCO_3$ on the curing characteristics, DGEBA (1 mole), DDS (0.5 mole), and varying amounts of $CaCO_3$ ranging from 2 to 10% (w/w) were mixed thoroughly using acetone. The solvent was then removed under vacuum, and DSC scans were recorded using Perkin Elmer DSC 7. A heating rate of 10°C/min and a sample size of 5 ± 2 mg were used in each experiment.

The samples prepared by mixing 0, 2, 4, 6, 8, and 10% (w/w) of nano-$CaCO_3$ have been designated as ED, EDC-2, EDC-4, EDC-6, EDC-8, and EDC-10, respectively. The details of sample preparation and their designation are given in Table I.

Preparation of epoxy- nano-$CaCO_3$ composites

Diaminodiphenyl sulfone (DDS, 2.48 g, 0.01 mole) was dissolved in acetone and then the required amount of nano-$CaCO_3$ was added. The mixture was sonicated for ~30 min and then 6.96 g (0.02 moles) of DGEBA was added and mixed thoroughly and sonicated for another 30 min approximately. After thorough mixing, solvent was removed under

TABLE I
Details of Sample Preparation and Their Designation

Sample designation	Amount (g)		
	DGEBA	DDS	$CaCO_3$
ED	6.96	2.48	0
EDC-2	6.96	2.48	0.188
EDC-4	6.96	2.48	0.377
EDC-6	6.96	2.48	0.566
EDC-8	6.96	2.48	0.755
EDC-10	6.96	2.48	0.944

vacuum, and the mixture was then degassed to remove the dissolved oxygen. After degassing, mixture was poured into silicon mold (preheated at 80°C), and curing was done by heating in an air oven at 80°C (1 h); 100°C (1h); 120°C (1.5 h), and at 180°C (4 h). The samples were then taken out from the mold after cooling.

Characterization of epoxy- nano-$CaCO_3$ composites

Mechanical properties

Flexural testing.. For this purpose, the rectangular bars were prepared using a silicon mold. Flexural properties were determined in accordance to ASTM D 790 using Zwick Universal Testing Machine, Model, 2010. A three-point bending method utilizing center loading on a simply supported beam was used for flexural testing. The following conditions were used for testing:

Span length	=	70 mm
Crosshead speed	=	1.25 mm/min
Thickness	=	3.2 ± 0.5 mm
Width	=	12.2 ± 0.4 mm

Izod impact strength. For impact testing, Izod test was performed on the unnotched specimens as recommended by IMPATS-15 (ATSFAR). Specimen was held as a vertical cantilever beam with the original size of each specimen being about 27 mm × 12 mm × 3 mm. Four specimens of each type were tested in accordance with the same standard.

Dynamic mechanical thermal analysis (DMTA). Rheometric Scientific DMTA-4 spectrometer at a frequency of 1Hz, a strain of 1%, and a heating rate of 3°C /min was used for evaluating the dynamic mechanical properties of samples in the absence as well as in the presence of varying amounts of nano-$CaCO_3$. Rectangular specimens having dimensions of 29 mm × 13 mm × 4 mm were used for recording dynamic mechanical analysis (DMA) scans.
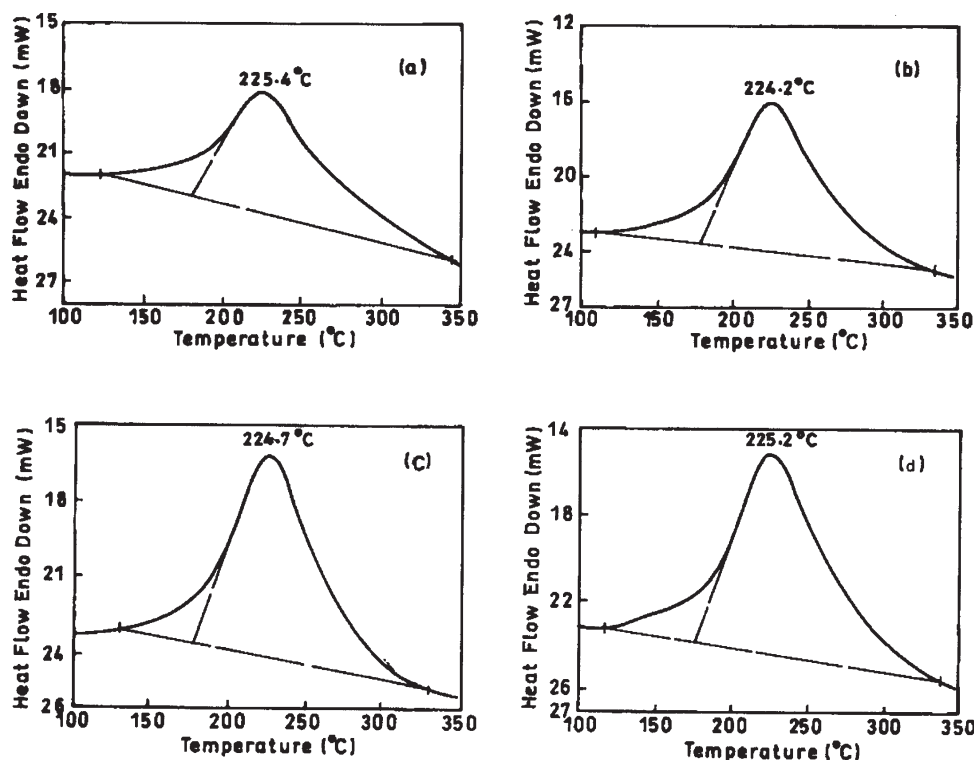
Figure 1 DSC scans of DGEBA : DDS (1 : 0.5 moles) in the presence of varying amounts of nano-CaCO$_3$. (a) ED, (b) EDC-2, (c) EDC-6, and (d) EDC-8.

Thermal analysis (TGA). Thermal stability of isothermally cured samples [(cured by heating in an air oven at 80°C (1 h), 100°C (1 h), 120°C (1.5 h), and 180°C (2 h)] was determined by recording TG/DTG traces in nitrogen atmosphere. A heating rate of 20°C/min and a sample size of 10 ± 2 mg was used in each experiment. Powdered samples were used for recording TG/DTG traces using Perkin Elmer thermal analyzer having TG 7 module. TG traces were obtained by plotting percent residual weight against temperature.

X-ray. Wide angle X-ray diffraction (WAXD) patterns were obtained by using Phillips X′ Pert PRO X-ray generator equipped with microprocessor controlled recorded unit. The scans were recorded at a scan rate of 0.8° with 2θ ranging from 2° to 30°.

Morphology. Morphological characterization of nanocomposites was done using scanning electron microscopy. Cryogenically fractured specimens were scanned using Zeiss EVO 50 scanning electron microscope operated at a voltage of 20 kV.

RESULTS AND DISCUSSION

Curing studies

In the DSC scans of all the samples, a broad exothermic transition due to curing was observed. The curing exotherm was characterized by noting the following temperatures:

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 the steepest portion of exotherm.

T_p = temperature of peak position of exotherm.

T_f = temperature of the end of curing exotherm.

ΔH = heat of curing was calculated by measuring the area under the exothermic transition.

Figure 1 shows the DSC scans of DGEBA : DDS (1 : 0.5 mole) in the presence of varying amounts of nanocalcium carbonate. In all the samples, a broad exothermic transition due to curing was observed. The results of DSC scans, i.e., characteristic curing temperatures (T_i, T_{onset}, T_p, and T_f), and heat of curing determined from the area under the exothermic transition are summarized in Table II. T_i, T_{onset}, and T_f decreased upon incorporation of 2% (w/w) CaCO$_3$ (EDC-2). Further increase in the amount of CaCO$_3$ did not show any effect on these temperatures. Peak exotherm temperature (T_p) was not affected by the incorporation of varying amounts of calcium carbonate. As expected, ΔH showed a decrease except in EDC-4, where it was significantly higher. From these results, it can be concluded that the incorporation of CaCO$_3$ did not hinder the curing reaction of DGEBA-DDS system.

Figure 2 shows the DSC scans of epoxy-nanocomposites obtained by curing isothermally in an oven at 80°C (1 h), 100°C (1 h), 120°C (1.5 h), and 180°C

TABLE II
Results of DSC Scans of DGEBA/DDS Mixture in the Presence of Calcium
Carbonate (Heating Rate 10°C/min in Nitrogen Atmosphere)

Sample designation	Nano-CaCO$_3$ [%]	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
ED	0	120.4	182.3	225.4	346.5	340.5
EDC-2	2	112.5	177.4	224.2	335.4	384.9
EDC-4	4	112.4	176.7	224.6	335.1	497.9
EDC-6	6	112.1	178.0	224.7	335.3	333.5
EDC-8	8	114.3	175.3	225.2	335.4	382.3
EDC-10	10	112.3	173.6	224.6	335.1	358.6

(4 h), mixture of epoxy/CaCO$_3$ (2%– 10% w/w) using DDS as curing agent. A shift in the base line was observed in the DSC scans of all the samples. Absence of exothermic transition shows that the samples are cured. From the DSC scans, glass transition temperature was noted as midpoint inflexion and the results are given in Table III. A significant increase in T_g was observed upon incorporation of nano-CaCO$_3$. For DGEBA : DDS (1 : 0.5) (sample ED), T_g was observed at 58°C and it increased with increasing amount of CaCO$_3$. Addition of 2% nano-CaCO$_3$, i.e., sample EDC-2 had a T_g of 88.9°C and it increased to 142°C as the amount of CaCO$_3$ was increased to 10%. These results clearly show that the incorporation of nano-CaCO$_3$ reinforces the matrix, increases its rigidity, and restricts the mobility of chains.

Mechanical properties

Mechanical properties are dependent on factors like filler content, particle size and shape, the degree of adhesion between filler and the matrix, and filler dispersion in the polymer matrix.

The flexural strength is equal to the maximum stress in the outer layer at the moment of break. It is calculated by using the following equation:

$$\text{Flexural strength} = \frac{3PL}{2bd^2}$$

where P is the load at a given point on the load deflection curve (kg); L is the support span length (mm); b is the width of specimen (mm); d is the thickness (depth) of specimen (mm).

Flexural modulus

It is the ratio of the stress to the corresponding strain defined by the initial linear portion of the load deformation curve, and is expressed as MPa.

$$\text{Flexural modulus} = \frac{L^3 M}{4bd^3}$$

where $M = $ (load $\times$ magnification factor)/extension.

The results of flexural properties are summarized in Table IV. Flexural modulus increased significantly upon incorporation of CaCO$_3$ filler, and it was maximum at a loading of 4% (Sample EDC-4). Further increase resulted in a decrease; however, the values were still much higher as compared to neat samples. Flexural strength also showed a similar trend. The decrease in flexural properties at higher filler content
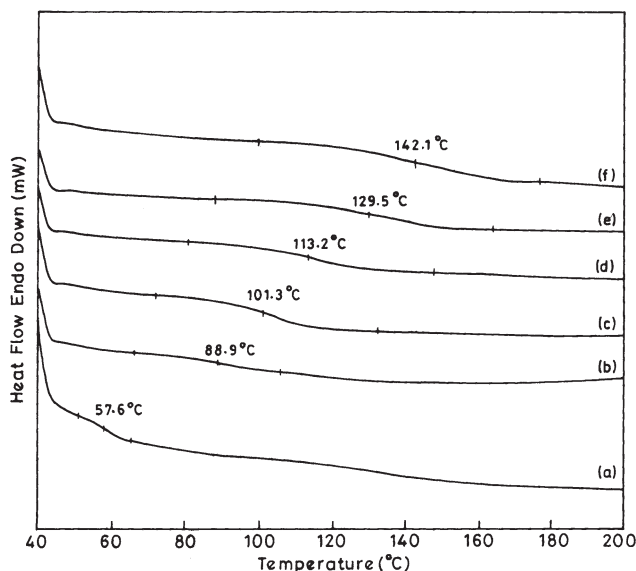

Figure 2 DSC scans of DGEBA : DDS (1 : 0.5 moles): nano-CaCO$_3$ composites. (a) ED, (b) EDC-2, (c) EDC-4, (d) EDC-6, (e) EDC-8, and (f) EDC-10.

TABLE III
Results of T_g of Epoxy Resin in the Presence of
Varying Amounts of Nano-CaCO$_3$

Sample designation	T_g (°C) (from tan δ plots)	T_g (°C) (from DSC)
ED	81	58.0
EDC-2	91	88.9
EDC-4	183	101.3
EDC-6	198	113.2
EDC-8	214	129.5
EDC-10	219	142.1

TABLE IV
Results of Flexural Properties and Impact Strength
of Epoxy Resins Cured in Presence of DDS
and Nano-CaCO$_3$

Sample designation	Flexural modulus (MPa)	Flexural strength (MPa)	Impact strength (kJ/m^2)
ED	3.9	18.6	10.2
ECD-2	2394.9	18.8	12.3
ECD-4	2681.8	24.7	18.9
ECD-6	2524.4	23.8	17.7
ECD-8	2099.4	21.7	13.2
ECD-10	1998.5	20.4	6.2

could be done due to poor dispersion or interface infraction.

Surprisingly, we find an increase in impact strength upon incorporation of filler, which again was maximum at a loading of 4%. Further increase of filler content resulted in a decrease in impact strength. This suggests that too many nano-CaCO$_3$ particles results in aggregation in the matrix and degrades the toughness of epoxy resin composite, whereas nano-CaCO$_3$ exhibits reinforcing capacities when added in small amounts. From these results, it can be concluded that the maximum improvement in the properties of epoxy resins was observed at a filler loading (CaCO$_3$) of $\sim 4\%$ (w/w).

Dynamic mechanical thermal analysis

Figure 3 show the plots of storage modulus versus temperature in the absence/presence of nano-CaCO$_3$. DMA scans were recorded in the tempera-
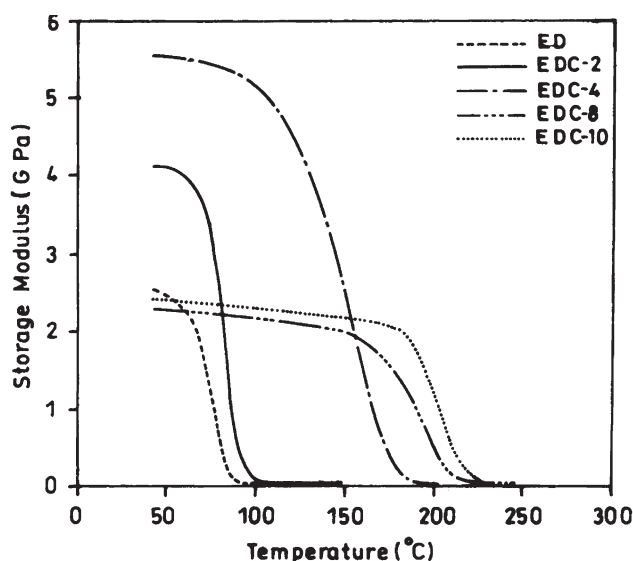
TABLE V
Results of Storage Modulus as a Function of Different
Temperature in ED and EDC Samples

Sample designation	Storage modulus (GPa) at temperature (°C)						
	50	60	80	100	110	120	130
ED	2.4	2.2	0.43	0.056	0.056	0.055	0.053
EDC-2	4.1	4.0	2.0	0.60	0.0516	0.049	–
EDC-4	5.5	5.5	5.4	5.1	4.8	4.4	4.0
EDC-8	2.29	2.27	2.24	2.21	2.15	2.12	2.09
EDC-10	2.4	2.38	2.32	2.26	2.23	2.20	2.18

ture range of 50–300 °C at a heating of 3°C/min. DMA scans for few samples were repeated to check the reproducibility of DMA data. Storage modulus (GPa) at different temperatures was noted for ED and EDC samples having varying amounts of CaCO$_3$, and the results are summarized in Table V. The values of storage modulus were significantly higher for composites above 100°C as compared to neat epoxy (ED sample) sample. Increase in storage modulus clearly indicates that the addition of nano-CaCO$_3$ resulted in an increase in hardness/modulus of the epoxy resin.

Figure 4 show the plot of tan δ vs. temperature for epoxy-nano-CaCO$_3$ composites. The peak position of the tan δ plots was used to indicate the glass transition temperature (T_g) of specimens, and the results are given in Table III. A significant increase in T_g i.e. ~ 150°C was observed upon addition of 10% CaCO$_3$. T_g for ED was 81°C, and it increased to 219°C upon addition of 10% filler (EDC-10). These results clearly show that the dimensional stability and maximum use temperature of epoxy resins can be enhanced upon incorporation of filler. The T_g obtained from tan δ plots are significantly different as compared to the values obtained from DSC scans. This could be
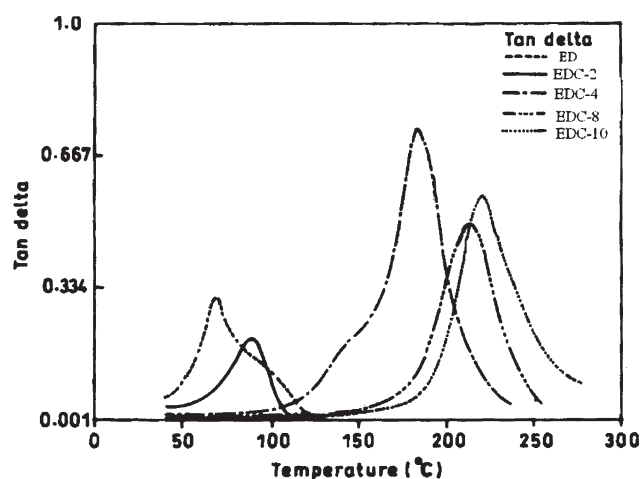
Figure 3 Plot of storage modulus vs. temperature for epoxy-nano-CaCO$_3$ (<50 nm) composites.

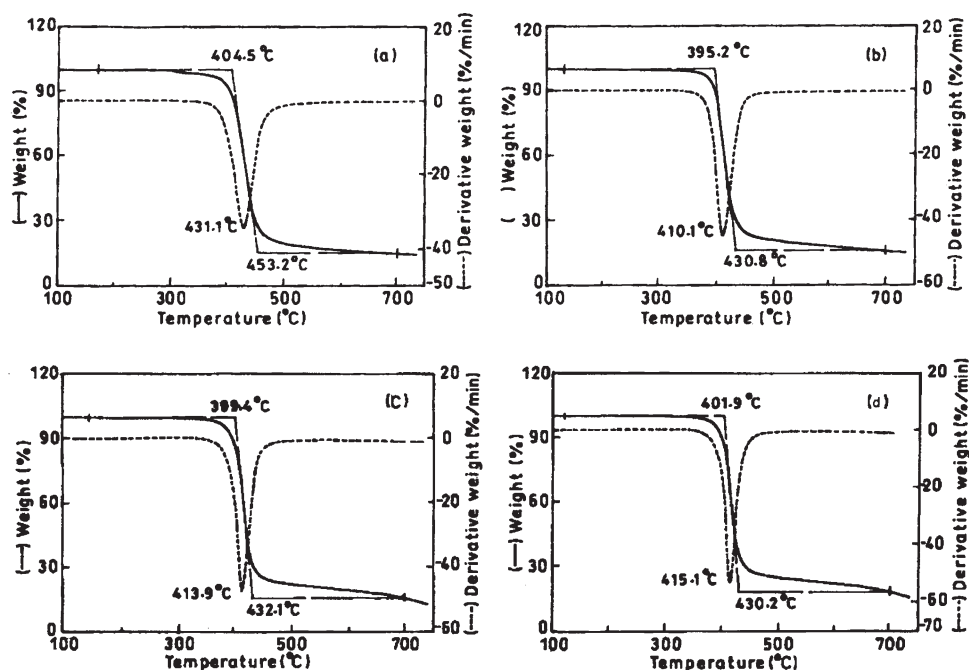**Figure 4** Plot of tan δ vs. temperature at frequency 1 Hz in the absence/presence of nano-CaCO$_3$.

Figure 5 TG/DTG traces of DGEBA : DDS (1 : 0.5 moles) in the absence/presence of nano-CaCO₃. (a) ED, (b) EDC-2, (c) EDC-6, and (d) EDC-8.

due to the significantly different condition used for isothermal curing and for making samples used for DMA scans. Postcuring results in a significant increase in the dimensional stability of these materials. Storage modulus for these samples was highest at a loading of 4% (EDC-4) and decreased with increase in the amounts of filler. This also supports that optimum condition of performance properties was observed at 4% filler content. This further supports the reinforcing effect of filler upto a filler content of 4%.

Thermal stability

Figure 5 show the TG/DTG traces of isothermally cured epoxy resin (DGEBA/DDS) in the absence/presence of varying amounts of CaCO₃. The results are summarized in Table VI. The relative thermal stability of cured resin was evaluated by comparing

initial decomposition temperature (IDT), the temperature of maximum rate of mass loss (T_{max}), the final decomposition temperature (FDT), and the percent char yield at 800°C. A single-step decomposition was observed in all the samples. All the formulations were stable upto 400 ± 5°C and started losing weight above this. A marginal decrease in IDT, T_{max}, and FDT was observed upon addition of varying amounts of CaCO₃ with a slight increase in percent char at 700°C. A decrease in IDT could be due to the moisture/coating of CaCO₃ filler. In order to verify this fact, TG/DTG trace of CaCO₃ was also recorded under similar conditions. A weight loss of ∼ 4% was observed in the temperature range of 200–600 °C and ∼ 5% in the temperature range of 600-700°C. Mass loss in the first step could be due to the moisture or coating, and the mass loss in the second step can be attributed to the loss of CO₂.

WAXD

Figure 6 shows the X-ray diffraction patterns of CaCO₃, neat epoxy, and epoxy filled with varying amounts of calcium carbonate. Neat epoxy showed an amorphous pattern, and XRD patterns of epoxy-nanocomposites show the characteristic peak due to CaCO₃ at 2θ of 31.7°, 29.4°, and 23° in epoxy- nanocomposites. The increase in CaCO₃ content in epoxy composite resulted in an increase in the intensity of characteristic peak at 2θ of 30.9° belonging to that of dolomite particles. In case of neat CaCO₃, intensity of peak at 2θ of 29.4° (due to calcite) was much

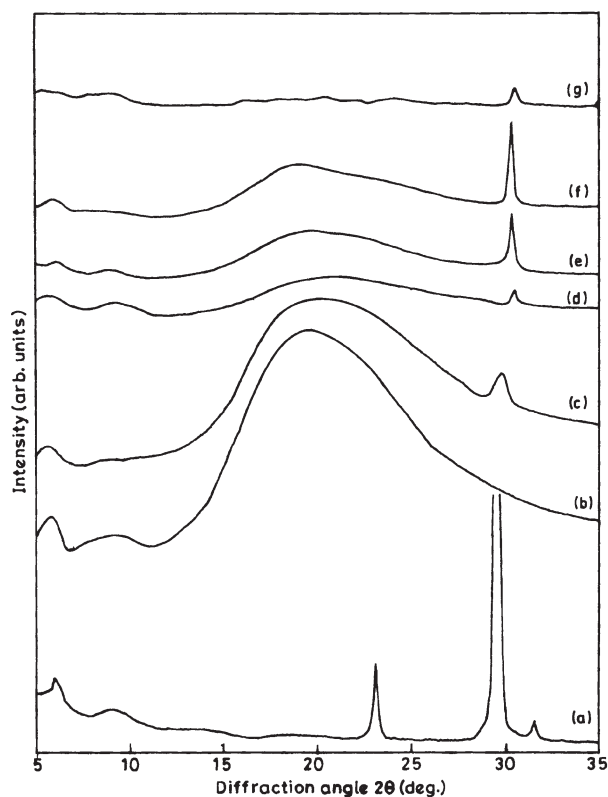**TABLE VI**
Results of TG/DTG Traces of DGEBA : DDS (1 : 0.5 moles) in the Absence/Presence of Varying Amounts of Nano-CaCO₃ (Heating Rate 20°C/min in Nitrogen Atmosphere)

Sample designation	IDT (°C)	T_{max} (°C)	FDT (°C)	Char yield at 800°C (%)
ED	404.5	431.1	453.2	15.6
EDC-2	395.2	410.1	430.8	16.0
EDC-4	399.4	414.7	432.0	16.1
EDC-6	399.4	413.9	423.1	16.0
EDC-8	401.0	415.1	430.2	17.9
EDC-10	397.7	412.3	429.6	20.6

Figure 6 Intensity vs. 2θ plots for $CaCO_3$, epoxy, and epoxy-$CaCO_3$ composites. (a) $CaCO_3$, (b) ED, (c) EDC-2, (d) EDC-4, (e) EDC-6, (e) EDC-8, and (g) EDC-10.

higher as compared to that of dolomite (31.7°). In case of composites, only one characteristic peak belonging to that of dolomite at 2θ of 30.9° was observed in all the samples, and the intensity increased with increasing amount of $CaCO_3$.[21] This shows that the crystal lattice of $CaCO_3$ changed from calcite to dolomite in epoxy composites.

Morphology

In order to investigate the dispersion/distribution of filler within the epoxy matrix, fractured surfaces of specimens were observed using scanning electron microscopy (SEM). Figure 7 shows the SEM images of the fractured surface of epoxy in the absence or presence of varying amounts of $CaCO_3$. It is obvious that a very good dispersion with a little agglomeration was observed as the concentration of $CaCO_3$ increased from 2% (w/w) to 8% (w/w). A very fine dispersion of filler was observed in EDC-10 sample.

CONCLUSIONS

From these results, it can be concluded that the incorporation of nano-$CaCO_3$ improves the rigidity, maximum use temperature, and toughness of epoxy resins. The maximum improvement in the properties
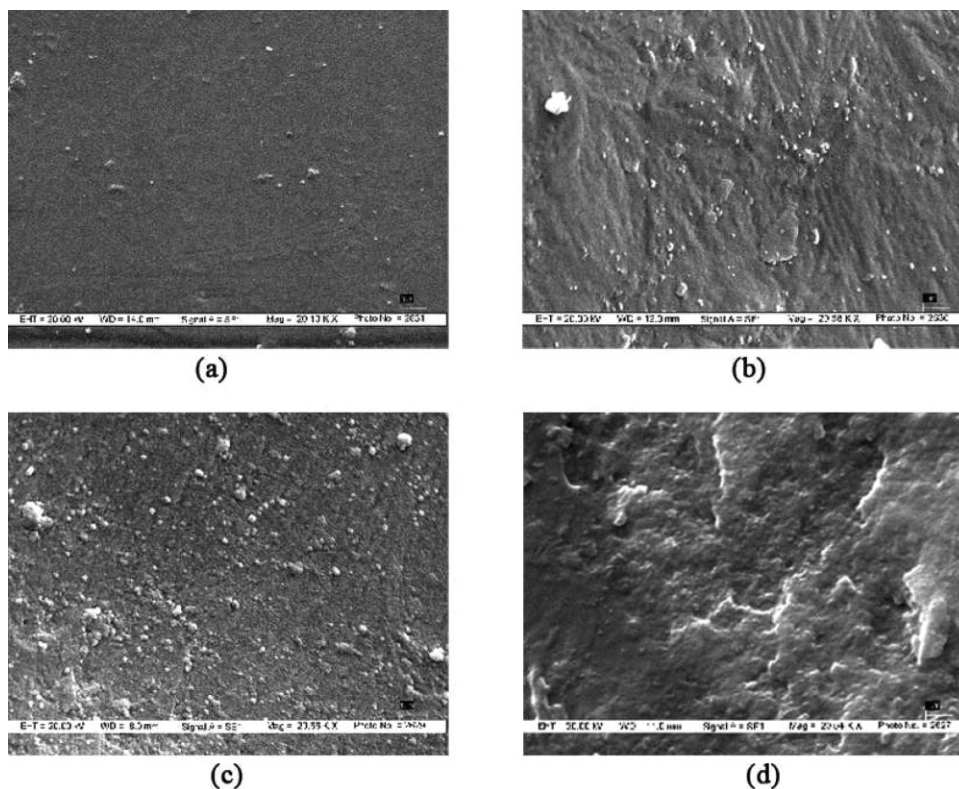

Figure 7 SEM images of fractured surfaces of neat epoxy and epoxy filled with varying amounts of nano-$CaCO_3$. (a) ED, (b) EDC-4, (c) EDC-8, and (d) EDC-10.

was observed at a filler loading ($CaCO_3$) of 4% (w/w) in the epoxy matrix

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