Cloisite Clay-Infused Phenolic Foam Nanocomposites

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ABSTRACT: A sonochemical technique was developed to infuse Cloisite clay nanoparticles into phenolic foam materials. Phenolic resin solution (Part A) was mixed with clay particles, and irradiated using a high intensity ultrasonic liquid processor. In the next step, the modified phenolic resin solution containing clay particles was mixed with Part B (containing phenol sulfonic acid, catalyst) through a high-speed mechanical stirrer. The reaction mixture was then cast into rectangular molds to make nanophased foam panels. Test coupons were cut precisely from the panels to carry out thermal, morphological, and mechanical characterizations. The as-prepared foam samples were characterized by scanning electron microscopy (SEM), X-ray diffraction, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The SEM studies have shown that the particles are well dispersed over the entire volume of the matrix with minimal agglomeration. The foam cells structures are well-ordered and uniform in size and shape. The TGA and DSC analyses show that the nanophased foams are thermally more stable than the corresponding neat system. Quasistatic compression tests have been carried out for both nanophased and neat foams systems. The test results show that there is a significant increase (approximately in the range of 150–180%) in the compressive strength and modulus of the nanophased foams over the neat system. This improvement in compressive properties has been noted repeatedly for multiple batches and with a minimum of three specimens tested from each batch. Details of the synthesis, thermal and mechanical characterization are presented in this paper. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 308–314, 2007

Key words: nanocomposites; fabrication; polymeric resins

INTRODUCTION

Polymeric foam technology is widely used in today's world and continues to grow at a rapid pace. Many reasons for this growth include lightweight, excellent strength to weight ratio, superior insulating abilities, energy absorbing performance, and comfort features. The polymeric foams are extensively used in transportation, bedding, packaging sporting goods, automobiles, insulation, flotation devices, decorative moldings, and flame retardants. Phenolic foams are the most efficient insulation materials that are commonly available and relatively inexpensive. They have outstanding fire characteristics and extremely low smoke emission and no dripping of molten plastic when exposed to flame. Phenolic foams are highly resistant to chemicals and solvents. They are particularly useful in applications where fire resistance is critical, such as building materials for civil construction, passenger and military aircrafts, and marines. In these structural applications polymeric foams are used as core materials in sandwich composites. An important objection in using sandwich composites in marine structures is their flammability and fire resistance.[1,2] Most unprotected composites ignite after a short time when exposed to fire because of the high flammability of the polymers. For this reason strict fire safety rules were imposed on the use of composites in the marine industry. However, structural applications of phenolic foam have been severely limited because of the extreme brittleness and friability, which causes serious problems when used in structural sandwich panels.

Over the past few decades, many efforts have been made to produce phenolic foams tougher,[3] using certain inert fillers such as carbon black, talk, mica, asbestos, wood, and cork. Typically, to improve the texture and homogeneity of foams core materials, but none of them has succeeded entirely in improving the toughness without increasing the density.[4,5]

Recently, researchers have shown a great deal of interest in improving physical, mechanical, thermal, and chemical properties of materials using nanoparticles as fillers. The infusion of nanoparticles in polymer materials has become attractive because of the unique properties displayed by the nanoparticles. Because of the nanometer size of these particles,
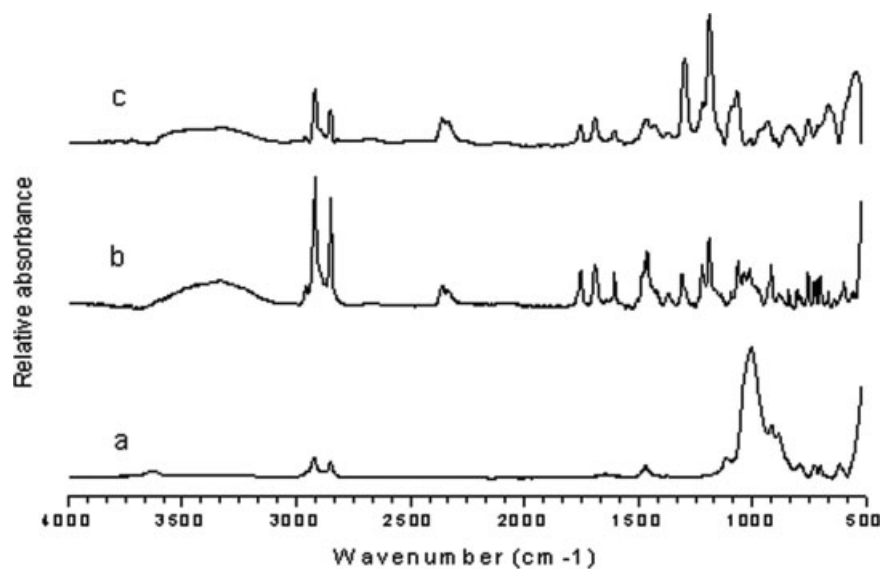
Figure 1 FTIR spectra of (a) Cloisite 10A clay, (b) neat phenolic foam, and (c) phenolic foam/2% Cloisite 10A clay.

their physicochemical characteristics differ significantly from those of molecular and bulk materials.[6,7] Nanoparticle–polymer composites synergistically combine the properties of both the host polymer matrix and the discrete nanoparticles. Such nanocomposite materials are expected to have novel thermal and mechanical properties.[8,9] Lee and Giannelis[10] were the first to study phenolic resin/clay nanocomposites by melt intercalation. Choi and Lee[11] further studied the morphology and curing behavior of phenolic resin/clay nanocomposites prepared by the same method as used by Giannelis and Lee. Recently, Jonathan and others[12] studied the phenolic resin/clay composite synthesized by *in situ* polymerization and reported the improvement in tensile properties for 2.7% loading. Zenggang and others[13] studied phenolic resin/montmorillonite composite by suspension condensation method and reported the significant improvement of the morphological changes in nanocomposite materials. Choi and research team[14] reported the thermal and mechanical properties of intercalated clay and phenolic resin prepared by melting method.

Many researchers have used different techniques to make nanocomposite materials. Acoustic cavitations technique is one of the efficient ways to disperse nanoparticles into the virgin materials.[15,16] In this technique, application of alternating acoustic pressure above the cavitation threshold creates numerous cavities in the solution. Some of these cavities oscillate at the frequency of the applied field (normally 20 kHz), while the gas content inside these cavities remains constant. However, some other cavities grow intensely under tensile stresses while yet another section of these cavities, which is not completely filled with gas, starts to collapse under the compression stresses of the

sound wave. In the latter case, the collapsing cavities produce tiny particles of "debris" and the energy of the collapsed one transformed into pressure pulses. It is noteworthy that the formation of the "debris" also facilitates the development of cavitation. It is assumed that acoustic cavitation in solutions develops according to a chain reaction. Therefore, individual cavities on real nuclei develop so rapidly that within a few microseconds an active cavitation region is created close to the source of the ultrasound probe. The evolution of cavitation process in the ultrasonically processed melt creates favorable conditions to intensify various physiochemical processes. Acoustic cavitation
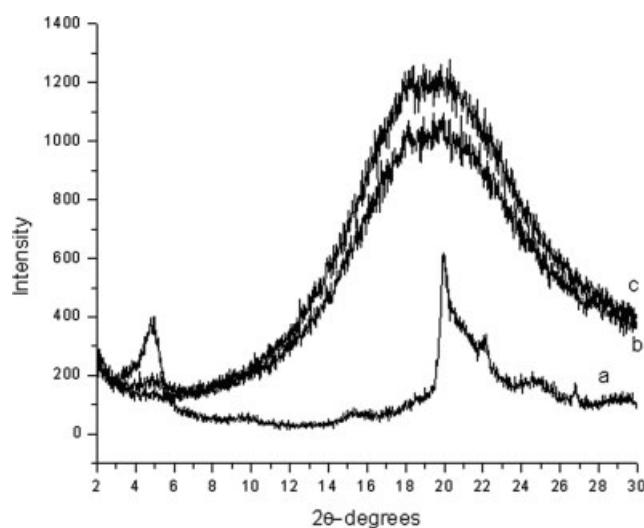

Figure 2 WAXRD patterns of (a) Cloisite 10A clay, (b) phenoilic resin/Cloisite 10A clay nanocomposite, and (c) neat phenolic resin.
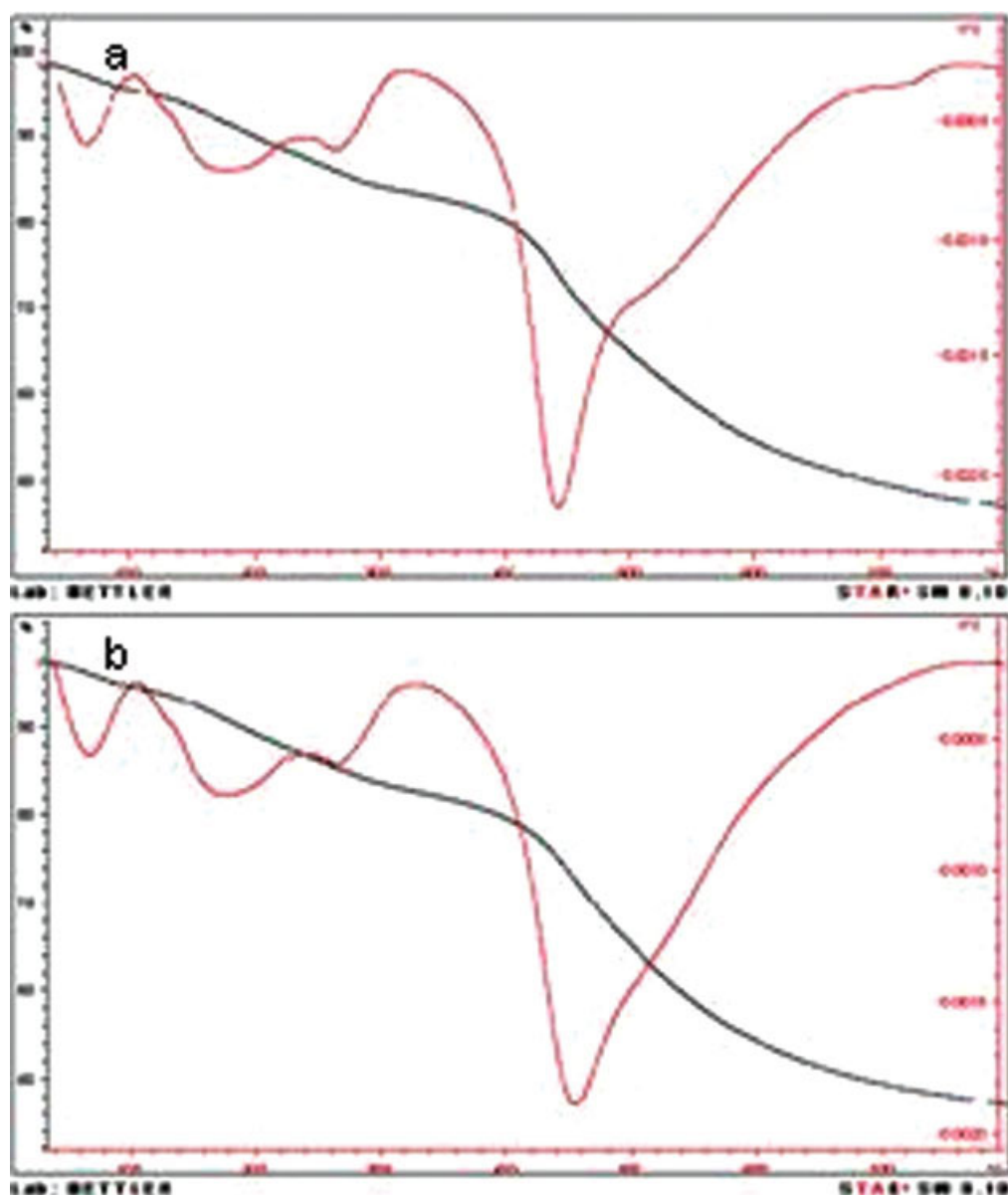
Figure 3 (a) TGA curve of neat phenolic foam; (b) TGA curve of 2% Cloisite 10A clay–phenolic foam. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

accelerates heat and mass transfer process such as diffusion, wetting, dissolution, dispersion, and emulsification.

The purpose of this study is to improve the thermal and mechanical properties of the nanocomposite foams using organically modified layered silicates in which nanometer-size silicates such as montmorillonite (Cloisite 10A clay) are dispersed in the phenolic polymer matrix through high-power ultrasound technique.

EXPERIMENTAL

Materials

Thermo Core is a two-part phenolic foam polymer acquired from American Foam Technologies (HC37,

Lewisburg, WV). Part A contains the phenolic resin solution and anionic and nonanionic surfactant. Part B is a catalyst solution, which contains the phenol sulfonic acid. Cloisite 10A was purchased from Southern Clay Products, Inc. (Gonzales, TX). It is a natural montmorillonite modified with dimethyl-benzyl-hydrogenated tallow quaternary ammonium chloride, possessing a cation exchange capacity (CEC of 125 meq/100 g).

Processing

Phenolic resin (Part A) is mixed with 2% of Cloisite 10A and irradiated with high intensity ultrasonic horn (Ti-horn, 20 kHz, 100 W/cm^2), at room temper-
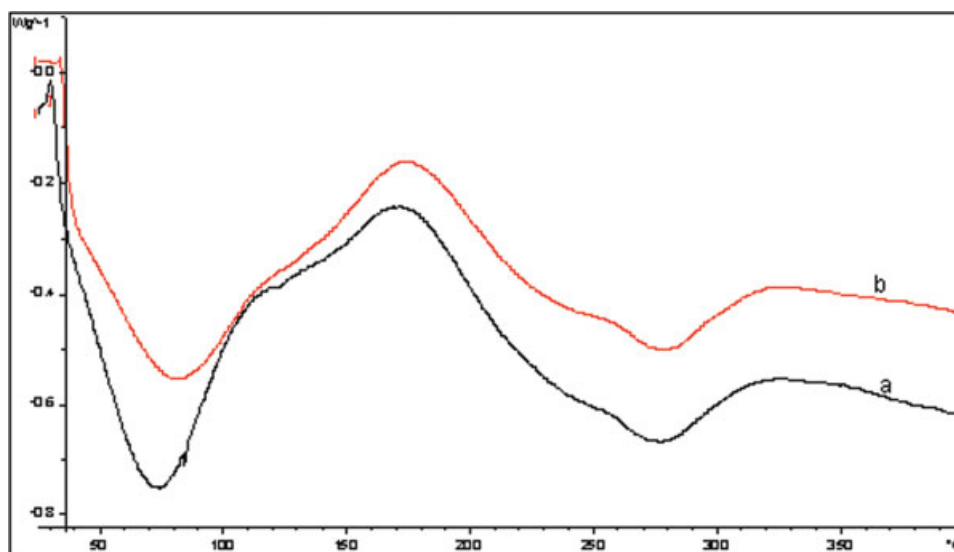
Figure 4 DSC results of (a) neat phenolic foam and (b) phenolic foam/Cloisite 10A clay nanocomposite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ature for 30 min. The reaction mixture was then mixed with phenol sulfonic acid and stirred with high-speed mechanical mixer for about 50 s and cured at room temperature for 24 h. The samples were cut precisely and used for the chemical and mechanical testing.

Characterization

FTIR spectroscopic study was carried out using a Thermo–Nicollet Nexus 470 FTIR Spectrometer and KBr pellets were made on a hand-press from a mixture of the sample and KBr powder. The X-ray diffraction (XRD) study was carried out with Rigaku D/MAX 2200 X-ray diffractometer to understand the intercalation and exfoliation clay structure in the polymer matrix. Samples were extracted from different locations of the panel and XRD tests were conducted on those samples at various surfaces. XRD peaks were found to be in all cases identical. Dimensions of sample were maintained at 17.5 mm (length) × 13.5 mm (width) ×1 mm (thickness). Thermogravimetric analysis (TGA) of various specimens was carried out under nitrogen gas atmosphere using a Mettler Toledo TGA/SDTA 851^e apparatus. The samples were cut into small pieces (10–20 mg) using a surgical blade. The TGA measurements were carried out for these samples from 30°C to 800°C at a heating rate of 10°C/min under nitrogen atmosphere. Differential scanning calorimetric experiments were carried out using a Mettler Toledo DSC 822^e with temperatures ranging from 30°C to 400°C at a heating rate of 10°C/min under nitrogen atmosphere. The morphological analysis was carried out using scanning electron microscopy (SEM; JEOL JSM 5800). The sample were precisely cut in to small

pieces and placed on a double-sided carbon tape and coated with gold/palladium to prevent charge buildup by the electron absorption.

Quasistatic compression

To explore the quasistatic compression response, the specimens were tested in the thickness direction using servo-hydraulically controlled Material Testing System MTS-810. An ASTM C365-57 standard was followed for the quasistatic compression test. The size of the specimen was 12.7 mm × 25 mm × 25 mm. The capacity of the MTS machine is approximately 10,000 kg. The test was carried out in displacement control mode at a crosshead speed of 1.27 mm/min. To maintain evenly distributed compressive loading, each specimen was sanded and polished with high accuracy so that the opposite faces were parallel to one another. A software Test Ware-SX was used to develop a program, which controlled the test conditions and recorded both the load and crosshead displacement data. The load-deflection data recorded by the data acquisition system was converted to stress–strain curve.

RESULTS AND DISCUSSION

FTIR-spectra of thermo core foam, Cloisite 10A and nanocomposite are presented in Figure 1. A minimum of 32 scans were averaged with a resolution of 2 cm^{-1} at 4000–500 cm^{-1} range. Both phenolic resin and nanocomposite, as shown in Figure 1(b,c) have the characteristic bands of phenolic resin 815 cm^{-1}, 1240 cm^{-1}, and 3300 cm^{-1}.[17,18] These correspond to the absorbance of phenyl ring γ (CH), the aromatic ether and —OH stretching, respectively. Besides
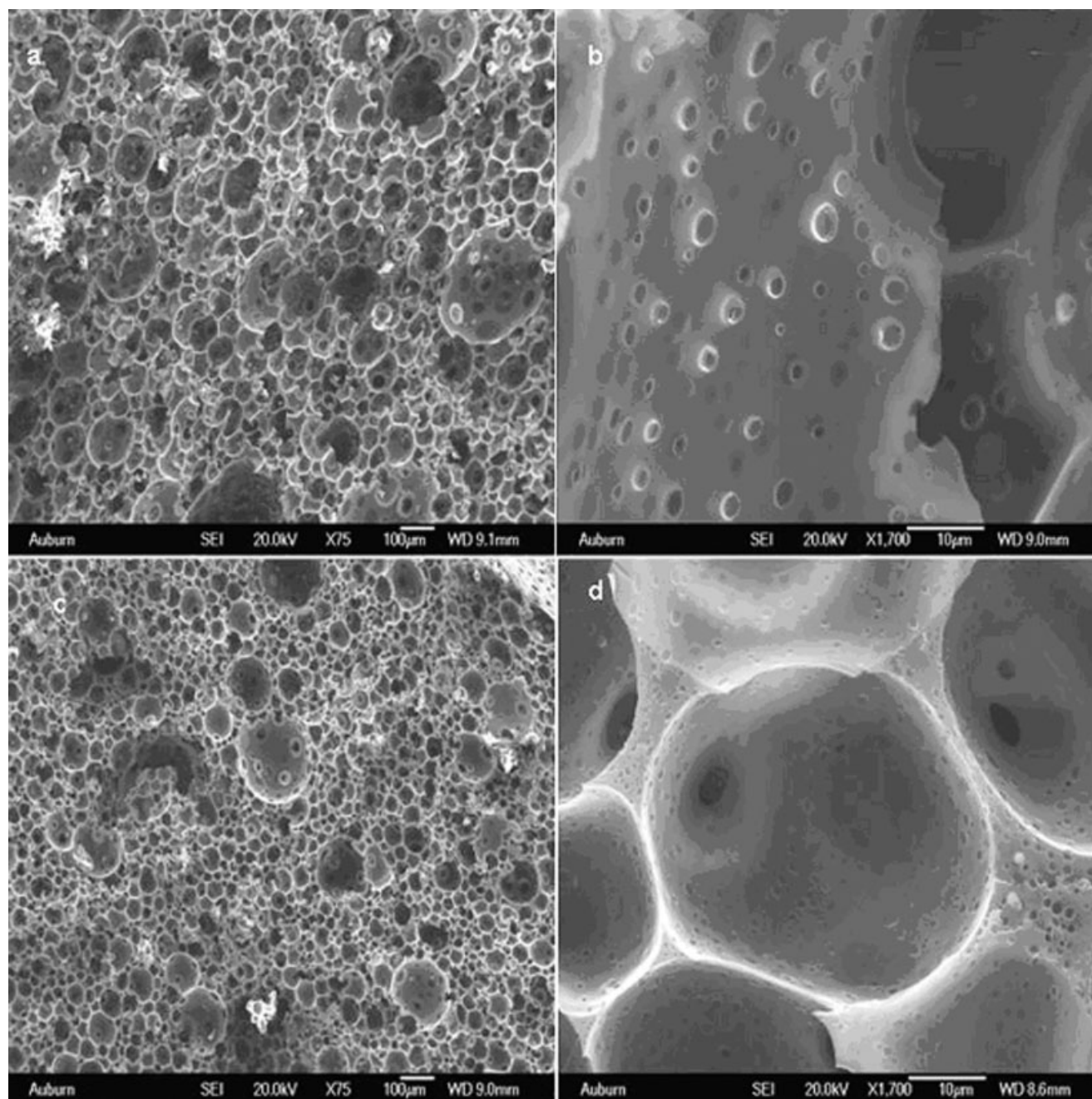
Figure 5 SEM micrograph of (a) neat phenolic foam, (b) neat phenolic foam at higher magnification, (c) nanophased phenolic foam, and (d) nanophased phenolic foam at higher magnification.

these bands, nanocomposite also has the characteristic bands of montmorillionite: 1038 cm^{-1} and 524 cm^{-1}, which correspond to the stretching vibrations of Si—O—Si and Al—O of montmorillionite. These results show that montmorillionite has been incorporated in phenolic resin.

Wide-angle X-ray diffraction (WAXD) technique was used to study the regular lattice arrangement of crystals. The gallery spacing of MMT, d, can be expressed by the Braggs equation $n\lambda = 2d \sin n\theta$, Where λ is the wavelength of X-ray, θ is the diffraction angle, and n is an integer 1,2,3, ... The WAXD patterns of the

Cloisite 10A and phenolic resin are presented in Figure 2. The 001 spacing of Cloisite 10A is about 2.5 nm, corresponding to the diffraction angle $2\theta = 4.1°$. The phenolic resin/Cloisite 10A clay nanocomposite shows a diffraction peak at $2\theta = 3.6°$ ($d_{001} = 3.5$ nm). The absence of diffraction peaks suggests that the clay has been completely exfoliated.[19,20]

Thermogravimetric analysis (TGA) was also carried out to obtain information on the thermal stability of the nanophased phenolic foams. Figure 3(a,b) depict the TGA of foams including neat and the nanophased phenolic foam. As seen in Figure 3(a,b),
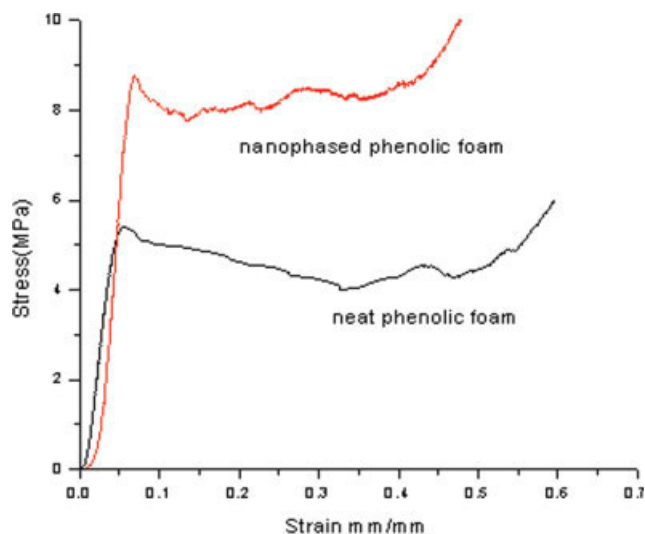
Figure 6 Quasistatic compressive behavior of neat phenolic foam and nanophased 2% Cloisite 10A clay phenolic foam. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the major structural disintegration for neat phenolic foam occurs at 443°C while it takes place 455°C, for that of 2% Cloisite 10A clay–phenolic foam. The 12°C increase in thermal stability could be due to the catalytic effect on the crosslinking and high cell density of the phenolic foam, caused by the clay nanoparticles. Similar results were observed in our earlier studies, as well.[18,21]

The glass transition temperature (T_g) of the cured resin was obtained from the DSC curves, and the scans were carried out at a heating rate of 10°C/min in a nitrogen atmosphere (Fig. 4). The T_g for neat phenolic system was found to be ∼ 270°C,[22] whereas for the nanocomposite foam it was ∼ 282°C, which is 12°C more than that of the neat phenolic system. This increase in T_g is attributed to the high crosslinking due to the presence of the clay particles. These results are consistent with the TGA data.

To further examine the phenolic foam and its clay-based nanocomposites, SEM analysis was also carried out. The micrographs for neat phenolic foam

and nanophased phenolic foam are shown in Figure 5. These foam materials have closed cell structures. The cell sizes measured from SEM micrographs were about 100 μm and 50 μm as shown in Figure 5(a,c) for neat and nanophased foam respectively. When the samples were examined at a higher magnification as shown in Figure 5(b,d) it was possible to see cells of much smaller sizes, 2 μm and 1 μm for neat and nanophased phenolic foam respectively. It was also observed as shown in Figure 5(c), that the neat phenolic foam has fewer cells compared to the nanophased phenolic foam. Phenolic foam containing 2% Cloisite 10A clay has a higher cell density and smaller cell size as compared to the neat phenolic foam, suggesting that the dispersed Cloisite 10A clay particles act as heterogeneous nucleation sites during cell formation.[23,24]

To study the effect of nanoclay on the mechanical properties the nanocomposite compressive tests were performed. The stress–strain cures of the neat phenolic foam and the nanophased Cloisite 10A clay phenolic foam are presented in Figure 6. The compressive strength and modulus calculated for neat phenolic foam are 5.4 MPa and 136.6 MPa, respectively. Whereas for the nanocomposite foams the strength and the modulus were 8.7 MPa and 248.8 MPa, respectively. These results were further converted to reduced compressive strength and modulus by dividing by density of the foam sample and were presented in Table I. When we compared these results with other researcher's results[25] of similar samples, it was found that the percentage of improvements were very well comparable to those results. It is also worth mentioning that we have not observed the clay particles coming out of the composite during the usage.

Nanophased 2% Cloisite 10A phenolic foam shows a substantially higher compressive strength and modulus compared with the neat phenolic foam. The nanocomposite foam shows about 160% increase in the strength and 182% increase in the modulus. This may attributed to the fact that for closed-cell structure foams, the elastic region is controlled by the stretching of the cell faces and edges. The stress plateau is associated with the collapse of the cells.

TABLE I
Comparison of Mechanical Properties with Other Similar Systems

	PU/5% clay nanocomposite foams (Ref. 25)						As prepared phenolic foam nanocomposite	
	(a) Polyol-180			(b) Polyol-100				
Property	Neat	(MMT–OH)	(MMT–Tin)	Neat	(MMT–OH)	(MMT–Tin)	Neat	Nanophased
Density (g cm^{-3})							0.237	0.314
Reduced compressive modulus (MPa/g cm^{-3})	1	16.5	16	195	120	90	413.502	764.331
Reduced compressive strength (MPa/g cm^{-3})	0.2	1.4	1.25	8.3	7.6	4.9	15.190	27.707

When the cells have completely collapsed, the cell walls touch each other and further strain caused sharp rise in stress. The peak stress of the nanophased phenolic foam is 60% higher than that of the neat foam. This improvement in the strength may be due to the high crosslinking and nucleation created by the Cloisite 10A clay particles.

CONCLUSIONS

- A sonochemical technique has been developed to produce nanophased phenolic foam
- Thermal analysis results clearly indicate that there is an increase in crosslinking and the foam cell density, due to the presence of Cloisite 10A clay particles.
- The glass transition temperature was also increased by 12°C.
- Mechanical tests showed that there was a significant increase in the strength and the modulus by 60 and 80%, respectively.

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