

Nanoclay modified silica phenolic composites: mechanical properties and thermal response under simulated atmospheric re-entry conditions

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Ablative nanocomposites based on nanoclay-dispersed addition curable propargylated phenolic novolac (ACPR) resin, reinforced with chopped silica fiber, were investigated for their thermal response behavior under simulated heat flux conditions corresponding to typical atmospheric re-entry conditions. Organically modified nanoclay (Cloisite 30B) was incorporated to different extents (1–10%) in the ACPR resin matrix containing silica fiber to form the composite. The composites displayed optimum mechanical properties at around 3 wt% of nanoclay loading. The resultant composites were evaluated for their ablative characteristics as well as mechanical, thermal and thermo-physical properties. The reinforcing effect of nanoclay was established and correlated to the composition. The mechanical properties of the composites and its pyrolysed product improved at moderate nanoclay incorporation. Plasma arc jet studies revealed that front wall temperature is lowered by 20°C and that at backwall by 10–13°C for the 3 wt% nanoclay-incorporated composites due to impedance by nanoclay for the heat conduction. Nanoclay diminished the coefficient of thermal expansion by almost 50% and also reduced the flammability of the composites. The trend in mechanical properties was correlated to the microstructural morphology of the composites. The nanomodification conferred better strength to the pyrolysed composites. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: ablatives; addition cure phenolics; plasma arc jet; nanoclay

INTRODUCTION

Polymer nanocomposites (PNCs) are emerging materials in automobile, household and biomedical areas. However, their potential in space science and technology is not yet fully exploited.^[1–6] Modification of various thermosets and elastomeric insulating systems with different types of nanoparticles such as nanoclay, polyhedral oligomeric silsesquioxane (POSS), carbon nanotube (CNT) and carbon nanofibers is known to improve the ablative, thermal and mechanical performance.^[7–16] One of the important areas where PNCs are likely to find application is in ablative thermal protection systems in spacecraft and launch vehicles where significant weight saving through improved performance is expected through modification of the polymer matrix with suitable nanomaterials. Studies on the ablation characteristics and thermal performance of polymer nanocomposites have been reported by different researchers.^[17–19]

Phenolic resin and its derivatives are the most common thermoset matrices used in ablative composites.^[20–23] Conventional resole type phenolic resins are used in a wide range of applications encompassing commercial products as well as high performance applications in aerospace industry owing to their desirable features such as reasonably good mechanical properties, dimensional stability, flame retardance and resistance against various solvents.^[24–26] Some of the shortcomings of phenolic resin, which limit their application in many other critical areas are, their brittleness, lower shelf life and evolution of volatile by-products during curing,^[27] which motivated researchers to modify the

phenolic groups by appropriate synthetic strategy. Phenolic resins containing addition curable functional groups invoking new chemistry gain importance in this context.^[28]

In the present study, nanocomposites based on nanoclay-dispersed, addition curable phenolic resin/silica fiber have been investigated as ablative thermal protection system for atmospheric re-entry missions under moderate heat flux conditions. The effect of nanoclay incorporation on the physical, thermal and thermo mechanical performance and morphology of the composites has been investigated and correlated to the composition of the composites. Ablative performance, char strength and char morphology were also evaluated to assess the suitability of the composites as effective re-entry TPS.

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EXPERIMENTAL

Materials

Phenol, formalin (34–37%) and oxalic acid were procured from Nice Chemicals, India and were used as received. Potassium carbonate (Nice Chemicals, India) was powdered and dried at 120°C for 5 h prior to use. Propargyl bromide (80% solution in toluene, Alfa Aesar) was used as received. Chopped silica fiber (length: 4–7 mm, dia: 15–20 μ , silica content > 99%) was procured from M/s. ValetHitec Composites (Chennai, India). Nanoclay (Cloisite 30B $d_{001} = 11.7^\circ\text{A}$, CEC = 92.6 meq/100 g clay, specific gravity = 2.86) was procured from M/s. Southern clay product, USA and was vacuum dried at 80°C prior to use.

Instrumental

Spectroscopic characterization of the nanoclay-incorporated matrices was done using a Perkin Elmer FT-IR spectrophotometer. Differential scanning calorimetric (DSC) analysis was performed using a Setaram DSC Q-20, at a heating rate 10°Cmin⁻¹ in nitrogen atmosphere, and thermo gravimetric analysis (TGA) was performed using TA Instruments SDT Q-600 thermo gravimetric analyzer at a heating rate of 10°Cmin⁻¹ in nitrogen atmosphere. Rheological characterization was done with a Reologica Stresstech Rheometer model ReologicaViscotech QC using a 20-mm parallel plate assembly in oscillation mode at a frequency of 1 Hz and a controlled strain of 0.01. Mechanical properties were determined using an INSTRON UTM 4202. Thermomechanical analyser was used to measure the coefficient of thermal expansion using TA Instruments Q400, as per ASTM E831, at a ramp of 10°C/min under N₂ (50 ml/min) up to 300°C. The limiting oxygen index (LOI) was determined as per ASTM D 2863. Plasma Arc jet tests were conducted in a 250-kW plasma arc jet facility. The tests were conducted under identical, simulated environments at a peak heat flux of 125 W/cm² for 75 seconds. The microstructure of the composites was investigated using a scanning electron microscope, Carlzeiss, EVO 50.

Synthesis of novolac-propargyl ether resins

The propargyl ether novolac resin (ACPR) was synthesized by reacting the precursor novolac with propargyl bromide by a reported procedure.^[28]

Processing of composites

Composites of dimension 150 mm × 150 mm × 35 mm (l × b × t) were fabricated by compression molding of different compositions of nanoclay-incorporated (1, 3, 5 and 10 wt%) ACPR, and chopped silica fiber in the weight ratio of 30:70. Nanoclay was first dispersed in acetone (by ultrasonication in a bath for 30 min), and then it was added to the ACPR matrix followed by

mechanical stirring at room temperature for 1 h. The required quantity of silica fibre was then mixed well with the resin solution to prepare the prepreg mix. The prepreg mix after drying at 50°C in a vacuum oven for 2 h was filled in a rectangular mould and cured in a hydraulic press according to the cure schedule: 100°C for 10 min, 150°C for 1 h, 160°C for 2 h, 170°C for 2 h, 200°C for 1 h and at 250°C for 2 h. The composite blocks were removed from the mould after cooling to ambient temperature and were cut to the required size according to ASTM standards for various analyses.

RESULTS AND DISCUSSION

Cure characterization of propargyl ether novolac

Propargyl ether novolac resin was synthesized as per Scheme 1. The resin was characterized by hydroxyl value and FT-IR. From the hydroxyl value of the novolac and the propargyl derivative, the extent of propargylation was estimated as 85%. This composition was shown to have good thermal stability. The curing of ACPR and the effect of nanoclay on its cure reaction were studied by FTIR, DSC and Rheometry.

The FTIR spectra of ACPR uncured, and a cured composition of ACPR containing 10 wt% of nanoclay (ACPR 10) are given in Fig. 1. The peak at 2120 cm⁻¹ due to C≡C diminished and an additional peak appeared at 1736 cm⁻¹ substantiating the curing of ACPR and the resultant formation of cyclic ketone during curing.

Cure studies of the propargyl ether novolac by DSC show a proportionate lowering in the initial cure temperature with the increase in nanoclay, as evident from the thermograms shown in Fig. 2. Detailed cure and mechanistic aspects of propargyl ether novolac have been examined in a previous study.^[20]

The resin system containing 10% by weight of nanoclay exhibited an initial cure temperature of 172°C against the cure initiation of neat resin at 195°C. It is clear that, as the nanoclay content increases, a proportionate lowering in the initiation of curing temperature

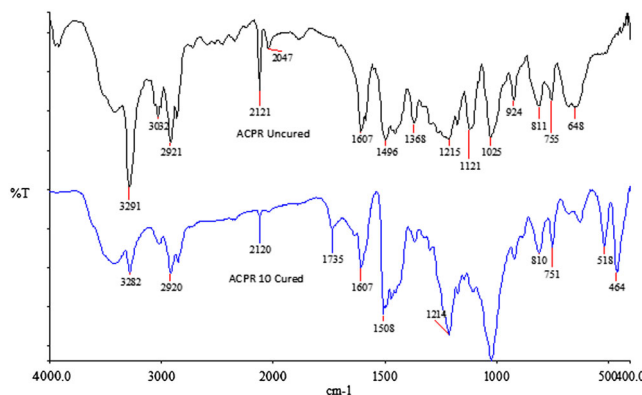
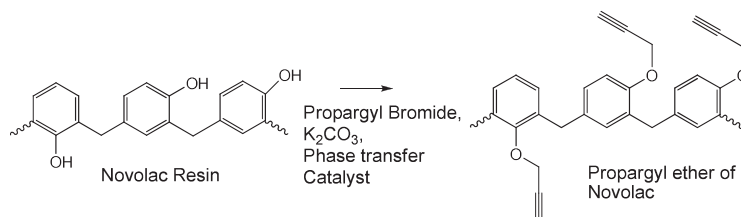


Figure 1. FTIR spectrum of uncured ACPR (neat); cured ACPR-10. This figure is available in colour online at wileyonlinelibrary.com/journal/pat



Scheme 1. Synthesis of propargyl ether of novolac.

occurs, which is a clear indication of nanoclay facilitating the Claisen rearrangement prior to cross-linking as shown in Scheme 2.

During heating around 150°C, the organo modifier in the nanoclay decomposes leading to the formation of strongly protonic catalytic sites (Lewis acids) on the clay surface. Catalysis of Claisen rearrangements, accomplished by a large number of organic and inorganic Lewis acids has been previously reported.^[29,30] The possible mechanism of catalysis by nanoclay invokes the active catalytic sites in the ene carbon as shown in scheme 3. Nanoclay contains aluminium (Al₃[⊕]) which act as strong cationic sites that can facilitate the Claisen rearrangement by way of coordinating with the π electron of C≡C which increases its electrophilicity.

It was observed that catalysis by nanoclay did not significantly affect the peak and final cure temperatures of the system as evident from Table 1.

The cure acceleration was confirmed in the rheological analysis of the resin also as shown in Fig. 3. The isothermal (220°C) rheogram implied an early gelation and cure stagnation for nanoclay containing system.

The modulus of the cured network increased with 3% nanoclay but at 10% nanoclay, it resulted in a lowering in the modulus. High nanoclay loading adversely affects the network integrity. This is due to the dispersion effect of the clay. The accelerated curing can be attributed to the clay mediated Claisen rearrangement of propargyl groups that precedes the crosslinking.

Mechanical properties

Dependence of mechanical properties of the composites on nanoclay content is shown in Fig. 4. Mechanical properties

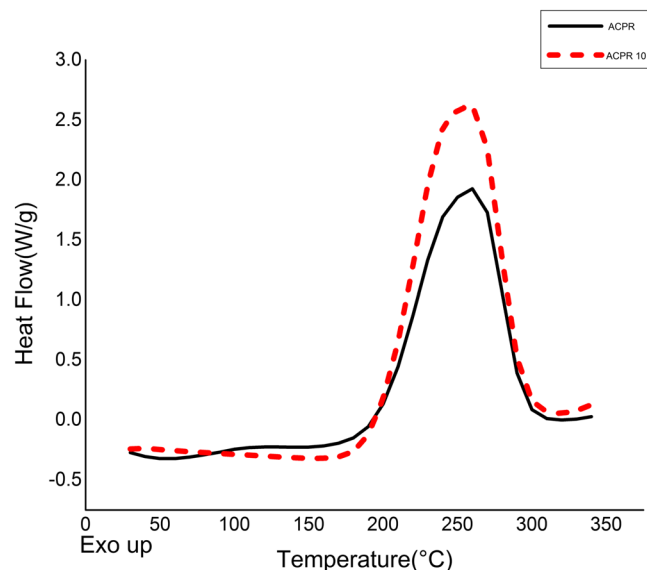
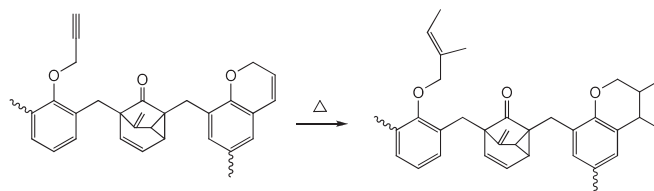


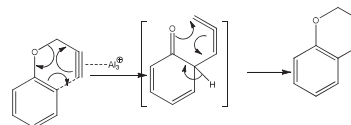
Figure 2. Cure characteristics of the virgin and nanoclay modified ACPR 10. This figure is available in colour online at wileyonlinelibrary.com/journal/pat



Scheme 2. Possible cure mechanism of addition cure phenolic resin via Claisen rearrangement.

improve on nanoclay addition in low proportions (typically 3%). Thus, optimum flexural strength and resilience were observed for 3 wt% nanoclay loaded systems. Further loading of nanoclay causes a decline in the strength of the composites, probably due to agglomeration of nanoclay in the matrix that act as failure points.

Incorporation of 3% nanoclay decreased the coefficient of thermal expansion of the composites by 50% compared to neat (ACPR- $12 \times 10^{-6}/^{\circ}\text{C}$ and ACPR3- $6 \times 10^{-6}/^{\circ}\text{C}$) which is a desirable feature for thermo structural materials.



Scheme 3. Possible mechanism of nanoclay catalyzing Claisen rearrangement.

Table 1. Cure characteristics of the nanommodified Novolac-propargyl ether

Sample	Clay loading	T _i (°C)	T _p (°C)	T _f (°C)
ACPR	0	195	258	315
ACPR 1	1	192	257	314
ACPR 3	3	190	258	316
ACPR 5	5	188	260	315
ACPR 10	10	172	261	318

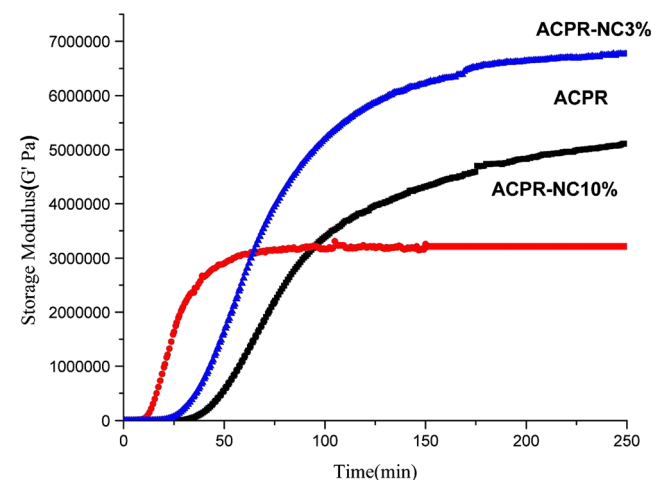


Figure 3. Isothermal rheogram of ACPR, ACPR 3 and ACPR10 at 220°C. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

Morphological evaluation of the freshly fractured surfaces reveals that the unmodified matrix (without clay) has a smooth crack surface, indicating crack propagation. In contrast, the nanocomposites exhibited a rougher fracture surface with increasing nanoclay content, as seen in Fig. 5. As evident in the micrographs, with the increase in nanoclay loading, the roughness exhibited by the nanocomposites also becomes prominent. Thus, the morphology reveals a smooth texture for ACPR and ACPR3 which got transformed to a rough one in the case with ACPR5 and ACPR10. The micro cracks have been pointed out in the image.

This morphology derives from the presence of organoclay layers that force the crack to propagate along a tortuous path, thereby dissipating energy during fracture. Fine micro-cracks indicate that the clay layers act as stress concentrators and promoted the formation of the micro-cracks during loading. An increase in clay content leads to an increase in the extent of microcracking, and thus, the fracture toughness. SEM image of ACPR10 clearly shows agglomeration of nanoclay which can be the reason for the lowering of mechanical properties at high nanoclay loading. This reduces the material resistance to fracture and forms an extension of the advancing crack.

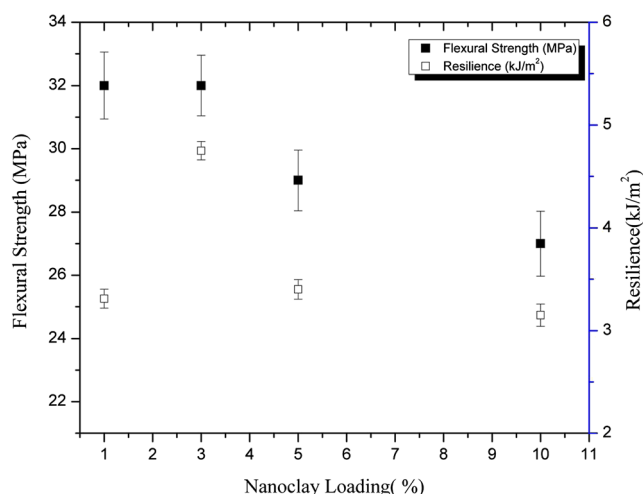


Figure 4. Dependence of flexural strength and resilience as nanoclay concentration. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

Thermo gravimetric analysis (TGA) of cured polymers

Cured ACPR and nanoclay incorporated ACPR were evaluated by TGA to investigate the influence of the nanoclay on the thermal stability and char residue. It was found that the presence of nanoclay does not bear significant influence on the thermal stability of the cured systems. Char residue was slightly enhanced (ACPR-50% and ACPR3-57%) owing to the thermally stable, inorganic residue of silicate layers that act as an effective barrier to the volatile products generated during decomposition.

Evaluation of ablative performance

Cylindrical composite specimens of length 20 mm and diameter 10 mm were encased in a guard of 35-mm diameter of the same material. The test specimens were exposed to plasma arc jet to evaluate their thermal response under a given heat flux condition. All specimens were embedded with K type thermocouples at locations TC1 (4.5 mm), TC2 (12.5 mm) and TC3 (20.0 mm). After embedding thermocouples, actual in-depth locations were identified by subjecting specimens for radiographic test.

Both neat and nanoclay-loaded composite specimens were exposed to a constant heat flux of 125 W/cm² for a period of 75 s and the temperatures near the front wall (at 4.5-mm depth) and at the backwall (20.0 mm) were recorded continuously. The initial heat transfer into the ablative occurs by pure conduction, and the resulting temperature rise causes material expansion (thermal expansion as well as vaporization of any traces of moisture). When the material reaches moderately high temperature (600–700°C), rapid thermochemical degradation of the polymer matrix occurs, resulting in the evolution of gases concomitantly, solid carbonaceous char residue is formed which is assisted by the strongly protonic catalytic sites on the organomodified clay.^[29] For the thermal protection to be effective, all these reactions must be strongly endothermic.

During plasma arc jet test, the unmodified ACPR/silica composite system showed a maximum frontwall temperature of 210°C (at 4.5 mm depth) whereas the nanoclay incorporated composite exhibited a lower temperature of 190°C at the end of 60 sec (not shown in figure). It is also observed that, the rise in backwall temperature started immediately (approximately after 18 sec) for the neat composite whereas the nanoclay incorporated system showed a delayed rise in temperature and

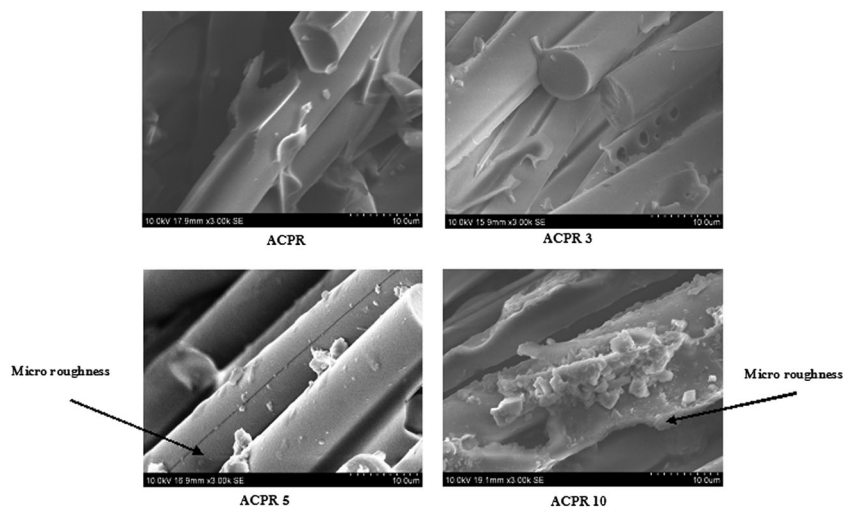


Figure 5. SEM images of fractured surfaces.

relatively lower rate of temperature rise at the back wall. Thus, with 3 and 10% loading of nanoclay, a significant reduction (around 13 and 10°C, respectively) in back wall temperature is observed compared to the unmodified system (Fig. 6).

The incorporation of organo-modified nanoclay in the polymer matrix creates a protective layer during combustion. On pyrolysis, the nanoclay layer builds up in the front and forms a protective layer and restricts the heat transfer into the material that impedes diffusion of oxygen into the material.^[28] Morphology evaluation of the pyrolysed specimens also corroborates this hypothesis.

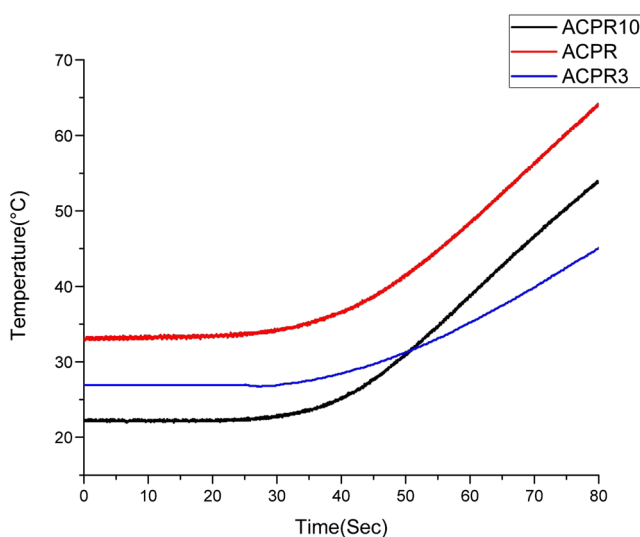


Figure 6. Backwall temperature profile during arc jet. This figure is available in colour online at wileyonlinelibrary.com/journal/pat



Figure 7. Specimens after arc jet evaluation. a) ACPR, b) ACPR 3 and c) ACPR 10. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

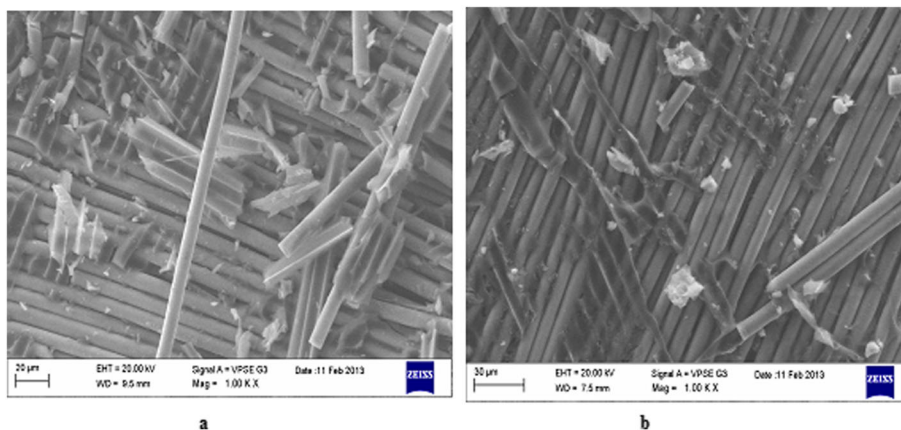


Figure 8. SEM images of fractured surfaces of charred specimens. a) ACPR and b) ACPR 3. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

Close examination of the surface of the test specimen (Fig. 7) after exposure to plasma arc jet clearly showed more cracks on the surface of the neat composite (weaker char) when compared to the nanomodified counterparts. Char depth of the systems was observed to be around 1 mm.

The char strength was evaluated by determining the compressive strength of the specimens after pyrolysis. The nano modified samples exhibited 33% enhancement in compressive strength of the char when compared to the neat (5.2 MPa, 4.8 MPa and 3.9 MPa for ACPR3, ACPR 10 and ACPR, respectively). Thus, nanomodified composites exhibited superior integrity for the char, which is advantageous for the performance of systems as an ablative thermal protection system. The volume shrinkage of the nanomodified systems, as measured from the dimensions after pyrolysis was determined to be less than 5% which is also lower when compared to the neat system (7%).

Morphology of the charred composites

The surface morphology of the charred specimens (shown in Fig. 8) indicates that the fiber breakage is less for ACPR3, enhancing the char integrity for the nanomodified system which is reflected in its compressive strength. Nanofillers prevent the propagation of crack by acting as a bridge between the fractured faces, thereby, enhancing the integrity of the char.

Flammability

Limiting oxygen index (LOI) value is often used to rate the relative flammability of composite materials. The flammability characteristics of the nanoclay modified addition cure phenolic-silica composite systems showed an increase in LOI (Table 2) which indicate that the propensity for combustion decreased with increase in

Table 2. Mechanical properties of the char

Reference	Compressive strength (MPa) before pyrolysis	Compressive strength (MPa) after pyrolysis	LOI (%)	Volume shrinkage (%)
ACPR	30 ± 1.0	3.9 ± 0.1	64	7%
ACPR 3	48 ± 1.1	5.2 ± 0.1	69	4%
ACPR-10	42 ± 1.2	4.8 ± 0.1	69	5%

the nanoclay content. This is due to the formation of char, at the expense of combustible volatiles, which in turn increases the amount of oxygen required to sustain combustion. Accumulated clay on the surface of the material acts as a protective barrier, which limits the heat transfer into the material and diffusion of oxygen.

CONCLUSION

Nanocomposites based on nanoclay-dispersed addition cure phenolic resin reinforced with chopped silica fiber were evaluated for their thermal response under moderate re-entry heating conditions. Incorporation of nanoclay facilitated the resin curing through catalysis of the rearrangement reaction. The composites displayed optimum non flammability and mechanical properties at around 3 wt% nanoclay loading. The presence of higher nanoclay content was detrimental for the mechanical properties of the composite. Plasma arc jet test results showed that the rate of backwall heating was slower for the nanoclay-incorporated systems. Nanoclay at lower loading strengthened the composites and was conducive for building a stronger char on pyrolysis. Apparently the thermal diffusivity decreased for the composites (lowering in backwall temperature). Study reveals that nanoclay modification of the new generation phenolic matrix based composites provides some scope for designing ablative type thermal protection systems with improved performance for possible aerospace applications.

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