16 Thermal Properties and Microstructures of Polymer Nanostructured Materials

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16.1 INTRODUCTION

The utility of introducing inorganic nanomaterials as additives into polymer systems has resulted in polymer nanostructured materials exhibiting multifunctional, high-performance polymer characteristics beyond what traditional polymer composites possess. Multifunctional features attributable to polymer nanocomposites consist of improved thermal resistance and flame resistance, moisture resistance, decreased permeability, charge dissipation, and chemical resistance. Through control/alteration of the additive at the nanoscale level, one is able to maximize property enhancement.
of selected polymer systems to meet or exceed the requirements of current military, aerospace, and commercial applications. The technical approach involves the introduction of nanoparticles into selected polymer matrix systems whereby nanoparticles may be surface-treated to provide hydrophobic characteristics and enhanced inclusion into the hydrophobic polymer matrix.

The objectives of this chapter are to summarize our research activities in the areas of (1) developing processes to disperse nanoparticles uniformly in the different types of polymers, (2) using wide-angle x-ray diffraction (WAXD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) techniques to characterize polymer nanocomposite structures, (3) studying the structure-property relationship of these types of new materials, and (4) evaluating the thermal performance of these materials for different applications using established laboratory devices.

Four different processing methods were used to disperse nanoparticles in a variety of polymers in this study: (1) high shear mixing for liquid resins, (2) three-roll milling for liquid resins, (3) Brabender-type mixing for high viscosity resins, and (4) twin screw extrusion for solid polymers. The degree of nanodispersion was characterized by WAXD, TEM, and SEM analyses. These imaging techniques allowed us to screen formulations and distinguish compositions that exhibited either favorable or unfavorable nanodispersed nanoparticle/polymer blends. Furthermore these analytical techniques facilitated and provided guidelines in the scale-up of favorable compositions.

Different types of polymers including (1) thermosets, (2) thermoplastics, and (3) thermoplastic elastomers are presented as examples in this chapter. Three types of nanoparticles including: (1) montmorillonite (MMT) organoclays, (2) carbon nanofibers (CNF), and (3) polyhedral oligomeric silsesquioxanes (POSS®) were used to disperse into the preceding polymers. Selected laboratory devices such as cone calorimeter, simulated solid rocket motor (SSRM), and subscale solid rocket motor were used to evaluate the materials performance for fire and rocket propulsion applications.

16.2 SELECTION OF NANOPARTICLES

16.2.1 MONTMORILLONITE NANOCLAYS

Exfoliation of montmorillonite (MMT) clays into polymer has been shown to increase mechanical properties, barrier performance, and application processing. Achieving exfoliation of organomontmorillonite in various polymer continuous phases is a function of the surface treatment of the MMT clays and the mixing efficiency of the dispersing apparatus/equipment. Surface treatment of MMT is classically accomplished with the exchange of inorganic counterions, e.g., sodium, with quaternary ammonium ions. The choice of the quaternary ammonium ion is a function of the hydrophilic/hydrophobic nature of the continuous phase; the hydrophilic/hydrophobic nature of the interface of MMT is balanced with the hydrophobic/hydrophilic nature of the continuous phase. A MMT clay, Cloisite® 30B, from Southern Clay products, had been used in several of our application studies and will be described in detail as an example for nanoclay. It is montmorillonite clay surface modified
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[Tallow bishydroxyethyl methyl, T(EOH)2M] manufactured by Southern Clay Products (SCP). The chemical surface structure of Cloisite 30B is shown in Fig. 16.1. Cloisite 30B is an additive for plastics to improve various plastic physical properties, such as reinforcement, heat distortion temperature, and barrier properties. It has a ternary ammonium salt modifier at 90 meq/100 g clay and is off-white in color. Its typical dry-particle size and physical properties are shown in Table 16.1 and Table 16.2, respectively.

Cloisite 30B in loadings of 5, 10, and 15 wt% was dispersed in a liquid phenolic resole (SC-1008, Borden Chemicals). SC-1008 is the phenolic resin matrix used in the manufacture of MX 4926, an ablative material for solid rocket nozzles. Mixing efficiency, in the phenolic, can be achieved with standard paint mixing or IKA’s (IKA Works, Inc., Wilmington, NC) high-shear mixing equipment that is designed to provide high-shear mixing if the phenolic resin is in solution. The TEM analyses allowed us to determine the degree of dispersion/exfoliation of the nanoclay before committing to a 20-lb run at Cytec Engineered Materials (CEM) of these nanoparticle/resin mixtures to make prepregs. This proved to be a very cost-effective and efficient technique for screening different formulations. This nanoclay has also been used for cyanate ester, thermoplastic elastomer, epoxy, and nylon in our research.

16.2.2 CARBON NANOFIBERS (CNF)

CNF are a form of vapor-grown carbon fiber, which is a discontinuous graphitic filament produced in the gas phase from the pyrolysis of hydrocarbons. In regard to properties of physical size, performance improvement, and product cost, CNF

![Figure 16.1 Chemical structure of Cloisite 30B.](image-url)

| TABLE 16.1 |
| Typical Dry-Particle Sizes for Cloisite 30B (Microns, by Volume) |
| 10% Less Than | 50% Less Than | 90% Less Than |
| 2 µ | 6 µ | 13 µ |
complete a continuum bounded by carbon black, fullerenes, and single-wall to multiwall carbon nanotubes on one end and continuous carbon fiber on the other.\textsuperscript{16} CNF are able to combine many of the advantages of these other forms of carbon for reinforcement in engineered polymers. The CNF have transport and mechanical properties that approach the theoretical values of single-crystal graphite, similar to the fullerenes, but can be made in high volumes at low cost—ultimately lower than conventional carbon fibers. In equivalent production volumes, CNF is projected to have a cost comparable to E-glass on a per-pound basis, yet possess properties that far exceed those of glass and are equal to, or exceed those of, much more costly commercial carbon fiber. Maruyama and Alam published an excellent review of carbon nanotubes and nanofibers in composite materials.\textsuperscript{17}

The CNF are manufactured by Applied Sciences, Inc./Pyrograf\textsuperscript{®} Products by pyrolytic decomposition of methane in the presence of iron-based catalyst particles at temperatures above 900\textdegree C. Pyrograf-III is a patented, very fine, highly graphitic CNF. Pyrograf-III is available in diameters ranging from 50 to 200 nm and a length of 50 to 100 µm. Therefore CNF are much smaller than conventional continuous or milled carbon fibers (5 to 10 µm) but significantly larger than carbon nanotubes (1 to 10 nm). Compared to PAN and pitch-based carbon fiber, the morphology of CNF is unique in that there are far fewer impurities in the filament, providing for graphitic and turbostatic graphite structures, and the graphene planes are more preferentially oriented around the axis of the fiber. Consequences of the circumferential orientation of high-purity graphene planes are a lack of cross-linking between the graphene layers, and a relative lack of active sites on the fiber surface, making it more resistant to oxidation, and less reactive for bonding to matrix materials. Also in contrast to carbon fiber derived from PAN or pitch precursors, CNF are produced only in a discontinuous form, where the length of the fiber can be varied from about 100 µm to several cm, and the diameter is of the order of 100 nm. The two commonly used CNF in our application studies are PR-19-PS and PR-24-PS.\textsuperscript{3–12}

The CNF exhibit exceptional mechanical and transport properties, allowing them excellent potential as a component for engineering materials. Table 16.3 lists the properties of vapor-grown carbon fibers, both as-grown and after a graphitizing heat treatment to 3000\textdegree C. Note that due to the difficulty of direct measurements on the nanofibers, the values in Table 16.3 are measured on vapor-grown fibers that have been thickened to several microns in diameter.\textsuperscript{16} Such fibers consist almost

---

**TABLE 16.2**

<table>
<thead>
<tr>
<th>Property</th>
<th>Cloisite 30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loose bulk density (lb/ft\textsuperscript{3})</td>
<td>14.25</td>
</tr>
<tr>
<td>Packed bulk density (lb/ft\textsuperscript{3})</td>
<td>22.71</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.98</td>
</tr>
<tr>
<td>(d_{001}) (Å)</td>
<td>18.5</td>
</tr>
</tbody>
</table>
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exclusively of chemical vapor deposition (CVD) carbon, which is less graphitic and more defective than the catalytically grown carbon core that constitutes the CNF. Thus the properties listed in the table represent an estimate for the properties of CNF.

One of the goals for CNF broad utility is to provide mechanical reinforcement comparable to that achieved with continuous tow carbon fiber at a price that approaches that of glass fiber reinforcement and with low-cost composite fabrication methods such as injection molding. Theoretical models suggest that reinforcement by discontinuous fibers, such as the CNF, can closely approach that of continuous fibers as long as the aspect ratio of the fibers is high and the alignment is good. Work is ongoing to improve the mechanical benefits of CNF through fiber surface modification to provide physical or chemical bonding to the matrix. Such modifications have resulted in strength and modulus improvements of four to six times the values of the neat resin; however, these values are still a modest fraction of what may be anticipated from idealized fiber/matrix interphase and alignment of the fibers within the matrix. The more immediate opportunities for use in structural composites lie in the prospect for modifying the properties of the matrix material. For example, use of small volume loadings of CNF in epoxy may allow for improvement of interlaminar shear strength of PAN or pitch-based composites. The CNF additives to fiberglass composites could provide benefits to a suite of properties, including thermal and electrical conductivity, coefficient of thermal expansion, and mechanical properties, as suggested by the data in Table 16.4.

### TABLE 16.3
Properties of CNF

<table>
<thead>
<tr>
<th>Property (Units)</th>
<th>As Grown</th>
<th>Heat Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (GPa)</td>
<td>2.7</td>
<td>7.0</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>400</td>
<td>600</td>
</tr>
<tr>
<td>Ultimate strain (%)</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Electrical resistivity (µΩ-cm)</td>
<td>1000</td>
<td>55</td>
</tr>
<tr>
<td>Thermal conductivity (W/m-K)</td>
<td>20</td>
<td>1950</td>
</tr>
</tbody>
</table>

### TABLE 16.4
Thermoset Polyester/Pyrograf-III Composite Properties

<table>
<thead>
<tr>
<th>Fiber Content (Wt%)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Electrical Resistivity (ohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17% PR-19</td>
<td>51.5</td>
<td>4.55</td>
<td>3.2</td>
</tr>
<tr>
<td>17% PR-19, OX</td>
<td>47.4</td>
<td>4.55</td>
<td>7.1</td>
</tr>
<tr>
<td>5% PR-19 in 10% ½&quot; glass</td>
<td>44.1</td>
<td>11.52</td>
<td>5.0</td>
</tr>
<tr>
<td>5% PR-19, OX in 10% ½&quot; glass</td>
<td>33.8</td>
<td>8.92</td>
<td>7.0</td>
</tr>
</tbody>
</table>
Figure 16.2 shows the SEM micrograph of a CNF bundle. Figure 16.3 shows the TEM micrograph of an individual CNF with the hollow core in two distinct regions, catalytic and deposited.

Recently Glasgow et al. demonstrated that the achievement of significant mechanical reinforcement in CNF composites requires high fiber loadings and is somewhat dependent on generating an appropriate interphase between the CNF and the matrix. Novel surface treatments under development have yielded good improvements in the tensile modulus and strength of CNF-reinforced polypropylene. Adding surface functional groups, particularly oxygen groups, also demonstrated benefits for interphase development. Carboxyl and phenolic groups contributing to a total surface oxygen concentration in the range from 5 to 20 atom percent have been added to CNF used to fabricate epoxy polymer matrix composites, providing
improved flexural strength and modulus. The effect of similarly functionalized CNF in bismaleimide (BMI) polymer matrix composites also shows promise. Data for polypropylene, epoxy, and BMI/CNF-reinforced composites indicate that higher fiber volume loadings will find a role in structural composite markets as price and availability improve.

16.2.3 Polyhedral Oligomeric Silsesquioxane (POSS)

Representing a merger between chemical and filler technologies, POSS nanostructured materials can be used as multifunctional polymer additives, acting simultaneously as molecular level reinforcements, processing aids, and flame retardants. POSS nanostructured materials have two unique structural features: (1) The chemical composition is a hybrid, intermediate (RSiO\(_{1.5}\)) between that of silica (SiO\(_2\)) and silicones (R\(_2\)SiO); (2) the POSS molecules are nanoscopic in size, ranging from approximately 1 to 3 nm. POSS have the multifunctional properties and an inorganic framework of silicon oxide. It has been proven that this is ceramic-like in nature, especially in severe environments. The other key factor for POSS property enhancement is the length scale effect.

Lee\(^{19}\) followed the approach in using POSS as an additive alloyed into epoxy systems and as a copolymer compatibilizer. A POSS-alloyed epoxy sample preparation procedure was developed. The epoxy was preheated for an hour, and then POSS in different weight percentages was added. The two epoxies used were the DER 332 system, which is the difunctional epoxy of the DGEBA variety and the tetrafunctional epoxy of 4,4'-methylene bisaniline. The trisilanolphenyl-POSS was selected for his work. A very low amount of loading (0.20 wt% to 1.00 wt%) of the POSS compound was used. At 0.20 wt% of POSS, he reported a significant increase in \(T_g\) from 84.2 to 92.1 as shown in Table 16.5. For the tetrafunctional epoxy also mixed with Jeffamine, the same increase in the glass transition temperature was observed.\(^{19}\) When a Dytek A curing agent was used on the DER-332 and 4,4

<table>
<thead>
<tr>
<th>POSS (wt %)</th>
<th>(T_g) DMTA ((\Delta T))(^*)</th>
<th>(T_g) DSC ((\Delta T))(^**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>84.2 (12)</td>
<td>86.6 (6)</td>
</tr>
<tr>
<td>0.20%</td>
<td>92.1 (10)</td>
<td>90.1 (5)</td>
</tr>
<tr>
<td>0.40%</td>
<td>91.2 (9)</td>
<td>91.4 (5)</td>
</tr>
<tr>
<td>0.60%</td>
<td>90.6 (9)</td>
<td>94.4 (6)</td>
</tr>
<tr>
<td>0.80%</td>
<td>91.6 (10)</td>
<td>91.1 (5)</td>
</tr>
<tr>
<td>1.00%</td>
<td>91.7 (12)</td>
<td>91.7 (7)</td>
</tr>
</tbody>
</table>

\(^*\) \(T_g\) is determined by using tan \(\delta\) curve; \(\Delta T\) is the full width at half the tan \(\delta\) peak.

\(^**\) \(\Delta T\) is endset temperature—onset temperature.
methylenebis (N-N-diglycidylaniline) epoxy system, he did not observe any change in DSC. The particular diamine used to cure the system is critical.

Hybrid Plastics’ SO1458 trisilanolphenyl-POSS (C_{42}H_{38}O_{12}Si_7) has been used in several of our studies. It is the material of choice for use in phenolic, cyanate ester, and thermoplastic elastomer. This was also used by Lee. Figure 16.4 shows the chemical structure of the trisilanolphenyl-POSS. POSS is currently very expensive at the research and development material level since it is a new nanoparticle with low-production volume.

16.3 DISCUSSION OF RESULTS

The challenges to form polymer nanocomposites are (1) choice of nanoparticles involving an interfacial interaction or compatibility with the polymer matrix, (2) proper processing techniques to uniformly disperse and distribute the nanoparticles or nanoparticle aggregates within the polymer matrix, and (3) selective analytical tools to characterize the morphology of the nanocomposites. We selected four application areas as examples for this chapter: (1) fire retardant nanocomposite coatings, (2) nanostructured materials for rocket propulsion systems with improved thermal insulation, (3) nanocomposite rocket ablative materials, and (4) nanomodified carbon/carbon composites. These examples are used to illustrate the processing techniques to form the resulting nanocomposite system, the analytical/imaging techniques used to characterize the nanocomposites, and the thermal property and performance characteristics of these nanocomposites for their specific applications.

16.3.1 TEM ANALYSES OF NANOPARTICLES

Three types of nanoparticles were dissolved in 0.5% isopropanol (IPA) solvent overnight to create specimens for TEM analyses. The TEM image in Fig. 16.5 shows that the Cloisite 30B nanocalay layers are in an intercalated state and the scale bar is 500 nm. Figure 16.6 shows the PR-24-PS CNF are entangled and the scale bar is 500 nm. Figure 16.7 shows the TEM images of trisilanolphenyl-POSS-SO1458 (C_{42}H_{38}O_{12}Si_7) showing micron and nanometer particles in the system and the scale bar is 1 µm. Neat nanoparticles dissolved in isopropanol solvent exhibit particle intercalation, entanglement, or a wide assortment of micron and nanometer particles.
FIGURE 16.5 TEM micrograph of Cloisite 30B nanoclays dissolved in IPA solvent with a scale bar of 500 nm.

FIGURE 16.6 TEM image of PR-24-PS CNF dissolved in the IPA solvent with a scale bar of 1 µm.

FIGURE 16.7 TEM images of 30B trisilanophenyl-POSS-SO1458 (C₄₈H₃₈O₁₂Si₇) dissolved in the IPA solvent with a scale bar of 1 µm.
16.3.2 Fire-Retardant Nanocomposite Coatings

Vinyl acetate-acrylic copolymer (PVA 5174), ammonium polyphosphate (APP), melamine and dipentaerythritol supplied by StanChem (Hartford, CT), and nanoclay (Cloisite Na+) supplied by Southern Clay Products were used as received. The nanoclay was dispersed in deionized water with Dispermat (high-shear mixer) at high speed for about an hour. The slurry was allowed to stay at room temperature overnight. The slurry was then mixed with PVA 5174 and/or intumescent components (APP, dipentaerythritol, and melamine) for about 2 hours for subsequent coating. Douglas fir plywood sized 10- by 10- by 1.8-cm was used as the substrate for all test specimens. A 5-ml plastic syringe was used to measure and place the amount of coating on the sample. It was evenly spread (visual monitoring only) with a brush that was presaturated with the coating. The coating thickness was monitored with a digital caliper for a dry thickness of 0.28 to 0.30 mm (0.011 to 0.012 inch). The edges were then fully coated and the coating was allowed to dry at room temperature for about 24 hours before testing. Samples were exposed to a mass loss calorimeter under a heat flux of 50 kW/m² for 15 minutes. The calorimetry data reported here are the average data of three replicates.\(^{20}\)

Figure 16.8 shows the heat release rates of PVA-clay fire-retardant (FR) coating systems with different clay loading at a heat flux of 50 kW/m². It is very clear that nanoclay plays a key role in reducing the flammability of these coating systems. With only 10% clay, the peak high release rate (PHRR) has been dramatically reduced by almost 50%. With more clay applied, the PHRR continues to drop.

![Figure 16.8 Comparison of HRR for PVA-clay FR coatings at 50 kW/m².](image_url)
Actually with 50% and 60% clay loading, the testing specimen could not be ignited throughout the 15-minute test. Figure 16.9 shows the mass loss of the PVA-clay FR coating systems. It can be seen that with the addition of clay, the residual mass has been raised from 32% to about 70%.

A discernable effect of the MMT clay on the HRR data is supported by examining Fig. 16.10. Without any MMT clay, the wood was severely burnt. As a result, a higher HRR was observed throughout the test. However, with the MMT clay loading up to 30%, it is clear that a uniform ceramic layer has been formed on the top of the wood block, which protects the wood from heat throughout the test. Therefore a lower HRR has been obtained.

FIGURE 16.9 Comparison of residual mass for PVA-clay FR coatings at 50 kW/m².

FIGURE 16.10 Digital photos of combustion residues of wood blocks coated with PVA 5174 (left), PVA – 3% MMT clay (center), and PVA – 30% MMT clay (right).
Nanoengineering of Structural, Functional, and Smart Materials

It has been shown that incorporation of MMT clay in the PVA coating systems has significantly improved its fire retardant properties at clay loading of 30% or higher. A thin section of the post-test specimen of PVA-clay nanocomposite FR coating system with 30% clay loading was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM micrographs in Fig. 16.11 show a post-test specimen of PVA-30% clay loading at low and high magnifications. It is evident that the MMT clay formed protective layers underneath the charred top surface of the coating. The TEM micrographs of PVA-30% clay post-test residue are shown in Fig. 16.12. Distinct nanoclay layers in the post-test ash residue of PVA-30% clay loading specimen were observed.

16.3.3 Nanostructured Materials for Propulsion Systems

Polymer chopped fiber-filled systems are used as insulative materials in rocket propulsion systems. This research program is aimed to develop new classes of nanostructured materials that are lighter and have better erosion and insulation characteristics than current insulative materials (Kevlar®-filled EPDM rubber). The TPSiV™ X1180 thermoplastic elastomer (TPE) is a polyamide-based vulcanized silicone thermoplastic resin manufactured by Dow Corning and was selected as a potential replacement material. Its typical uses include profiles for automotive fuel and vapor line covers, brake hose covers, and industrial application involving extruded profiles exposed to harsh environments. Table 16.6 shows the chemical compositions of three thermoplastic elastomer/nanoparticle blends that were produced by twin screw extrusion.
TEM analyses were conducted on the aforementioned three blends. Figure 16.13 shows the TEM images of the Dow Corning polyamide silicone TPSiV™ X1180 in two separate phases; the dark color is the silicone phase and the light color is the polyamide phase. Figure 16.14 shows the TEM images of the 7.5 wt% Cloisite 30B/92.5 wt% TPSiV™ X1180 blend. We speculate that the Cloisite 30B nanoclays are dispersed only in the polyamide phase, since the silicone phase is already cross-linked. TEM images of the 15 wt% PR-24-PS CNF/85 wt% TPSiV™ X1180 blend (Fig. 16.15) and 10% Ph$_{12}$T$_{12}$-POSS/90 wt% TPSiV™ X1180 blend (Fig. 16.16)

**TABLE 16.6**
Thermoplastic Elastomer/Nanoparticle Blends

<table>
<thead>
<tr>
<th>Material</th>
<th>TPE (wt%)</th>
<th>Nanoparticle (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TPSiV™ X1180 (90%)</td>
<td>Ph$<em>{12}$T$</em>{12}$-POSS (10%)</td>
</tr>
<tr>
<td>2</td>
<td>TPSiV™ X1180 (92.5%)</td>
<td>Cloisite 30B (7.5%)</td>
</tr>
<tr>
<td>3</td>
<td>TPSiV™ X1180 (85%)</td>
<td>PR-24-PS CNF (15%)</td>
</tr>
</tbody>
</table>
showed similar results. It was determined that the TPSiV™ X1180 TPE is difficult to process with any of the three selected nanoparticles. None was compatible with the resin system.

The preceding three blends with the baseline Kevlar-filled EPDM rubber was tested for ablation resistance using a subscale solid rocket motor. Figure 16.17 shows the ablation rate of the materials at low, medium, and high Mach no. regions inside the rocket motor. All three TPEs were out-performed by the baseline material. These observations clearly demonstrate that if the nanoparticles are poorly dispersed in the polymer matrix, no thermal performance improvement can be expected.

FIGURE 16.13 TEM micrographs of polyamide silicone TPSiV™ X1180 (scale bar 500 nm).

FIGURE 16.14 TEM micrographs of 92.5% polyamide silicone TPSiV™ X1180 with 7.5% Cloisite 30B (scale bar 500 nm).
16.3.4 Nanocomposite Rocket Ablative Materials

This program is aimed at developing nanocomposite rocket ablative materials for solid rocket nozzles. The candidate materials are evaluated for dispersion uniformity using WAXD and TEM prior to full ablation testing. Borden SC-1008 resole phenolic in isopropanol (IPA) is the baseline resin system. Our first attempts were to modify this resin by the incorporation of MMT organoclays. The surface treatment on these clays (usually with quaternary ammonium ions) is critical for blend compatibilization and ease of dispersion of the surface-treated clay into the hydrophobic phenolic resin matrix. This treatment is a quaternary ammonium ion (quat). These blends were dispersed using high-shear, nonsparking paint mixing equipment. Neat resin castings (without fiber reinforcement) were made for WAXD and TEM analyses.

**FIGURE 16.15** TEM micrographs of 85% polyamide silicone TPSiV™ X1180 with 15% PR-24-PS CNF (scale bar 1 µm).

**FIGURE 16.16** TEM micrographs of 90% polyamide silicon TPSiV™ X1180 with 10% Ph12 T12-POSS (scale bars are 1 µm and 500 nm).
MX-4926 is a rayon carbon fabric impregnated with SC-1008 containing carbon black (CB) particles. Based on TEM analyses, we concluded that CB particles in the baseline MX-4926 caused interference of the dispersions of all nanoparticles in the SC-1008. As a result, we eliminated CB in our subsequent blending experiments. Cloisite 30B in loadings of 5, 10, and 15 wt% were dispersed in the SC-1008. Figure 16.18

FIGURE 16.17 Ablation rate of polyamide silicone TPSiV™ X1180 with Cloisite 30B, Ph12T12-POSS, and PR-24-PS CNF as compared to EPDM/Kevlar in low, medium, and high Mach no. regions inside the rocket motor.

FIGURE 16.18 WAXD of 5, 10, 15 wt% Cloisite 30B in 95, 90, and 85 wt% SC-1008 phenolic resin, respectively.
shows the WAXD of the three nanoclay loadings in SC-1008 and indicated good dispersibility of the nanoclay into SC-1008. Figure 16.19, Fig. 16.20, and Fig. 16.21 show the TEM images of the 5 wt% Cloisite 30B: 95 wt% SC-1008 (Fig. 16.19), 10 wt% Cloisite 30B: 90 wt% SC-1008 (Fig. 16.20), and 15 wt% Cloisite 30B: 85 wt% SC-1008 (Fig. 16.21). The TEM images indicate intercalation and not

FIGURE 16.19 TEM images of 5 wt% Cloisite 30B in 95 wt% SC-1008 (scale bar 1 µm).

FIGURE 16.20 TEM images of 10 wt% Cloisite 30B in 90 wt% SC-1008 (scale bar 1 µm).

FIGURE 16.21 TEM images of 15 wt% Cloisite 30B in 85 wt% SC-1008 (scale bar 500 nm).
exfoliation of the nanoclay in the resin system. The TEM analyses assisted in
determining the degree of dispersion/exfoliation of the nanoclay before committing
to a 20-lb run at Cytec Engineered Materials of these nanoparticle/resin mixtures
to fabricate prepregs. This procedure is a very cost-effective and efficient technique
for screening different formulations.

We selected SC-1008 with 5, 10, and 15 wt% Cloisite 30B to replace 15 wt%
of carbon black in the original MX-4926 formulation. CEM prepared three versions
of MX-4926 alternates, designated by MX-4926 ALT 5%, MX-4926 ALT 10%, and
MX-4926 ALT 15%. Three loadings of PR-24-PS in 20, 24, and 28 wt% were
dispersed in SC-1008 without the rayon carbon fiber reinforcement. Three loadings
of trisilanolphenyl-POSS in 2, 6, and 10 wt% were also dispersed in SC-1008. The
POSS/SC-1008 mixture was used with the rayon carbon fabric to produce prepregs.
Table 16.7 shows the chemical compositions for the laminates used for ablaton
testing. Figure 16.22 compares the densities of three types of Nanocomposite Rocket
Ablative Materials (NRAMs) with nanoclay, CNF, and POSS at various loading
levels of nanoparticles. All CNF-NRAMs and POSS-NRAMs have densities lower
than MX-4926.

A small-scale supersonic liquid-fueled rocket motor (SSRM) burning kerosene
and oxygen was used to study the ablation and insulation characteristics of the ablative.
It has been demonstrated as a cost-effective laboratory device to evaluate different

<table>
<thead>
<tr>
<th>Material ID</th>
<th>Density (g/cc)</th>
<th>Rayon Carbon Fiber Reinforcement (wt%)</th>
<th>Resin SC-1008 Phenolic (wt%)</th>
<th>Filler (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MX-4926 (Control)</td>
<td>1.44</td>
<td>50</td>
<td>35</td>
<td>15 carbon black (CB)</td>
</tr>
<tr>
<td>MX-4926 ALT Clay 5%</td>
<td>1.42</td>
<td>50</td>
<td>47.5</td>
<td>2.5 Cloisite 30B</td>
</tr>
<tr>
<td>MX-4926 ALT Clay 10%</td>
<td>1.43</td>
<td>50</td>
<td>45</td>
<td>5 Cloisite 30B</td>
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<tr>
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<td>1.43</td>
<td>50</td>
<td>42.5</td>
<td>7.5 Cloisite 30B</td>
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<tr>
<td>PR-24-PS 20%/SC-1008</td>
<td>1.35</td>
<td>None</td>
<td>80</td>
<td>20 PR-24-PS CNF</td>
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<tr>
<td>PR-24-PS 24%/SC-1008</td>
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<td>76</td>
<td>24 PR-24-PS CNF</td>
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<td>PR-24-PS 28%/SC-1008</td>
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<td>None</td>
<td>72</td>
<td>28 PR-24-PS CNF</td>
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<tr>
<td>MX4926 ALT SO-1458 2%</td>
<td>1.41</td>
<td>50</td>
<td>49</td>
<td>1 Trisilanolphenyl-POSS</td>
</tr>
<tr>
<td>MX4926 ALT SO-1458 6%</td>
<td>1.38</td>
<td>50</td>
<td>47</td>
<td>3 Trisilanolphenyl-POSS</td>
</tr>
<tr>
<td>MX4926 ALT SO-1458 10%</td>
<td>1.40</td>
<td>50</td>
<td>45</td>
<td>5 Trisilanolphenyl-POSS</td>
</tr>
</tbody>
</table>
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Ablatives under identical conditions for initial material screening and development.\textsuperscript{3-6} Figure 16.23 shows the peak erosion of MX-4926 and MX-4926 ALTs at the three heat fluxes with Al\textsubscript{2}O\textsubscript{3} particles. As expected, peak erosion decreases as heat flux decreases. At high heat flux (1000 Btu/ft\textsuperscript{2}-sec) the MX-4926 and MX-4926 ALTs show more difference in peak erosion performance, while the medium- and low-heat flux conditions show little difference in peak erosion. MX-4926 ALT 5 and 10% Cloisite

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1622.png}
\caption{Density of MX-4926 and NRAMs with different nanoparticle loadings.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1623.png}
\caption{Peak erosion for the nanoclay NRAM composites}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1624.png}
\caption{Peak erosion for the nanoclay NRAMs at 250, 625, and 1000 Btu/ft\textsuperscript{2}-s with particles.}
\end{figure}
30B samples are not as erosion resistant as the control MX-4926. The MX-4926 ALT 15% shows better erosion characteristics than MX-4926 by 14%. Figure 16.24 shows all nanoclay NRAM composites have a lower maximum backside heat-soaked temperature rise than MX-4926 by 28%. Surface temperature of MX-4926 ALTs are lower than MX-4926.

Figure 16.25 shows both PR-19-PS and PR-24-PS CNF NRAMs (without rayon carbon fabric) have significantly less ablation resistance than MX-4926 at
1000 Btu/ft\(^2\)-s by about 42% lower. Figure 16.26 shows both PR-19-PS and PR-24-PS CNFs also have substantial lower maximum backside heat-soaked temperature rise than MX-4926 by about 68% at all three levels of heat fluxes. Surface temperatures of the CNF samples were hotter than the MX-4926 and MX-4926 ALTs. This suggests we may have better radial heat transfer than axial heat transfer supported by the glowing heat of the surface observed during materials testing.

Figure 16.27 shows the ablation rates of MX-4926 and all three groups of NRAMs: clay-NRAM [(HE)\(_2\)MT nanoclay], CNF-NRAM (PR-24), and POSS-NRAM (SO-1458).
The ablation rate of MX-4926 is about 0.4 mm/s. For the clay-NRAM group, only the 7.5 wt% clay-NRAM has a lower ablation rate than MX-4926. For the CNF-NRAM group, all three loadings have lower ablation rate than MX-4926 with 28% CNF-NRAM being the lowest. For the POSS-NRAM group, all three loadings have lower ablation rate than MX-4926 with 5% POSS-NRAM being the lowest. The loadings of POSS are 1, 3, and 5 wt%, the lowest of the three NRAM groups. The loadings of clay are 2.5, 5, and 7.5 wt%, the medium of the three NRAM groups. The loadings of CNF are 20, 24, and 28 wt% without the rayon carbon reinforcements, the highest of the three NRAM groups. Figure 16.28 shows the residual masses of MX-4926 and all the NRAMs. The residual mass of MX-4926 is about 92%. The POSS-NRAM group has the most residual mass, about 93% for all three loadings. The clay-NRAM group has about the same residual mass as the MX-4926. The CNF-NRAM group has about 86 to 88 wt% residual mass, the lowest of all.

Figure 16.29 shows the maximum backside heat-soaked temperature rise of MX-4926 and the NRAMs. All NRAMs have lower maximum backside heat-soaked temperature rise than MX-4926. The backside heat-soaked temperature rise of MX-4926 is about 106°C. It is obvious that the CNF-NRAM group has substantial lower maximum backside heat-soaked temperature rise than MX-4926, from 54° to 72°C. The POSS-NRAM group has the second lowest than MX-4926, from 75° to 86°C. The clay-NRAM group has the third lowest than MX-4926, from 82° to 98°C.

An IR pyrometer was used to measure the surface temperatures of all materials during SSRM firings. Figure 16.30 shows the surface temperatures of MX-4926 and the NRAMs. Surface temperatures of MX-4926 are about 1700°C. Surface temperatures of the CNF-NRAM samples were hotter than the MX-4926, clay-NRAMs, and POSS-NRAMs. This suggests we may have better axial heat transfer than radial heat transfer, supported by the glowing heat of the surface observed during material testing.
This phenomenon was observed by other researchers\textsuperscript{21} and needs further study. The surface temperatures of clay-NRAMs and POSS-NRAMs are lower than MX-4926. There is essentially no effect of the amount of nanoclay in the clay-NRAMs. The amount of POSS in the POSS-NRAMs has a significant effect on the surface temperature of the POSS-NRAMs.

16.3.5 \textbf{NANOMODIFIED CARBON/CARBON COMPOSITES}

The objective of this materials program is to develop an improved carbon/carbon (C/C) composite with enhanced thermo-oxidative resistance at intermediate temperatures (700\textdegree{} to 1200\textdegree{}F).\textsuperscript{3-9} We proposed that a nanophase be introduced into the C/C

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure16.29}
\caption{Backside temperature rise of MX-4926 and NRAMs with different types of nanoparticle at various loading levels.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure16.30}
\caption{Surface temperature of MX-4926 and NRAMs with different types of nanoparticle at various loading levels.}
\end{figure}
composites (CCC), prior to cure, to provide improved and maintained mechanical strength by preventing oxidation of the composites. The candidate materials are evaluated for dispersion using WAXD and TEM prior to full scale-up. Baseline phenolic resin 134A, and cyanate ester resins PT-15 and PT-30 were used as matrix resins. Lab scale dispersion of (1) PT-30 cyanate ester (CE) resin with different wt% POSS, nanoclays, and CNF, (2) PT-15 CE resin with different wt% of POSS and nanoclays, and (3) 134A phenolic resole resin with different wt% POSS and nanoclays were conducted. The morphology of selective resin/nanoparticle systems were characterized using TEM and SEM analyses. Detailed processing and characterization of PT-30/nanoparticle, PT-15/nanoparticle, 134A/nanoparticle systems are reported elsewhere.9 A brief discussion of PT-30/nanoparticle and PT-15/nanoparticle is included in this section.

Cloisite 30B was first dispersed in THF before blending with the PT-30 resin. Cloisite 30B is uniformly dispersed in PT-30/30B THF system. In higher magnification, Cloisite 30B is in an intercalated state in the PT-30 cyanate ester resin where scale bars are 500 nm (left), 200 nm (center), and 100 nm (right).

Different weight percent (wt%) of the seven POSS chemicals were blended with PT-30 for a total of 15 blends using a lab scale high shear mixer. Appearance in terms of transparency, translucency, or opaqueness was examined during mixing, before and after curing, and was recorded for all blends and densities. Based on visual observations trisilanolphenyl-POSS is the only potential POSS compound that works well with PT-30 using direct melt blending process. All other blends were either opaque or transluscent and large, poorly dispersed particles were observed. Phase separation had clearly taken place.

Selective candidates were cured for TEM analyses. PT-15 and PT-30 were cured thermally. The SO1458 POSS particles, when directly blended into PT-30 resin, show very few undissolved POSS particles in the resin matrix, as shown in Fig. 16.32. Some molecular dispersion in the PT-30/SO1458 POSS (95/5) was achieved, as shown in Fig. 16.32. Significant Si is detected in the resin matrix where no phase separation can be detected. SO1458 is the preferred POSS system for PT-30 resin.
**FIGURE 16.32** TEM micrographs of PT-30/SO1458 POSS (95/5) in high magnification showing molecular dispersion of SO1458 POSS with some POSS particles in the PT-30 cyanate ester. Significant Si is detected in the resin matrix.
PT-30/PR-19-PS and PT-30/PR-24-PS were blended in 99.5/0.5 and 99/1 wt% (Fig. 16.33), and a total of four CNF blends were prepared.

PT-15 was blended with several clays (Nanomer® I.28E, Nanomer I.30E, PWG, Cloisite 10A, and Cloisite 30B) using different mixing methods, and a total of 34 blends were recorded. Resulting samples were either opaque or translucent. PT-15/30B (97.5/2.5) THF, PT-15/10A (97.5/2.5) THF, and PT-15/I.30E (97.5/2.5) THF blends were prepared using THF as a carrier medium in these samples to facilitate clay dispersion. When Cloisite 30B, Cloisite 10A, and Nanomer I.30E were compared in higher magnification TEM micrographs, Cloisite 30B was dispersed slightly more uniformly than the other two clays. Cloisite 30B was in a partial exfoliated state in PT-15, as shown in Fig. 16.34. Small tactoids are present in this nanodispersion. Figure 16.35 shows higher magnification TEM micrographs of PT-15/Cloisite 30B.
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(97.5/2.5) THF showing that Cloisite 30B clays are exfoliated in PT-15 cyanate ester.

Cloisite 30B is our preferred clay for the PT-15 resin. PT-15 was blended with poly(phenyl silsesquioxane), PPSQ, in THF and trisilanol-phenyl POSS in different wt%, and a total of 13 blends were recorded. Only PT-15/trisilanol phenyl POSS in 99/1 and 97/3 were completely transparent. TEMs of PT-15/SO1458 (97/3) and PT-15/SO1458 (95/5) blends were prepared. Figure 16.36 shows molecular dispersion of SO1458 POSS in the PT-15/SO1458 (97/3) system. Where particles are noted, one finds their Si content is higher than in the open resin matrix. Significant Si is detected in the resin matrix in regions where no particles are observed. Clearly the POSS is partially dissolved in the matrix and partially nano-dispersed, resulting in molecular dispersion of SO1458 in PT-15. This is a good candidate system for a conversion to CCC. SO1458 POSS is the preferred POSS system for the PT-15 resin.

A summary of all the nanomodified carbon/carbon composite (NCCC) candidates and CC139 (baseline commercial carbon/carbon composite prepared with 134A phenolic resin) with their weight loss percentage, density, and ranking based on weight loss data is shown in Table 16.8. Sample designation of −1, −2, −3, and −4 are as follows: RT, 700°F, 1200°F, and retained. An air leakage was detected in our first set of experiments, and as a result the 134A/CLO/3-1A, 134A/CLO/3-2A, 134A/CLO/3-3A, 134A/POSS/3-1A, 134A/POSS/3-2A, 134A/POSS/3-3A, PT15/POSS/5/-1B, PT15/POSS/5/-2A, PT15/POSS/5/-3A, PT30/PR24PS/1-1A, and PT30/PR24PS/1-2A specimens were overexposed to unrealistic thermo-oxidative conditions. They are denoted with an asterisk (*) in Table 16.8. The 134A/CLO/3-4B and 134A/POSS/3-4D specimens were retested for the 1200°F condition using the fourth spared panels of the 134A/CLO/3 and 134A/POSS/5 candidates marked as “−4.” The PT15/POSS/5-4 spared specimen was lost, and as a result the PT15/POSS/5 candidate was unable to be retested for the 1200°F conditions of this project. Regrettably the behavior of molecularly dispersing POSS into PT-15 (Table 16.8, entries 9 to 12) could not be assessed for improved thermo-oxidative stability due to specimens overexposed or lost.
Based on the thermo-oxidative analyses, the PT30/CLO/5 candidate is the most thermo-oxidative resistant material; weight losses were 5.2%, 5.1%, and 3.7% at room temperature (RT), 700°F, and 1200°F conditions, respectively. It is ranked as the best or 1. The PT15/CLO/5 candidate is the second best thermo-oxidative resistant and weight losses were 6.5%, 5.1%, and 3.7% at RT, 700°F, and 1200°F conditions, respectively. The PT30/PR24PS/1 NCCC has a low 6.8% weight loss and is the third best thermo-oxidative resistant NCCC candidate. The standard CC139 is the fourth material with a weight loss of 8.9%, 9.0%, and 13.6% for RT, 700°F, and 1200°F, respectively. The 134A/CLO/3 and 134A/POSS/3 had high weight loss of 30.5% and 23.3%, respectively.

Weight losses of different NCCCs were compared, as shown in Fig. 16.37. It is evident that the cyanate ester resin–based PT30/PR24PS/1, PT30/CLO/5, and PT15CLO/5 specimens have better thermo-oxidative resistance than the phenolic resin–based CC139 standard CCCs. The phenolic resin–based 134A/CLO/3 and 134A/POSS/3 specimens have worse thermo-oxidative resistant characteristics than
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From our TEM analyses we concluded that the nanoparticles were dispersed very well in the PT-30 and PT-15 cyanate resin systems and poorly in the 134A phenolic resin system. Figure 16.38 shows a comparison of the density of the different NCCCs. It is also evident that PT15/CLO/5-3B,C has the highest density (1.684 g/cc), followed by PT30/CLO/5-2B,C and PT30/PR24PS/1-3B,C (1.656 g/cc), than the CC139 specimens (1.627 to 1.638 g/cc), while the densities of 134A/POSS/3-4D and 134A/CLO/3-4B were 1.603 g/cc and 1.585 g/cc, respectively. Figure 16.39 shows a comparison of densities versus weight loss of the different NCCCs.

### TABLE 16.8
Summary of Thermo-oxidative Data and Ranking

<table>
<thead>
<tr>
<th>P/N</th>
<th>Initial wt. (g)</th>
<th>TGA recorded wt. (g)</th>
<th>Weight Loss (%)</th>
<th>Sample Density (g/cc)</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>134A/CLO/3-1A'</td>
<td>2.053</td>
<td>1.728</td>
<td>−15.8</td>
<td>1.619</td>
<td></td>
</tr>
<tr>
<td>134A/CLO/3-2A'</td>
<td>2.145</td>
<td>1.772</td>
<td>−17.4</td>
<td>1.581</td>
<td></td>
</tr>
<tr>
<td>134A/CLO/3-3A'</td>
<td>2.056</td>
<td>1.152</td>
<td>−44.0</td>
<td>1.567</td>
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</tr>
<tr>
<td>134A/CLO/3-4B</td>
<td>2.036</td>
<td>1.414</td>
<td>−30.5</td>
<td>1.585</td>
<td>6</td>
</tr>
<tr>
<td>134A/POSS/3-1A'</td>
<td>1.958</td>
<td>1.441</td>
<td>−26.4</td>
<td>1.616</td>
<td></td>
</tr>
<tr>
<td>134A/POSS/3-2A'</td>
<td>1.989</td>
<td>1.216</td>
<td>−38.9</td>
<td>1.575</td>
<td></td>
</tr>
<tr>
<td>134A/POSS/3-3A'</td>
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<td>1.666</td>
<td>−13.8</td>
<td>1.611</td>
<td></td>
</tr>
<tr>
<td>134A/POSS/3-4D</td>
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<td>1.573</td>
<td>−23.2</td>
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<td>5</td>
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<tr>
<td>PT15/POSS/5-1B'</td>
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</tr>
<tr>
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<td>Lost</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>PT15/CLO/5-1</td>
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<td>−6.5</td>
<td>1.630</td>
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<td>−3.4</td>
<td>1.643</td>
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<tr>
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<td>2.24</td>
<td>−6.8</td>
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</tr>
<tr>
<td>PT15/CLO/5-3B</td>
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</tr>
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<td>PT30/PR24PS/1-1A'</td>
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<td>−5.1</td>
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<td>1</td>
</tr>
<tr>
<td>PT30/CLO/5-3B,C</td>
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<td>2.265</td>
<td>−3.7</td>
<td>1.618</td>
<td>1</td>
</tr>
<tr>
<td>CC139-1A</td>
<td>2.673</td>
<td>2.436</td>
<td>−8.9</td>
<td>1.627</td>
<td>4</td>
</tr>
<tr>
<td>CC139-2A</td>
<td>2.506</td>
<td>2.881</td>
<td>−9.0</td>
<td>1.638</td>
<td>4</td>
</tr>
<tr>
<td>CC139-3A</td>
<td>2.536</td>
<td>2.191</td>
<td>−13.6</td>
<td>1.630</td>
<td>4</td>
</tr>
</tbody>
</table>

* An air leakage was detected in these experiments. RT, 700°F, and 1,200°F specimens were designated as −1, −2, and −3, respectively.

the CC139 standard. From our TEM analyses we concluded that the nanoparticles were dispersed very well in the PT-30 and PT-15 cyanate resin systems and poorly in the 134A phenolic resin system. Figure 16.38 shows a comparison of the density of the different NCCCs. It is also evident that PT15/CLO/5-3B,C has the highest density (1.684 g/cc), followed by PT30/CLO/5-2B,C and PT30/PR24PS/1-3B,C (1.656 g/cc), than the CC139 specimens (1.627 to 1.638 g/cc), while the densities of 134A/POSS/3-4D and 134A/CLO/3-4B were 1.603 g/cc and 1.585 g/cc, respectively. Figure 16.39 shows a comparison of densities versus weight loss of the
different NCCCs. A trend of higher density NCCCs exhibiting lower weight loss while lower density NCCCs show higher weight loss is proposed. Lower weight loss for NCCC from cyanate ester resin systems is expected due to little or no volatiles from cured cyanate esters as well as proposed improved thermo-oxidative stability attributable to the presence of a nanophase in the NCCC cyanate ester materials.

FIGURE 16.37 Comparison of weight loss with different NCCCs.

FIGURE 16.38 Comparison of density with different NCCCs.
16.4 SUMMARY AND CONCLUSIONS

We have been developing polymer nanocomposites to enhance materials properties for high-temperature applications. The following conclusions are presented:

1. The feasibility of using polymer nanocomposite for high-temperature applications was clearly demonstrated.
2. MMT organoclays, CNF, and POSS can be easily incorporated into various polymers using conventional processing and manufacturing techniques to form nanocomposites.
3. The degree of dispersion of nanoparticles in the polymer matrix is essential to achieve the desired properties enhancement.
4. SEM and TEM analyses techniques have been demonstrated to be effective and efficient screening tools to determine nanodispersion in the polymer matrix.

PROBLEMS

1. What are the shortcomings of using wide-angle x-ray diffraction (WAXD) to determine the degree of dispersion in polymer-clay nanocomposites? How can one compensate for the shortcomings of this technique?
2. What is the disadvantage of using transmission electron microscopy (TEM) to determine the degree of nanoparticle dispersion in polymer nanocomposites? How can one compensate for this technique?
3. Discuss other types of techniques that one can use to study the morphology of these polymer nanocomposites.
4. What other types of nanoparticles can be used to enhance the thermal and mechanical properties of polymer nanostructured materials? Explain and give examples.

5. Discuss the similarities and differences of different types of nanoparticles and give examples.

6. Discuss other thermal applications of polymer nanostructured materials in the literature.

7. How can one enhance the interfacial interaction and compatibility with different nanoparticles in a specific polymer matrix?

Readers should read the references in this chapter and current nanocomposite literature to answer the preceding questions.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Charles Y-C Lee of AFOSR for sponsoring several of our research activities through the AFOSR STTR programs. Support from Dr. Shawn Phillips of AFRL/Edwards AFB and W. Casey West of StanChem are appreciated. The authors also would like to express their appreciation to numerous colleagues that have contributed to our nanomaterials research.

REFERENCES

2. Cloisite® 30B technical data sheet, Southern Clay Products, Gonzales, TX.