ADVANCED FIBER-REINFORCED COMPOSITES BASED ON NANOCOMPOSITE MATRICES

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INTRODUCTION

Composite materials have largely demonstrated their potential in terms of weight reduction, improved corrosion and fatigue resistance, and design flexibility. Autoclave processing of long-fiber-reinforced composites ensures the production of high quality parts that have all the above-mentioned advantages. The high cost of the equipment, raw materials, and long processing times involved have restricted the application of high performance composites to aerospace and aeronautic applications where performances and light weight are more important than the cost [1]. Recent developments in aeronautical, transportation, and commodity applications have made this class of material comparable to metals and ceramics.

The diffusion of nanocomposites is necessary to develop new correlations and new models for the processes. Owing to the recent developing of these new materials, few data and processing model are yet available. Most of these models refer to the injection molding of thermoplastic layered silicate nanocomposites; in this case, it has been shown that the available processing models can be slightly modified to take into account the changes in the rheological behavior caused by the use of layered silicates, analogous attempts were made on modeling liquid molding processes with nanocomposite resins [2]. It has been pointed out that the most critical parameters to obtain a valid model of nanocomposite processes are the rheological behavior, which is strongly influenced by the presence of the nanocharges, the diffusion of the resins in the fiber bed, and the determination of the main physical properties of the nanocomposite resin.

Regarding the materials, many chances of improvement exist. For high performance applications, for example, there is a need to have injectable and, at the same time, toughened resin. For low performance applications, there is the need of having fast, reliable, and economic materials and compounds. But, the most important development is represented by the use of nanotechnologies applied to composites. Nanotechnologies can represent a great opportunity for composites. In this field, there are still opened many possibilities. The current research is more dedicated to nanotailored fiber-reinforced composites that can offer multifunctional performances, whereas nanocomposite resins can provide new and improved properties to composite parts.

Researchers and companies usually practice this bottom-up approach in designing, processing, and manufacturing fiber-reinforced composites. When designing a composite, the material properties are tailored for the required performance at all length scales. From the choice of the adequate matrix and fiber materials and the layup of the laminate (meter scaled) up to the design and optimization of the fiber/matrix interface and interphase (microscaled), the integrated approach used in composites processing is a remarkable example in the successful use of the bottom-up approach [3]. When to these levels, a nanoscaled one is added, applying nanotechnology to composite materials, tremendous opportunities for innovative approaches in the processing, characterization, and analysis/modeling of this new generation of composites can be found. To better understand the meaning of this approach, Fig. 1 represents the shift from the higher dimension level represented by a fiber fabric to the micrometer level represented by the fiber diameter up to the nanometer level represented in this picture by the carbon nanotubes (CNTs).

Considering that nanosized particles usually tend to stay in agglomerates because of their huge surface area and, on the other hand, that the exploitation of their benefits is possible only if they are evenly dispersed into the matrix, it is clear that the most important challenge in nanocomposite development is the study of the dispersion. In fact, a really good technique for this goal needs to produce an even dispersion of the particles and to be intrinsically up-scalable to the industrial level, in order to avoid that a good laboratory result did not get employed outside of Universities and did not carry a real benefit for the entire human community.

Many techniques have been employed to improve the dispersion of nanoparticles inside the matrix. In the case of the processing of thermosetting-based nanocomposites, most of the approaches involve different steps that include mechanical stirring [4–7], high energy sonication, and solution-evaporation processing [8–12]. During last years, the possibility in employing the calendering technique for the dispersion of nanoparticles was successfully investigated [5,13–15]. Moreover, covalent and noncovalent functionalization of the nanofillers with the initiators of thermosetting curable systems has been the focus of recent investigations, which has also been exploited to prepare nanocomposites with superior conductive properties [16].

Advanced composites are increasingly used in aerospace, naval, and automotive fields. Their high mechanical performances, together with their low weight, make the employment of these materials a key factor for the development of a competitive high performance product.

For this reason, researcher all over the world are working on it. In particular, whereas companies are developing new materials for fiber production and new fabric layout,

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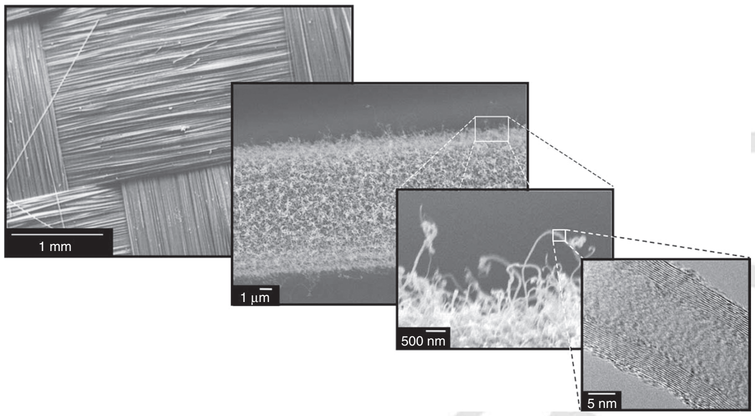

Figure 1. Example of multiscaled fiber-reinforced nanocomposite [3].

researchers in Universities are focusing their attention on the polymeric matrix of the fiber-reinforced polymers (FRPs), studying new formulations essentially based on the employment of nanocomposites, see for instance [17]. In fact, the idea is to transfer the improved mechanical characteristics and the new functional properties obtained, thank to the interaction of the nanoparticle with the polymer to a fiber-reinforced composite in which the nanocomposite is the polymeric matrix.

PROCESSES FOR PRODUCTION OF FIBER-REINFORCED NANOCOMPOSITES

The development and production of fiber-reinforced composites based on nanocomposite matrices (fiber-reinforced nanocomposites, FRN) are basically performed utilizing the same techniques commonly employed for commercial FRPs. Nonetheless, thermosetting suspensions on behalf of homogeneous liquid thermosets, which are commonly more viscous, may create pitfalls in the processing that can lead to a laminate of poor quality. A heterogeneous dispersion throughout the laminate, a reagglomeration of the nanoparticles, and a poor impregnation of the fibers are some of the most common trouble that a composite manufacturer could face.

Hand layup represents the most common technique to produce fiber-reinforced composites, and their application to nanoreinforced matrices can be hindered only by the increasing of the viscosity because of the presence of the nanofiller themselves. As an example, Norkhairunnisa *et al*. [18] produced glass fiber composites based on epoxy filled with organo-modified montmorillonite (OMMT) and did not encounter significant problems because of the presence of the nanoparticles. The same finding was recovered by Chang and Chow [19] who studied the weathering on glass fiber/epoxy/OMMT and by Chow [20].

Many studies have been conducted on FRNs produced by liquid molding techniques [21–28]. Gojny *et al*. [21] in one earlier work on this topic developed a glass fiber composite where the matrix was constituted by an epoxy with amino-functionalized double-wall carbon nanotubes (DWCNT-NH_2). In spite of the increase in viscosity that they observed, the production of a laminate via resin transfer molding (RTM) technique with an epoxy 0.3 wt% CNTs was achieved. Nonetheless, they advise that much higher filler contents lead to processing problems due to a dramatically increasing viscosity. Interestingly, they did not notice any filtering effect by the glass fibers, with a nanotube concentration even over the entire laminate.

In a following study [22], they compared different fillers, CNTs, carbon blacks (CBs), and fumed silica nanoparticles, added to the epoxy matrix for the production of a RTM-based glass fiber composite. They remarked that nanoparticles significantly influence the viscosity of the matrix, complicating the RTM processing, as well as extending both the degassing and the injection time. In the case of electrically active fillers, the mold was modified to apply an electrical field during the curing process, in order to induce a preferred orientation of the CNTs perpendicular to the fiber plane. Even in this study, they could not observe any filtering effect of the glass fiber bundles on the nanoparticles, although, especially in the case of CNTs, they found a reagglomeration behavior during the RTM injection.

Thostenson and Chou in their studies [23–25] successfully produced multiwalled carbon nanotube (MWNT)-based glass fiber-reinforced polymer (GFRP) via vacuum-assisted resin transfer molding (VARTM), adding a resin distribution layer to assist infiltration and hermetically sealing the layup in a vacuum bag. In order to compensate the increase of the viscosity because of the presence of the nanotubes, they heated the nanocomposite matrix up to 50–60°C.

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Filament winding is another technique that can be utilized in the presence of a nanocomposite matrix. Hussain *et al*. [29] developed a filament-wound glass/epoxy composite with 10% of nanosized alumina, observing that, despite the increased viscosity, the possibility in producing a workpiece of good quality was the same of the one with the neat epoxy.

Spindler-Ranta and Bakis [30] utilized an epoxy 1 wt% SWNTs system to produce a carbon fibers filament-wound composite. Although the composite was successfully produced, this study concluded that SWNT did not produce any significant effect in the composite produced. Zhou *et al*. [31] produced, by means of filament winding technique, a carbon fiber/epoxy composite, with silicon carbide nanoparticles dispersed in the liquid epoxy resin, before the wetting of the fiber strands. They found a general increase of the mechanical properties of the composite.

Many papers were published on fiber-reinforced nanocomposites produced by preparing prepregs with the nanofilled matrix and allowing them to cure in autoclave. Yokozeki *et al*. [32] studied nanocomposite laminates manufactured from prepregs that consist of traditional carbon fibers and epoxy resin filled with the CNTs. Although they did not mention experimental details on the prepregs processing, they were able to obtain a three-phase composite with increased fracture toughness and decreased residual thermal strain. Chen *et al*. [33] work on the development of basalt fibers/epoxy prepreg with a functionalized MWNTs embedded in the matrix, observing an enhancement of the mechanical properties. Srikanth *et al*. [34] produced nano silica-modified carbon–phenolic composites for enhanced ablation resistance. They utilized four different matrices adding 0.0 (neat phenolic), 0.5, 2.0, and 4.0 wt% of nano silica powder in the phenolic resin. Viscosity of the mixture was controlled adding ethanol, and each composition was applied to the carbon fabric with a brush and allowed to dry at room temperature to form the prepregs.

As already mentioned, most of the techniques utilized for the production of fiber-reinforced nanocomposites are based on the production of a nanocomposite blend—before—and to use this blend to impregnate the fibers just like for the neat resin—afterward. The advantage of this approach comes from the fact that only well-established techniques are utilized for the production of nanocomposites, especially those that can produce large volume per hour material, and for the production of composite laminate. Nonetheless, this approach can lead to some problems all connected to the different rheological behavior of a nanocomposite with respect to the neat resin, which can affect the flowing rate and the homogeneity of the dispersion in a liquid molding process or the impregnation effectiveness in all the techniques (Fig. 2). Q3

However, other techniques with a different approach have been developed. Thostenson *et al*. [35] let CNTs grow directly on carbon fibers using chemical vapor deposition. The experimental details they utilized were those of Li *et al*. [36], which basically consist in applying a layer of catalyst to bundles of carbon fiber using magnetron sputtering. Prior to the application of the catalyst, the carbon fiber bundles were heat treated at 700°C in a vacuum to remove any polymer sizing applied to the fiber. The outcome of this process is shown in figure. Q4 As a result, they found that the presence of the CNTs at the fiber/matrix interface improves the interfacial shear strength of the composites (Fig. 3).

He *et al*. [37] prepared a CNT/carbon fiber multiscale reinforcement, grafting amino-functionalized MWNTs onto the surfaces of carbon fibers, via chemical process that consists of several steps. First, they functionalized the nanotubes at the end caps of the surface with hexamethylene diamine (HMD) using condition previously studied [38,39]. After a treatment in acetone to remove the sizing agent, carbon fibers were first oxidized and then treated in dimethylformamide (DMF) so that the carboxyl groups obtained through oxidation on fiber surfaces could be transformed into carbonyl chloride groups. Finally, carbon fibers were mixed with the functionalized MWNTs in DMF solvent to graft onto fiber surfaces through nucleophilic substitution reaction between amine groups and acyl chloride groups. As a result, they produced a uniform distribution of the nanotubes along the carbon fiber length.

Bekyarova *et al*. [40] reported an approach to the development of advanced structural composites based on CNT–carbon fiber reinforcement, which utilized electrophoresis for the selective deposition of multi- and single-walled CNTs on woven carbon fabric. The CNT-coated carbon fabrics were consequently infiltrated with epoxy resin using VARTM. As a result of the complete integration of the nanotubes into the fiber bundles, the CNT/carbon fabric/epoxy composites showed a significant enhancement (about 30%) of the interlaminar shear strength (ILSS) with respect to that of carbon fiber/epoxy composites without CNTs and demonstrated significantly improved out-of-plane electrical conductivity.

When dealing with CNTs and carbon nanofibers (CNF), another approach can be utilized, as a very effective alternative to the use of these nanoreinforcements, which is constituted by the employment of buckypapers. Buckypapers are CNT free-standing mats of tangled CNT ropes

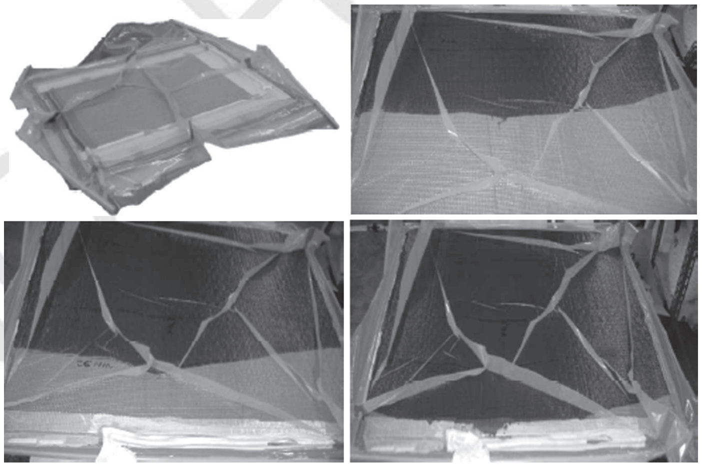


Figure 2. Liquid molding process of CNT-epoxy matrix during impregnation of a glass fiber laminate [26].

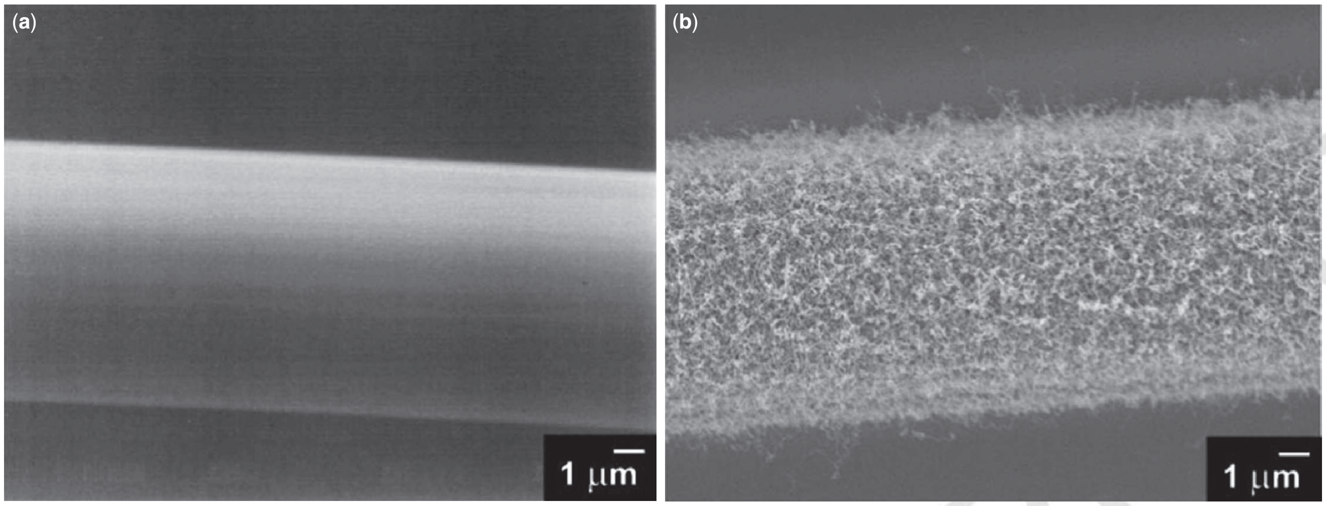


Figure 3. SEM micrographs of carbon fibers (a) before and (b) after nanotube growth.

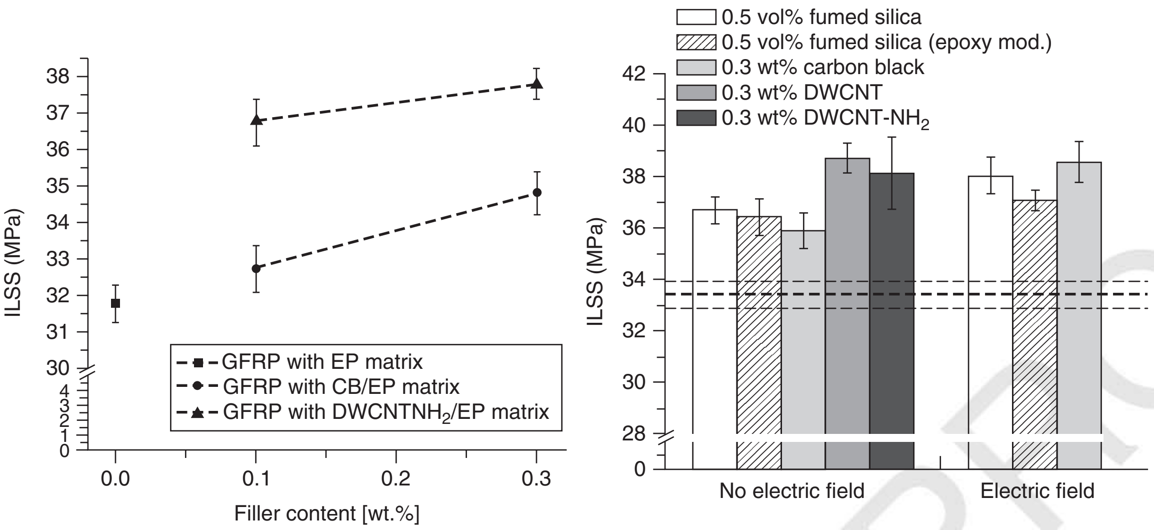
[41] that can be produced by the filtration of CNT suspensions. Such membranes were also produced using CNFs (carbon nanofiber sheets, CNSs). CNT buckypapers and CNSs were successfully applied to composite laminates by means of traditional processing techniques. Wu *et al*. [42] placed CNT buckypapers and CNSs on the surface of an epoxy/carbon fiber-reinforced composites using hand layup followed by vacuum bagging. CNSs were also used as traditional fiber mats. Gou *et al*. [43] incorporated CNSs into glass fiber-reinforced polyester composites through RTM process. The composite laminates consisted of eight plies of CNSs and eight plies of glass fiber mats. These researches clearly pointed out how these sheets can be handles as traditional fiber reinforcements.

NANOSTRUCTURED FIBER-REINFORCED COMPOSITES WITH IMPROVED MECHANICAL PROPERTIES

Beside the well approaches that can be considered for the improvement of mechanical properties in fiber-reinforced composites (selection of fiber reinforcements that optimized properties, toughening of the matrix, and optimization of the fiber–matrix interface to enhance the stress-transfer properties), attempts to incorporate both nanoscale and microscale reinforcements have been extensively considered during the last two decades. Even if the replacement of FRPs by nanocomposites can be regarded as improbable because of the highly developed and well-established conventional fiber reinforcement of polymers and their still unsurpassed level of material properties, the incorporation of nanofillers to give three-phase composites is expected to improve specific mechanical properties such as fracture toughness and the compressive strength [17]. Candidates in the collectivity of nanoparticles with a high potential for the enhancement of mechanical and physical properties of polymers are nanoclays, CNTs, and nanofibers, whereas, among the different matrices, epoxy, phenolic, and polyester resins in conventional fiber-reinforced composites have been widely reported in the literature.

Fiber-reinforced epoxy composites filled with nanoparticles give the opportunity to improve the bulk composite properties with the minimal sacrifice of other properties of the composites. Among nanoreinforcements, MWNTs stand out because of the ultrahigh strength/stiffness, large aspect ratio, and relative affordability. The introduction of carbon-based nanoparticles in carbon fiber-reinforced epoxy has been extensively studied. One key area where nanocomposites can make a significant impact is in addressing interlaminar toughness in the fiber-reinforced composites. Interlaminar toughness improvement of fiber-reinforced composites has been in the research focus for a considerable time because it is directly related to the dynamic as well as the damage tolerance performance of the composite. Veedu *et al*.[44] reported significant improvements in the interlaminar fracture toughness, hardness, delamination resistance, in-plane mechanical properties, damping, thermoelastic behavior, and thermal and electrical conductivities. They presented an approach to the three-dimensional through-the-thickness reinforcement, without altering the two-dimensional (2D) stack design, on the basis of the concept of interlaminar CNT forests that provided enhanced multifunctional properties along the thickness direction. Gojny *et al*. [21] investigated the ILSS of nanoreinforced FRPs in epoxy resin. The produced CNT and CB epoxy composites exhibit a significant increase in fracture toughness as well as an enhancement of stiffness, especially for the functionalized nanotubes (Fig. 4a). In a following work, they compared the influence of CNTs with CB and fumed silica as fillers for improving the ILSS of a glass fiber-reinforced composite [22]. Moreover, they applied a z-direction electric field while curing to the laminate. They reported that all fillers showed a significant increase in ILSS. In particular, they observed that the application of the electric field yielded in a further slight increase in ILSS, in particular, in the case of carbon-based fillers (Fig. 4b).

Zhao *et al*. [45] fabricated CNTs and continuous carbon fiber (T300)-reinforced unidirectional epoxy resin matrix



(**a**) (**b**)

Figure 4. Interlaminar shear strength (ILSS) of (a) GFRPs based on CB and DWCNT-NH2 [21]. (b) Fumed silica, CB, and unmodified and amino-modified CNT with and without the application of the electric field (the dashed line in this case represents the neat epoxy matrix).

composites. They prepared CNTs by catalytic decomposition of benzene using floating transition method at 1100–1200°C. The CNTs used were straight with diameter 20–50 nm, internal diameter 10–30 nm, and length 50–1000 μm. The volume fraction of continuous carbon fiber in the composites without CNTs was 60%. The flexural strength of the composites reached the maximum value of 1780 MPa when the weight percent of CNT in epoxy resin matrix was only 3%. The study concluded that flexural strength and modulus of the composites increased first and then decreased with the increasing of CNT contents in epoxy resin matrix.

Hsiao *et al*. [46] and Meguid and Sun [47] investigated the tensile and shear strength of nanotube-reinforced composite interfaces by single shear-lap testing. They observed a significant increase in the interfacial shear strength for epoxies with contents between 1 and 5 wt% of MWNTs when compared with the neat epoxy matrix. In particular, instead of processing and characterizing CNT/polymer composites, Hsiao *et al*. [46] explored the potential of CNT to reinforce the adhesives in joining two composite structures. In this study, different weight fractions of MWNT were dispersed in epoxy to produce toughened adhesives. The reinforced adhesives were used to bond the graphite fiber/epoxy composite adherents. This experimental study showed that by adding 5 wt.% MWNT in the epoxy adhesive, effectively transferred the shear load from the adhesive to the graphite fiber system in the composite laminates and improved the average shear strength of the adhesion by 46% (±6%). Despite the promising results, the researchers concurred that further experiments involving increasing MWNT weight fractions and more detailed SEM observations are required in order to understand and model the role of the MWNT in enhancing adhesion.

Various studies can be found in the literature regarding the incorporation of CNFs in polymeric matrices and the final mechanical and/or electrical properties of these materials [48–55]. In all cases where nanosized fillers are involved, the development of high performance CNF/polymer composites requires homogeneous dispersion of CNFs in the polymeric matrix and is crucial to the composite performance. The quality of the stress transfer between the nanofibers and the matrix material is also reported to play an important role in the composite properties interface quality in order to achieve efficient load transfer from the matrix to the CNFs. Iwahori and Ishikawa [49] reported that compressive strength improvements in carbon fiber-reinforced polymer (CFRP) laminates by using cup-stacked-type CNF-dispersed epoxy as three-phase composites. More recently, Yokozeki and Iwahori [56] investigated the damage accumulation behaviors in carbon fiber-reinforced nanocomposite laminates under tensile loading. The nanocomposite laminates used the study were manufactured from prepregs consisting of traditional carbon fibers and epoxy resin filled with CNTs. Thermomechanical properties of unidirectional carbon fiber-reinforced nanocomposite laminates were evaluated, and cross-ply laminates were subjected to tension tests in order to observe the damage accumulation behaviors of matrix cracks. It was suggested that the dispersion of CNTs resulted in fracture toughness improvement and residual thermal strain decrease, which was considered to cause the retardation of matrix crack formation.

If we consider the effect of the graphene nanoplatelets (GNPs) carbon source, it is well accepted that the high aspect ratio and excellent electrical conductivity of GNPs make them an effective reinforcement for polymer composites in providing high electrical conductivity. From the point of view of mechanical properties, few examples are reported in the literature in which the epoxy matrix in carbon fiber–epoxy composites was modified with graphite nanoplatelets. Cho *et al*. [57,58] studied the effect of the introduction of graphite nanoparticles in the epoxy matrix by sonication, followed by a vacuum-assisted wet layup process. The composites reinforced with nanoparticles showed enhanced compressive strength and in-plane shear properties.

Using nanoclays in the epoxy matrix, Rice and coworkers [59] found no major improvements of the mechanical properties of carbon fiber-reinforced laminates, even though 2 wt% of organosilicate induced a modulus improvement of 12% of the nanocomposite as compared with the pure epoxy [60]. Similarly, Chowdhury *et al*. [61] employed VARTM process to manufacture woven CFRP matrix composites. They investigated the effects of nanoclay particles on flexural and thermal properties. Different weight percentages of a surface-modified montmorillonite mineral were dispersed in SC-15 epoxy using sonication route. Flexural test results of thermally postcured samples indicated a maximum improvement in strength and modulus of about 14 and 9%, respectively. Li *et al*. [62] successfully prepared layered silicate/glass fiber/epoxy hybrid composites using a VARTM process. The results indicated that introducing a small amount of organoclay to the glass fiber/epoxy composites enhanced their mechanical and thermal properties, confirming the synergistic effects of glass fibers and clays in the composites.

Several other studies have reported on properties enrichment because of the addition of nanoclay in the composite matrices. For instance, Schmidt [63], Mark [64], and Hussain *et al*. [29] demonstrated the possible technology of dispersing Al_2O_3 particles in the matrix and investigated their effect on the mechanical properties of CFRPs. The incorporation of the filler particles resulted in higher fracture toughness by improving significantly the toughness of the matrix and the crack deviation.

Mohan *et al*. [65] evaluated the tensile performance of S2-glass epoxy composites dispersed with alumina nanoparticles up to 1.5% weight fraction and found an increase of 12% in tensile modulus and 8% in tensile strength. Kornmann *et al*. [66] successfully synthesized Q5 epoxy-layered silicate nanocomposites based on DGEBA and an anhydride curing agent.

Karaki *et al*. [67] incorporated layered clay, alumina, and titanium dioxide into an epoxy matrix and fabricated continuous carbon fiber-reinforced polynanomeric matrices to study tension–tension fatigue behavior. Wang *et al*. [68] demonstrated that the exfoliated clay with only 2.5 wt% in epoxy showed a significant improvement in fracture toughness and concluded that an increase in the microcracks and the fractured surface due to crack deflection resulted in the toughness increase.

Siddiqui *et al*. [69] investigated the mechanical properties of nanoclay-dispersed CFRP and showed that the interlaminar fracture toughness of nanoclay-dispersed CFRP is higher than that of the conventional CFRP. Seferis *et al*. [70] demonstrated the ability to incorporate nanosized alumina structures in the matrix and interlayer regions of prepreg-based carbon fiber/epoxy composites. Subramaniyan *et al*. [71] observed that the addition of 5 wt% of nanoclay increased the elastic modulus of epoxy resin under compression by 20% and the compressive strength of glass fiber composites with nanoclay when made by wet layup technique increased by 20–25%.

Beside the epoxy matrices, phenolic resins represent another important thermoset polymer used as matrix in FRPs. The literature reports a few examples of the use of nanoreinforced matrices, basically based on CNTs and CNFs, in FRPs for the enhancement of the mechanical properties, while more papers reported, for example, the modification of phenolic matrix in carbon–carbon (C–C) composites.

In Tzeng and Lin [72], the C–C composites were obtained by pyrolyzing the phenolic resin composites. For the phenolic resin composites, limited strength enhancement was measured. However, better reinforcing results were obtained for CNF reinforcement as compared to the CNT reinforcement because of the better interfacial bonding. CNF reinforcement also showed better results for the modulus measurement than those of CNTs. Property enhancement of carbon fabric/phenolic composites is possible through carbon nanomaterial dispersion in the matrix. The effect of CNF dispersion in phenolic resins/carbon fabric composites was also investigated by Joshi and Bhattacharyya [73], in which the dispersion efficiency in different systems and conditions was studied and the effect of nanofiber concentration on the properties was determined. It was proved that carbon nanomaterial incorporation influences the mechanical properties of the composites and gives better thermal stability.

CNF dispersion also shows better adhesion of phenolic resin to the fabric under fracture surface study. It has been observed that nanofiber alters the interface behavior of the carbon fiber and phenolic resin matrix. This may give better load transfer into the reinforcement and results in a synergistic effect of nanofiber into the property alteration beyond common mixture rules.

Zou *et al*. [74] studied the use of both hydrophobic epoxy resin mixed with surface-modified nanoclay and hydrophilic phenolic resin mixed with unmodified raw nanoclay. Long carbon fibers are also added into the nanocomposites to produce hybrid composites. A series of epoxy–clay and epoxy–clay–carbon fiber composites were prepared. Phenolic raw clay nanocomposites and phenolic carbon fiber–raw clay hybrid composites were prepared and were confirmed that adding nanoclay into the phenolic matrix can enhance the flexural properties and Tg substantially. Other examples are represented by the use of silica reinforcement in CFRP. Lin *et al*. [75] investigated the thermal and mechanical properties of a novel carbon fiber-reinforced phenolic/silica nanocomposite composite fabricated by sol–gel method. Different mixing ratios of the phenolic resins and the sol–gel solutions were adopted for preparing the nanocomposites. The influence of different mixing ratio on the properties of the fabricated composite materials is investigated, and the incorporation of inorganic phase into the matrix confirmed the increase in the flexural modulus of the fabricated composites.

The same approach was used by Chen-Chi *et al*. [76], who reported that phenolic resin–silica nanocomposites can be used to fabricate C–C composites. The effect of inorganic silica on the microstructure, the mechanical properties change of 2D microstructure, and physical and mechanical properties of C–C composites during Q6 the CVI densification composites were studied. Results show that the densities of the C–C composites increased with increasing silica content and the porosity decreased with increasing silica fiber-reinforced phenolic resin–silica nanocomposites content. The existence of silica enhances the stiffness of the fabricated C–C composites but does not affect the strength significantly.

Another property that was considered as improved selecting nanoreinforced phenolic-based composites was the wear resistance in tribological behavior. Wang *et al*. [77] considered the use of graphite and nano-SiO_2 to improve the friction and wear behavior of basalt fabric-reinforced phenolic composites. The tribological properties of the resulting composites under different sliding conditions were investigated systematically on a model ring-on-block test rig. Experimental results showed that graphite was more beneficial than nano-SiO_2 in improving the tribological properties of basalt fabric composites (BFC) when they were singly incorporated. Moreover, the friction and wear behavior of the filled composites were improved further when nano-SiO_2 and graphite were added together, indicating that there was a synergistic effect between them. The tribological tests under different sliding conditions revealed that the BFC/Gr/SiO_2 composites seemed to be more suitable for the tribological applications under higher sliding speed and load.

Among all these resin materials, vinyl ester nanocomposites have significant importance because of their wide range of applications. Until now, most of the work that is carried out related to polymer nanocomposites basically consists of layered silicate in polymer matrix. There is very little information available about continuous FRP nanocomposites. In the paper of Hossain *et al*. [78], emphasis is given in manufacturing S2-glass fiber-reinforced vinyl ester nanocomposites through an affordable process and studying the structures, thermal, and mechanical properties of these nanocomposites. In this article, the effects of silicate nanoparticles in both neat vinyl ester resin and S2-GFRP matrix composites were investigated. Silicate nanoparticles were incorporated into neat organic vinyl ester resin at various weight percentages. The ILSS, flexural properties, and fracture toughness of nanocomposites were also determined for both conventional composites and nanocomposites. Owing to the incorporation of silicate nanoparticles in vinyl ester resin, an improvement in both mechanical and thermal properties was observed. Addition of 1% nanoclay particles, S2-glass/vinyl ester–clay nanocomposites attributed to almost 8, 17, and 23% improvement in the ILSS, flexural strength, and fracture toughness than the conventional S2-glass/vinyl ester composites.

Owing to the bigger volumetric shrinkage during the copolymerization between unsaturated polyester (UP) and styrene and the brittleness of cured UP, many researches have been done to modify this resin in order to improve its mechanical properties. In the paper of Yuan *et al*. [79], three series of glass fiber-reinforced UP/organic rectorite (OREC) (GF/UP/OREC) composites were manufactured by selecting two types of fibers, different gelation time of UP matrix and different content of OREC. The results have shown that the mechanical properties and the resistance to hot–wet and alkali of UP composites can be improved by adding appropriate OREC without reference to the gelation time of UP matrix or the type of glass fibers and the best mechanical properties of UP composites can be obtained by adding 2 wt% OREC because of the high stiffness and uniform dispersion of OREC.

Another result is the one obtained by Zhou *et al*. [80], who investigated the use of the addition of the CNF in GF-reinforced UP. The CNFs improved both the thermal and mechanical properties of the UP resin. In this study, a new approach was used to prepare polymer composites reinforced by both nanoparticles and continuous fibers. CNFs were prebound onto glass fiber mats, and then UP composites were prepared by VARTM. The mechanical and thermal properties of these composites were measured and compared with those of the composites synthesized by premixing CNFs with the polymer resin. Flexural strength and modulus of composites improved with the incorporation of nanoparticles. Specifically, the property improvement was higher in the case of the composites prepared by the new prebound method. It was also found that CNFs increased the glass transition temperature and reduced the thermal expansion coefficient of UP composites.

MULTIFUNCTIONAL NANOSTRUCTURED FIBER-REINFORCED COMPOSITES

Besides the use as mechanical reinforcements, nanosized fillers can offer opportunities in creating fully new properties because of intrinsic characteristics of the nanoparticles utilized or improve properties that are not directly related to a mechanical property. For this reason, many nanofillers are considered multifunctional.

For example, the polymeric nanocomposite materials for applications in the field of electromagnetic (EM) interference protection are obtained by adding one or more nanofillers during the processing, which increase the conductivity shielding or attenuating the incident EM waves.

Thanks to their high electric conductivity, carbon-based nanofillers (i.e., CNTs, CNFs, and graphenes) allow the exploitation in many different applications involving the tailoring of the electrical properties of the fiber-reinforced composite. In fact, in last decade, researchers have demonstrated that it is possible to successfully employ electrically conductive nanoparticles to obtain a polymeric nanocomposite with enhanced electrical conductivity [6,81,82]. If such nanocomposite is used as a matrix of a nonconducting fiber composite, such as glass or aramid fibers, it is possible to obtain a fiber-reinforced composite with improved electrical properties, which can be employed for advanced applications.

On the basis of the physico-mechanical properties of nanostructured carbon materials, it results clear that the transfer of such features to polymeric materials suitable for real applications holds a deep scientific interest. However, for the time being, just a very limited number of studies have been done on the harnessing of these properties into functional nanostructured carbon-based polymer composites: an important step was actually done in understanding that such composites exhibit extraordinarily low electrical percolation threshold (0.1 vol%) because of the large conductivity and aspect ratio of carbon nanofillers, thus suggesting a possible introduction of percolating network within an insulating material rendering it a conductor.

For instance, electrically active carbon nanoparticles can be employed to design a radar absorbing structures (RAS) based on a fiber-reinforced composite. Oh *et al*. [83] studied the microwave EM absorptance of a glass/epoxy composite filled with CB, where the content of the nanoparticles and the thickness of the laminate were modulated in order to maximize the performance in terms of absorbance in the X-band frequency range. Chin and Lee [84] tested a composite RAS based on a UP resin and CB (Fig. 3). In both cases, absorbance levels as high as 90% were obtained adding few points percent of CB and optimizing the thickness of the laminate.

Lee *et al*. [85] exploited the high aspect ratio of CNTs to design RAS with load-bearing ability in the X-band, fabricating a glass/epoxy plain weave composites containing a low content of MWNTs to induce dielectric loss. The optimization of the design of the RAS, consisting of two-layered MWNT-added glass/epoxy fabric composite, was performed by linking a genetic algorithm with a program for the reflection/transmission of EM waves in a multilayered RAS. As a result, the developed RAS was verified to have 90% absorption of EM energy for the entire X-band. In a further study, the same research group [86] compared the absorbance efficiency of CNTs with CNFs and CB, demonstrating that similar good efficiency can be obtained with a much less content when handling CNT and especially the CNFs that they used.

The same polymeric system can be exploited to develop composite EM wave shielding enclosures. Das *et al*. [87] evaluated the electromagnetic interference (EMI) shielding effectiveness of natural rubber and ethylene vinyl acetate (EVA) composites filled with CB and short carbon fiber. They reported that the maximum SE is obtained with EVA-based composites having 30 phr SCF, remarking that short carbon fiber is more effective than CB for the same filler loading and polymer used.

Annadurai *et al*. [88] studied microwave shielding materials based on ethylene propylene diene monomer (EPDM) rubber composites with ferrite and CB, demonstrating how both filler are suitable as EMI shielding materials in the radar and television industries.

Park *et al*. [89] investigated the applicability of glass fabric composite materials to EM wave shielding enclosure. To this aim, they added to the epoxy matrix CNTs at several contents and showed that the MWNT-added composites had more than 90% shielding of EM energy over the 300 MHz to 1 GHz frequency range.

Another promising field in which nanotechnology, and in particular electrically active nanofillers, can play a very interesting role is the strain and damage self-sensing properties of a composite material. Although the use of techniques that exploit electrical properties of the composite has been widely recognized as a noninvasive way to monitor damage in carbon fiber-reinforced plastic, due to the good electrical conductivity of carbon fibers themselves [90–96], this approach cannot be employed with nonconducting fibers, for example, glass or aramid. Moreover, it is intrinsic anisotropic, that is, it is very sensible for the in-plane stress; it gives less information regarding the out-plane fracture mechanism. Several works have been published in the past years on the exploitation of carbon nanoparticles for enhancing the electrical conductivity of the matrix [21–25,27,28,97–106].

Kupke *et al*. in their studies [97,98] showed how CB can be successfully used for the development of electrically conductive glass fiber-reinforced epoxy resin and how this material shows a piezoresistive behavior.

In their review, Fiedler *et al*. [99] first introduced the concept of conductive modification with nanotubes as having potential for damage sensing. Thostenson and Chou [23] developed a glass fiber composite based on an epoxy resin filled with MWNTs in which the enhanced electrical conductivity was exploited as a sensor to evaluate the onset and evolution of damage caused by a mechanical stress (Fig. 5a). They established that the change in the order of magnitude of the reinforcements, from conventional microsized fibers to CNTs, allows unique chance for the creation of multifunctional *in situ* sensing capability. In fact, CNTs dispersed in the matrix can attain a percolating nervelike network of sensors throughout the composite laminate.

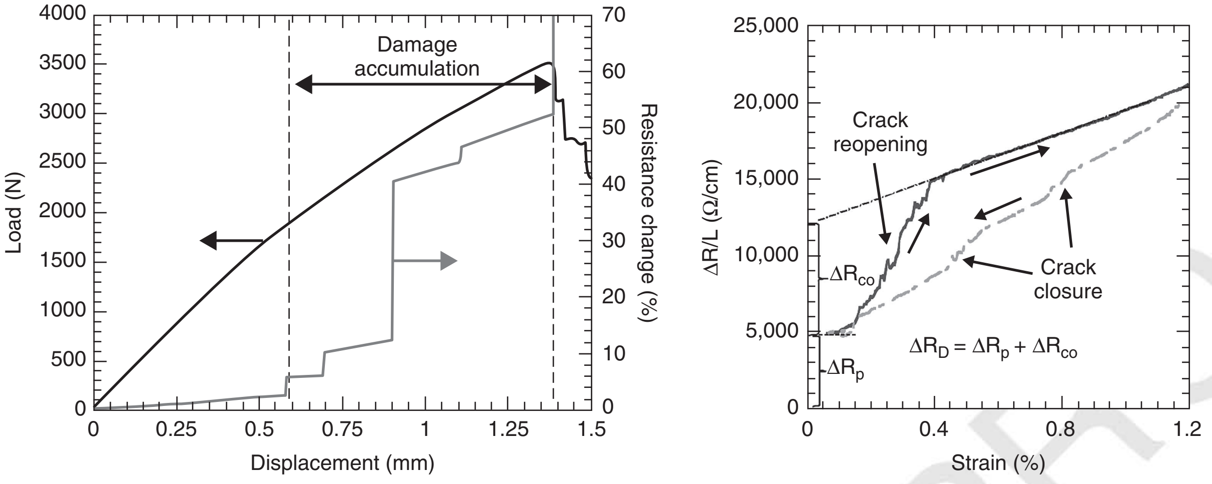
In a following study [24], they utilized the CNT conductive networks as a sensors for detecting damage accumulation during cyclic loading of advanced fiber composites. They showed that the resistance–strain relation has a substantial hysteresis due to the formation of cracks that are opened and closed during cyclic loading (Fig. 5b).

Boger *et al*. [100] modified an epoxy resin with two different types of CNTs and with CB in order to achieve good electrical conductivity and utilized these nanocomposites as matrices for glass fiber composites. These materials were tested by incremental tensile tests and fatigue tests and the ILSS, simultaneously with the monitoring of the electric conductivity, demonstrating how the sensitivity of this new method is higher compared to other damage sensing methods.

Fernberg and Joffe [101] studied a glass epoxy system showing that changes of electrical resistance, during tensile loading of composites containing CNT-doped matrix, give highly relevant information about the damage state of the material. In particular, they focused their attention on the different mechanisms that contribute to changes of the electrical resistance, that is geometrical changes of the specimen, piezoresistive material response, and accumulation of microdamages.

Park *et al*. [102] compared the effect in detecting the presence of damage via electric conductivity measurements of CNTs, CNFs, and CB.

Monti *et al*. [27] developed a glass fiber-reinforced nanocomposite produced via RTM and based on UP resin and helical ribbon CNFs. They found that good sensing characteristics pertain to this composite both when a continuous stress was applied and in the case of impact. In particular, regarding the impact load, a strong correlation



(**a**) (**b**)

Figure 5. (a) Load/displacement and resistance response of a CNT-based GFRP [23] and (b) resistance change during a loading–unloading cycle [25].

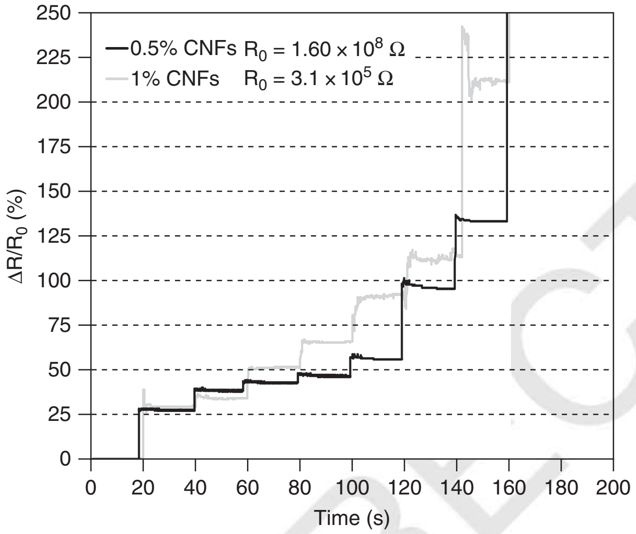


Figure 6. Electrical resistance variation of a CNF-based GFRP as a consequence of subsequent impacts [27].

was reported between the step increase in the electrical resistance of the sample and the impact itself (Fig. 6).

Carbon nanoparticles are supposed to have an intrinsically high thermal conductivity [107,108]. This property can be used to rise up the thermal conductivity of a fiber-reinforced composite in which carbon nanoparticles are embedded. Kim *et al*. [109] developed a carbon fiber/phenolic composite, in which the matrix was doped with MWNTs, by a solvent-assisted sonication technique. They demonstrated that 7 wt% of CNTs dispersed homogeneously in a phenolic resin acted as an effective thermal bridge between adjacent carbon fibers and resulted in an enhancement of the thermal conductivity. Wang and Qiu [110] studied low viscosity polyester/vinyl ester resins filled with CNTs as a matrices for glass fiber composites and found that thermal conductivity was significantly improved, both verified by theoretical calculation and experimental characterization: incorporation of 3 wt% CNTs has resulted in 1.5-folds enhancement of thermal conductivity.

Montmorillonite can also be considered as multifunctional nanoreinforcement. In fact, they can be successfully used as a mechanical reinforcement and for other applications. As an example, Chang and Chow [111] studied glass fiber/epoxy composites with several contents of OMMT, in order to obtain a composite with improved weathering characteristics. They demonstrated to have produced glass fiber/epoxy/OMMT (1–3 wt%) exfoliated structures while glass fiber/epoxy/OMMT (4 wt%) showed intercalated structures. The retention ability in flexural modulus and strength of epoxy hybrid nanocomposites after being subjected to accelerated weathering is considerably excellent. However, the fracture toughness of the glass fiber/epoxy/OMMT nanocomposites was reduced on exposure to UV radiation. In another work [20], Chow studied the same system to obtain a glass fiber-reinforced composite with reduced water absorption. In fact, this reduction is attributed to the increasing of tortuosity path for water penetration in the epoxy composites by the hybrid of glass fiber and OMMT.

NANOSTRUCTURED FIBER-REINFORCED COMPOSITES WITH ENHANCED FLAME RETARDANT PROPERTIES

FRP composites have become very attractive candidates to replace metallic materials in many important sectors of the industry. They are used in the production of aircrafts, buildings, ships, and offshore structures. However, there is an urgent need to improve their fire retardant properties. The use of thermosetting polymers is widely diffused in all those applications where a protection against fire is required. If compared to thermoplastics, thermosettings can ensure insulation at higher working temperature because they do not melt. In any case, they are organic materials: when heated up above critical temperatures, they degrade giving volatile combustible products. These toxic gases constitute a serious hazards for human life.

The possibility to improve the thermal stability and reduce the flammability of a polymeric matrix is generally based on two approaches. One deals with the use of flame retardant additives such as halogen-containing compounds [112–115]. One of the main drawbacks related to the use of these additives is that during combustion they can release toxic and corrosive products [116–118]. The other approach is basically related to the use of high char retention thermosetting matrices such as phenolics, benzoxazines (BZ), or cyanate esters (CE) [119].

One of the most accurate way to study the flame retardant properties of polymers and reinforced polymers is the cone calorimetry [120,121]. The measurement of the decreasing oxygen concentration in the combustion gases of a sample subjected to a given heat flux (typically in the range of 10–100 kW/m^2) is used to calculate the quantity of heat released per unit of time and surface area. In fact, the gross heat of combustion of any organic material can be related to the amount of oxygen required for combustion. In a typical cone calorimeter experiment, the heat release rate (HRR) is recorded as a function of time: the value of its peak heat release rate (PHRR) is usually taken into account in order to evaluate the fire behavior. The loss of mass after burning is also another important parameter. Moreover, to understand the mechanisms of material flammability, many other useful information can be obtained from cone calorimetry [122].

Polymer-layered silicate nanocomposites (PLSNs) can be considered as a new class of flame retardant systems [123]. In fact, they show increased resistance and decreased gas permeability and flammability [118,124]. While classic halogen-free flame retardants such as aluminum hydroxide and magnesium hydroxide require a filler content of more than 60 wt% to achieve acceptable flame retardant properties, a 5–10 wt% nanoclay content is able to reduce the maximum rate of heat release by 70% [31,118,125,126]. However, because of industrial requirements and regulation constraints, the exploitation of the synergy between traditional flame retardants and PLSNs has also been proposed and investigated [127–139].

Studies carried out on lamellar nanocomposites showed that the fire retardant mechanism proposed for PLSNs tested in a cone calorimeter is related to the formation of a homogeneous silicate-carbonaceous char layer that works as a heat shield during burning. This is widely accepted as the main flame retardant mechanism common in nanocomposites. In PLSNs, such a phenomenon is driven by the ablative reassembling of the inorganic nanoclay platelets [124,140–144]. Also, in lamellar nanocomposites, the thermal oxidation of the char is hindered because of the oxygen barrier effect due to inorganic layers reassembling on the surface of the ablating material. Schartel *et al*. [145] deeply investigated the properties of epoxy-layered silicate nanocomposites. According to this research, during combustion, in order to obtain a homogeneous residue surface skin exhibiting the desired flame retardancy, it is critical to obtain a homogeneous nanoscaled dispersion of nanoclay layers: the better the nanocomposite formation through a greater dispersion of nanofiller, the higher the efficiency in terms of fire retardancy. The same conclusion is reported by several other authors [115,121,146,147].

Indeed, the morphology of the nanocomposite strongly changes by virtue of ablative reassembly [144,148]. Only a few studies have addressed the study of the evolution of barrier formation [149]. In most sources, only the visual appearance (SEM or TEM analysis) is used for the interpretation of these mechanisms [149–151]. However, it is commonly believed that a closed homogeneous silicate-carbonaceous surface layer yields an effective reduction in PHRR. Cracks in the residue layer or even the formation of single islands lead to an ineffective protection. Literature also reports that intense flaming occurred in PLSN samples tested in a cone calorimeter because some cracks were not closed by increased addition of nanoclay platelets. The fact that the cracks were not closed, even though the thickness of the layer increased, clearly means that the enrichment in layered silicates on the surface is a very complex phenomenon. Different mechanisms such as ablation, migration, bubbling, and accumulation are believed to play a role in distinct morphologies [144,149, 152–154]. All these phenomenons probably occur simultaneously in PLSNs, with the importance of each mechanism specific to each system. Schartel and collaborators [145] also reported that epoxy-layered silicate nanocomposites tested in a cone calorimeter did not reach temperatures high enough to initiate crystallographic changes all over the sample. Both XRD and SEM results did not show sintering of the inorganic silicates. According to SEM analysis, the fire residue is a silicate-carbonaceous material, in which silicate platelets with their typical sharp contours are stacked together by the carbonaceous char. In depth, temperature profiles acquired in the neat resin and in nanocomposites tested by cone calorimetry were also studied. During burning with an external heat flux of 70 kW/m^2, the surface of the nanocomposite reached temperatures around 380°C higher than the surface temperatures of the burning neat polymer. The corresponding reradiation from the surface is increased by a factor of around 4–5 because it increases with T^4. The increased reradiation from the hotter surface is accompanied by a reduced heat flux transferred into the material; thus, the mass loss rate is reduced.

Carbon nanofilaments such as nanotubes or nanofibers are also being considered as candidates for flame retardant additives. Kashiwagi *et al*. [155–158] found that CNTs effectively act as flame retardant fillers. They attribute the improved flame resistance to the formation of a continuous protective nanotube network structure working as a heat shield. Such a protective barrier slows down mass loss rate and material flammability. Consistent with this mechanism, the flame retardancy improved with better dispersion, higher loading, and a higher interface area (aspect ratio) of the nanotubes. Also, CNTs embedded in the charred surface reemit much of the incident radiation into the gas phase from its hot surface, reducing the transmitted flux to the inner layers of the material, and slowing down the polymer pyrolysis rate [159,160]. However, in terms of processing, the addition of CNTs in a thermosetting matrix significantly increases its viscosity.

In addition, it is difficult to uniformly disperse and distribute CNTs into polymer matrix because of strong Van der Waals force between them. Another carbon nanoadditive of interest is graphite oxide (GO). GO can be obtained when bulk graphite is exposed to strong oxidizers such as nitric acid. The oxidation prevents graphene stacking and affords easy dispersion in organic media. The enhanced processability of GO allows it to be incorporated into polymer matrices, and the scalability and low cost of this process make it attractive for industrial applications [161]. The flammability of GO has been studied in poly(acrylic ester): the addition of GO was found to reduce the PHRR by as much as 45% with only 1 wt% GO content [162,163].

In order to improve the flame retardant properties of a composite, the use of buckypapers constitutes a very effective alternative at the use of CNTs directly dispersed in the matrix. Dense nanotube networks and small pore size within the buckypaper provide low gas and mass permeability, which means buckypaper may act as an inherent flame retardant shield when applied onto the polymeric material surface. CNF-based papers were also studied as fire retardant sheets. Wu *et al*. [42] compared the flame retardant properties of buckypapers produced with SWNTs, MWNTs, and CNFs placed on the surface of an epoxy/carbon fiber-reinforced composite. The composites with and without buckypaper skins were fabricated using hand layup followed by vacuum bagging. Cone calorimetry testing was carried out at a heat flux of 50 kW/m^2. MWNT-based buckypaper acted as an effective fire shield to reduce heat, smoke, and toxic gases generated during fire combustion. SWNT-based buckypaper was burnt out after combustion and did not affect the flammability of the composite. In the case of CNF paper-based composite, the big pore size of the network resulted in high gas permeability leading to a poor flame retardant efficiency (Fig. 7).

Zhuge and collaborators confirmed such a result [165]: the existence of a CNF paper placed on the surface of a glass fiber-reinforced composite laminates was not effective in improving the fire performance of the composites. However, the use of a CNF sheet placed on the surface of a composite resulted to be more effective than in the case in which the CNFs were directly dispersed in the matrix of the laminate [159]. CNSs were also used as traditional fiber mats. Gou *et al*. [43] incorporated CNSs into glass fiber-reinforced polyester composites through RTM process. The composite laminates consisted of eight plies of CNSs and eight plies of glass fiber mats. The fire retarding performance of the laminates was evaluated with cone calorimeter tests with an external radiated heat flux of 50 kW/m^2. The fire retardancy of the laminates was enhanced through the barrier effect of the embedded multiply CNSs. However, the CNS on the top surface of the laminates did not contribute to the fire retardancy. It was also found that the CNS plies survived the test except the one on the top surface of the laminates.

To further optimize the fire retardancy of the carbon nanofilament papers, the use of hybrid systems consisting of two or more types of nanoparticles exploiting the synergistic effect of different nanoparticles resulted to be extremely effective. Zhao *et al*. [166] developed two kinds of clay/CNF hybrid sheets containing 0.05 and 0.20 wt% of Cloisite Na$^+$ clay. These sheets were integrated onto the surface of laminated composites by traditional RTM process. Cone calorimeter tests performed at a heat flux of 50 kW/m^2 showed that hybrid sheets survived on the combustion surface of composites and significantly reduced the HRR by approximately 60.5%. It is believed that nanoclay platelets can protect CNFs from severe burning. A similar research carried out by Tang and collaborators [164] confirmed these results: the PHRR of composites coated with clay/CNF paper decreased by 67% compared to the control composite.

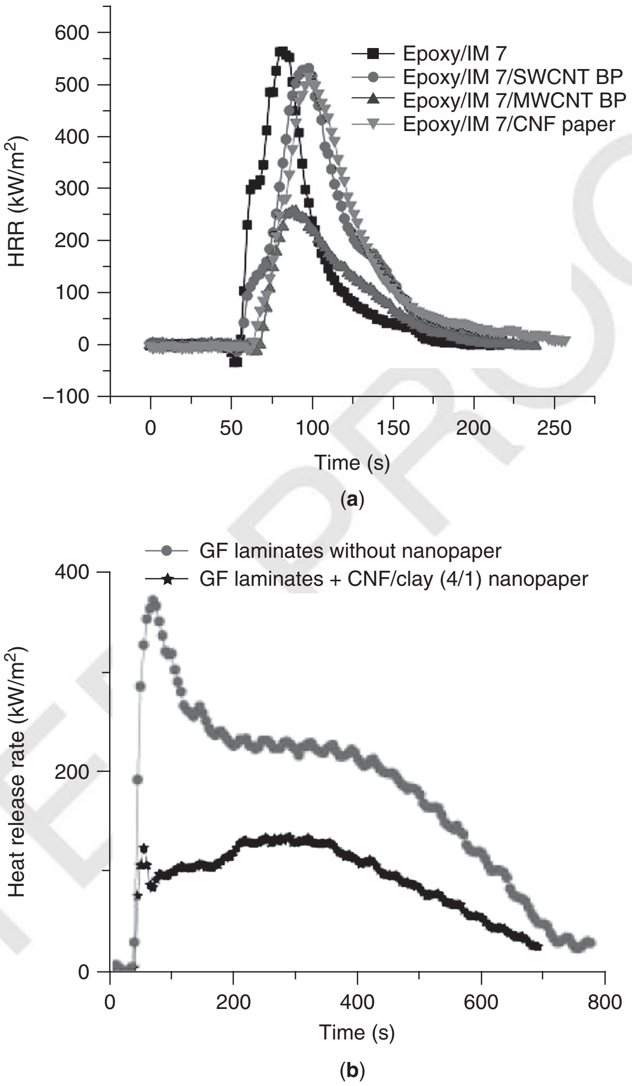


Figure 7. Comparison of heat release rate curves of heat emission curves for Epoxy/IM-7, Epoxy/IM-7/SWNT-BP, Epoxy/IM-7/MWNT-BP, and Epoxy/IM-7/CNF paper [42]. HRRs of composite laminates coated with hybrid nanopapers: 0−120 s [164].

As it was pointed out at beginning of this section, in addition to the use of fire retardant fillers, another way to reduce the flammability of a polymer composite is based on the use of high cross-linking density and high char retention thermosetting matrices: phenolic represents the most popular alternative to epoxy or polyester. In spite of some unfavorable properties such as brittleness, phenolic is a large commodity resin system with production volumes in excess of 5 million tons/year worldwide. Closely related phenolic materials such as BZ and CE are emerging systems with remarkable properties such as fire, smoke, and toxicity (FST) behavior: if compared to traditional phenolics, these systems release little or no volatiles during curing but, at date, they are still expensive [167]. Phenolic resins exhibit exceptional thermal stability, high dimensional stability, and thermal insulation. All these properties can be directly related to their high cross-link density and their chemical structure [168]. When exposed at high heat fluxes, the high cross-linking density of phenolics improves the mechanical performance of the residual char, leading a better protection of the inner layers of the virgin material [169]. Nevertheless, several investigations were also carried out with the aim to further improve the already high thermal stability of phenolics by means of nanofillers [170–172].

Fibrous reinforcements such as carbon, glass, silicon dioxide, and refractory oxides are typically added to phenolics. E-glass/phenolic composites are gaining popularity in marine, transportation, military, and construction industry because of their excellent FST properties [167] and their reasonable cost. The use of nano-modified phenolic resins as matrices for fiber-reinforced composites represents a very promising way to maximize their fire retardant properties. However, such a technology can be considered at its infancy: a few examples of fiber-reinforced composites impregnated with nanocomposites based on phenolics are reported in literature [2,173–179].

Koo *et al*. [2] carried out a wide series of researches in which a resole (Borden Chemical SC-1008) was nano-modified using several types of nanofillers such as Q7 CNF, nanoclay, and POSS. A family of these nanocomposites based on the use of nanoclay (Cloisite 30B) was used to impregnate a carbon/phenolic composite (Cytec MX-4926) [180]. Cone calorimeter tests (at a heat flux of 75 kW/m^2) were performed both on the traditional composite and on the nanoclay-loaded laminate. Compared with the traditional carbon/phenolic composite, the nanostructured system exhibited a 25% lower PHRR. Tate and collaborators [181] dispersed a nanoclay (Cloisite Na$^+$) in a water-based phenolic resin (Cellobond J2027L) using high shear mixer. Water-based Cellobond liquid phenolic resole resins have been available in the United Kingdom for over 20 years, being used in several markets such as mass transit, aircraft, marine, automotive, architectural, mining, and tunneling. The nano-modified phenolic resin was successfully used to manufacture E-glass-reinforced composites using low cost VARTM process. Mass loss calorimeter tests were conducted on the laminates at a heat flux of 35 kW/m^2. With respect to control E-glass/phenolic composite, it was observed that a 7.5 wt% loading of Cloisite Na$^+$ improved the flammability properties by almost 33%. Nano-modified phenolics were also combined to asbestos fibers. Even if asbestos is banned in many western countries, by virtue of its remarkable high temperature properties, some nations still continue to use asbestos in the production of special components: as an example, asbestos can be used to fabricate high performance thermal protection heat shields for space vehicle and engines. The flame retardant properties of an asbestos cloth impregnated with a resole layered silicate nanocomposite were investigated by Bahramian and collaborators [182]. At first, they produced the PLSN using a resole and a laboratory modified natural clay. Then, asbestos cloth was impregnated by the phenolic nanocomposite. All laminates were cured in autoclave and tested by cone calorimetry at a heat flux of 80 kW/m^2. According to experimental results, the laminate obtained impregnating the fiber asbestos cloth with the PLSN exhibited a 35% lower HRR and a 22% lower mass loss than the asbestos cloth/phenolic composite. The study of the morphology on postburnt surfaces showed that the spatially uniform distribution of the silicate platelets led to a uniform char.

CONCLUSIONS AND PERSPECTIVES

Nanostructured materials exhibit significantly different properties that are dictated by size, shape, and chemical composition. Having established many of their properties during the last two decades, scientists switched attention to their incorporation in polymeric systems.

The incorporation of nanofillers into the polymer composites induces new properties and functions based on synergetic effects. Several recent perspective articles highlight current progress and emerging issues related to polymer nanocomposites. This review provides a variety of industrial scalable processes and techniques such as solution mixing, *in situ* polymerization, and covalent grafting for fabricating such nanostructured-based composites. The composites exhibited improved electrical conductivity, mechanical strength, or thermal stability. With the rapid development of nanostructured materials science and technology, nanostructured-based composites become one of the most important class of materials. The developments in the design of nanostructured-based systems will continue to emerge as we venture into the 2D domain of carbon nanostructures in the near future. With the multidisciplinary efforts from chemistry, physics, and materials science, we believe that many applications of these materials will become reality in future.

REFERENCES

1. Mahrholz T, Mosch J, Rostermundt D, Riedel U, Herbeck L, Sinapius M. Fiber-Reinforced nanocomposites for spacecraft structures: manufacturing, characterization and application. Proceedings of the European Conference on Spacecraft Structures, Materials and Mechanical Testing-Noordwijk, The Netherlands; 2005, ESA SP-581 #168.1.
2. Koo JH. Polymer nanocomposites: processing, characterization, and applications. New York, McGraw-Hill, 2006.
3. Thostenson ET, Li C, Chou T-W. Nanocomposites in context. Compos Sci Technol 2005;65:491–516.
4. Thostenson ET, Chou T-W. On the elastic properties of carbon nanotube-based composites: modeling and characterization. J Phys D 2003;36(5):573–582.

5. Sandler J, Shaffler MSP, Prasse T, Bauhofer W, Schulte K, Windle AH. Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties. Polymer 1999;40(21):5967–5971.
6. Bryning MB, Islam MF, Kikkawa JM, Yodh AG. Very low conductivity threshold in bulk isotropic single-walled carbon nanotube-epoxy composites. Adv Mater 2005;17(9):1186–1191.
7. Corcione CE, Prinari P, Cannoletta D, Mensitieri G, Maffezzoli A. Synthesis and characterization of clay-nanocomposite solvent based polyurethane adhesives. Int J Adhes Adhes 2008;28:91–100.
8. Corcione CE, Fasiello A, Maffezzoli A. Synthesis and characterization of bohemite reinforced epoxy nanocomposites. J Nanostruct Polym Nanocompos 2007;3:82–89.
9. Suh DJ, Lim YT, Park OO. The property and formation mechanism of unsatured polyester-layered silicate nanocomposite depending on the fabrication methods. Polymer 2000;41:8557–8563.
10. Miyagawa H, Drzal LT. Thermo-physical and impact properties of epoxy nanocomposites reinforced by sigle-wall carbon nanotubes. Polymer 2004;45(15):5163–5170.
11. Lau KT, Lu M, Lam CK, Cheung HY, Sheng FL, Li HL. Thermal and mechanical properties of single-walled carbon nanotube bundle-reinforced epoxy nanocomposites: the role of solvent for nanotube dispersion. Compos Sci Technol 2005;65:719–725.
12. Kim B, Lee J, Yu IS. Electrical properties of single-wall carbon nanotube and epoxy composites. J Appl Phys 2003;94(10):6724–6728.
13. Gojny FH, Wichmann MHG, Kopke U, Fiedler B, Schulte K. Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content. Compos Sci Technol 2004;64:2363–2371.
14. Gojny FH, Wichmann MHG, Fiedler B, Schulte K. Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites-a comparative study. Compos Sci Technol 2005;65:2300–2313.
15. Thostenson ET, Chou T. Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites. Carbon 2006;44:3022–3029.
16. Zhu J, Kim J, Peng H, Margrave JL, Khabashesku VN, Barrera EV. Improving the dispersion and integration of single-walled carbon nanotubes in epoxy composites through functionalization. Nano Lett 2003;3:1107–1113.
17. Njuguna J, Pielichowski K, Alcock JR. Epoxy-based fibre reinforced nanocomposites. Adv Eng Mater 2007;9(10):835–847.
18. Norkhairunnisa M, Bakar Azhar A, Wen Shyang C. Effects of organo-montmorillonite on the mechanical and morphological properties of epoxy/glass fiber composites. Polym Int 2007;56:512–517.
19. Chang LN, Chow WS. Accelerated weathering on glass fiber/epoxy/organo-montmorillonite nanocomposites. J Compos Mater 2010;44(12):1421–1434.
20. Chow WS. Water absorption of epoxy/glass fiber/organo-montmorillonite nanocomposites. Express Polym Lett 2007;1(2):104–108.
21. Gojny FH, Wichmann MHG, Fiedler B, Bauhofer W, Schulte K. Influence of nano-modification on the mechanical and electrical properties of conventional fibre-reinforced composites. Compos Part A 2005;36:1525–1535.
22. Wichmann MHG, Sumfleth J, Gojny FH, Quaresimin M, Fiedler B, Schulte K. Glass-fibre-reinforced composites with enhanced mechanical and electrical properties—Benefits and limitations of a nanoparticle modified matrix. Eng Fract Mech 2006;73:2346–2359.
23. Thostenson ET, Chou TW. Carbon nanotube networks: sensing of distributed strain and damage for life prediction and self healing. Adv Mater 2006;18:2837–2841.
24. Gao LM, Thostenson ET, Zhang ZG, Chou TW. Sensing of damage mechanisms in fiber-reinforced composites under cyclic loading using carbon nanotubes. Adv Funct Mater 2009;19:123–130.
25. Thostenson ET, Chou TW. Real-time *in situ* sensing of damage evolution in advanced fiber composites using carbon nanotube networks. Nanotechnology 2008;19:215713.
26. Monti M. Advances in polymer nanocomposites with high aspect ratio carbon nanoparticles for damage tolerance sensing in fiber reinforced composites. PhD dissertation. University of Perugia; 2009.
27. Monti M, Natali M, Petrucci R, Kenny JM, Torre L. Carbon nanofibers for strain and impact damage sensing in glass fiber reinforced composites based on an unsaturated polyester resin. Polym Compos 2011. In press. Q8
28. Monti M, Natali M, Petrucci R, Kenny JM, Torre L. Impact damage sensing in glass fiber reinforced composites based on carbon nanotubes by electrical resistance measurements. J Appl Polym Sci 2011. In press.
29. Hussain M, Nakahira A, Niihara K. Mechanical property improvement of carbon fiber reinforced epoxy composites by Al2O3 filler dispersion. Mater Lett 1996;26:185–191.
30. Spindler-Ranta S, Bakis CE. Carbon nanotube reinforcement of a filament winding resin. Proceedings of 47th International SAMPE Symposium, Volume 47; 2002, p. 1775.
31. Zhou Y, Baseer MA, Mahfuz H, Jeelani S. Fabrication and evaluation on nano-phased unidirectional carbon fiber reinforced epoxy. 5th Annual SPE Automotive Composites Conference; 2005; Troy, MI.
32. Yokozeki T, Iwahori Y, Ishiwata S. Matrix cracking behaviors in carbon fiber/epoxy laminates filled with cup-stacked carbon nanotubes (CSCNTs). Compos Part A 2007;38:917–924.
33. Chen W, Shen H, Auad ML, Huang C, Nutt S. Basalt fiber–epoxy laminates with functionalized multi-walled carbon nanotubes. Compos Part A 2009;40:1082–1089.
34. Srikanth I, Daniel A, Kumar S, Padmavathi N, Singh V, Ghosal P, Kumar A, Rohini Devi G. Nano silica modified carbon–phenolic composites for enhanced ablation resistance. Scr Mater 2010;63:200–203.
35. Thostenson ET, Li WZ, Wang DZ, Ren ZF, Chou TW. Carbon nanotube/carbon fiber hybrid multiscale composites. J Appl Phys 2002;91:6034.
36. Li WZ, Wang DZ, Yang SX, Wen JG, Ren ZF. Controlled growth of carbon nanotubes on graphite foil by chemical vapor deposition. Chem Phys Lett 2001;335:141–149.
37. He X, Zhang F, Wang R, Liu W. Preparation of a carbon nanotube/carbon fiber multi-scale reinforcement by grafting multi-walled carbon nanotubes onto the fibers. Carbon 2007;45:2559–2563.
38. Gromoc A, Dittmer S, Svensson J, Nerushev OA, Garcia SAP, Jimenez LL, *et al*. Covalent amino-functionalization of single-wall carbon nanotubes. J Mater Chem 2005;15:3334–3336.
39. Okpalugo TIT, Papakonstantinou P, Murphy H, Mclaughlin J, Brown NMD. High resolution XPS characterization

of chemical functionalized MWNTs and SWNTs. Carbon 2005;43:153–159.

40. Bekyarova E, Thostenson ET, Yu A, Kim H, Gao J, Tang J, Hahn HT, Chou T-W, Itkis ME, Haddon RC. Multiscale Carbon Nanotube-Carbon Fiber Reinforcement for advanced epoxy composites. Langmuir 2007;23:3970–3974.
41. Liu J, Rinzler AG, Dai HJ, Hafner JH, Bradley RK, Boul PJ, *et al*. Fullerene pipes. Science 1998;280:1253–1256.
42. Wu Q, Zhu W, Zhang C, Liang Z, Wang B. Study of fire retardant behavior of carbon nanotube membranes and carbon nanofiber paper in carbon fiber reinforced epoxy composites. Carbon 2010;48:1799–1806.
43. Gou J, Tang Y, Zhuge J, Zhao Z, Chen R-H, Hui D, Ibeh C. Fire performance of composite laminates embedded with multi-ply carbon nanofiber sheets. Compos Part B 2010;41:176–181.
44. Veedu VP, Cao A, Li X, Ma K, Soldano C, Kar S, Ajayan PM, Ghasemi-Nejhad MN. Multifunctional composites using reinforced laminae with carbon-nanotube forests. Nat Mater 2006;5:457.
45. Zhao DL, Qiao RH, Wang CZ, Shen ZM. Microstructure and mechanical property of carbon nanotube and continuous carbon fiber reinforced epoxy resin matrix composites. Proceedings of the Asian International Conference on Advanced Materials (AICAM 2005), 2005 Nov 3–5, pp. 517–520.
46. Hsiao K, Alms J, Advani SG. Use of epoxy/multiwalled carbon nanotubes as adhesives to join graphite fibre reinforced polymer composites. Nanotechnology 2003;14:791.
47. Meguid SA, Sun Y. On the tensile and shear strength of nano-reinforced composite interfaces. Mater Des 2004;25:289.
48. Xu J, Donohoe JP, Pittman CU. Preparation, electrical and mechanical properties of vapor grown carbon fiber (VGCF)/vinyl ester composites. Compos Part A 2004;35:693.
49. Iwahori Y, Ishikawa T. Proceedings of the 3rd Japan–Korea Joint Symposium on Composite Materials; 2002, p. 191.
50. Iwahori Y, Ishiwata S, Sumizawa T, Ishikawa T. Mechanical properties improvements in two-phase and three-phase composites using carbon nano-fiber dispersed resin. Compos Part A 2005;36:1430.
51. Higgins BA, Brittain WJ. Polycarbonate carbon nanofiber composites. Eur Polym J 2005;41:889.
52. Njuguna J, Pielichowski K. Polymer nanocomposites for aerospace applications: characterization. Adv Eng Mater 2004;6:204.
53. Andrews R, Jacques D, Minot M, Rantell T. Homogenous composite of poly(propylene) and multiwall carbon nanotubes Macromol. Mater Eng 2002;287:395.
54. Thostenson ET, Ren ZF, Chou T-W. Advances in the science and technology of carbon nanotubes and their composites: A review. Compos Sci Technol 2001;61(13):1899–1912.
55. Njuguna J, Pielichowski K. Polymer nanocomposites for aerospace applications: properties. Adv Eng Mater 2003;5:769.
56. Yokozeki Y, Iwahori S. Ishiwata, Matrix cracking behaviors in carbon fiber/epoxy laminates filled with cup-stacked carbon nanotubes (CSCNTs). Compos Part A 2007;38:917.
57. Cho J, Chen JY, Daniel IM. Mechanical enhancement of carbon fiber/epoxy composites by graphite nanoplatelet reinforcement. Scr Mater 2007;56:685–688.
58. Cho J, Chen JY, Daniel IM. Processing and characterization of carbon fiber/epoxy composites reinforced with graphite nanoplatelets. ASME 2007 International Mechanical Engineering Congress and Exposition (IMECE2007) 11: Micro and Nano Systems, Parts A and B; 2007.
59. Rice BP, Chenggang C, Cloos L, Curliss D. Carbon fiber composites prepared from organoclay-aerospace epoxy nanocomposites. 46th International SAMPE Symposium and Exhibition; 2001 May 6–10; Long Beach, Volume 1, 2001, p. 355.
60. Chen C, Curliss D. Organoclay-aerospace epoxy nanocomposites. SAMPE J 2001;37:11.
61. Chowdhury FH, Hosur MV, Jeelani S. Studies on the flexural and thermomechanical properties of woven carbon/nanoclay-epoxy laminates. Mater Sci Eng A 2006;421:298.
62. Lin L, Lee J, Hong C, Yoo G, Advani SG. Preparation and characterization of layered silicate/glass fiber/epoxy hybrid nanocomposites via vacuum-assisted resin transfer molding (VARTM). Compos Sci Technol 2006;66:2116–2125.
63. Schmidt H. New type of non-crystalline solids between inorganic and organic materials. J Non Crystal Solids 1985;73:681–691.
64. Mark JE. Ceramic reinforced polymers and polymer modified ceramics. Polym Eng Sci 1996;36:2905.
65. Mohan RV, Kelkar AD, Akinyede O. Vartm processing and characterization of composite laminates from epoxy resins dispersed with alumina particles. Proceedings of 50th International SAMPE Symposium and Exhibition; 2005 May 1–5; Long Beach, 2005, p. 2425.
66. Kornmann X, Rees M, Thomann Y, Necola A, Barbezat M, Thomann R. Epoxy-layered silicate nanocomposites as matrix in glass fibre-reinforced composites. Compos Sci Technol 2005;65:2259.
67. Karaki T, Killgore JP, Seferis JC. Characterization of fatigue behavior of polynanomeric matrix. SAMPE, 49th International Sympos Exhibition Conference Proceedings, 2004. p. 2195. Q9
68. Wang K, Chen L, Wu J, Toh ML, He C, Yee AF. Epoxy nanocomposites with highly exfoliated clay: mechanical properties and fracture mechanisms. Macromolecules 2005;38:788.
69. Siddiqui NA, Woo RSC, Kim J, Leung CCK, Munir A. Mode I interlaminar fracture behavior and mechanical properties of CFRPs with nanoclay-filled epoxy matrix. Compos Part A 2007;38:449.
70. Hayes BS, Nobelen M, Dharia AK, Seferis JC, Nam J. Development and analysis of nano-particle modified prepreg matrices. Proceedings of 33rd International SAMPE Technical Conference—Advanced Affordable Materials Technology; 2001 Nov 5–8; Seattle, 2001, p. 1050.
71. Subramaniyan AK, Bing Q, Nakima D, Sun CT. Effect of nanoclay on compressive strength of glass fiber composites. Proceedings of the 18th Annual Technical Conference of the American Society for Composites, Gainesville, 2003, Paper 194.
72. Tzeng S-S, Lin Y-H. Mechanical properties of carbon-carbon composites reinforced with carbon nanotubes or carbon nanofibers. ICCM-16th International Conference on Composite Materials, Japan; 2007.
73. Joshi M, Bhattacharyya A. Carbon nanofiber reinforced carbon/polymer. Compos NSTI-Nanotech 2004;3:308–311.
74. Zhou G, Movva S, Lee LJ. Nanoclay and long-fiber-reinforced composites based on epoxy and phenolic resins. J Appl Polym Sci 2008;108:3720–3726.

75. Lin J, Ma CM, Tai W, Chang W, Tsa C. Carbon fiber reinforced phenolic resin/silica ceramer composites-processing, mechanical and thermal properties. Polym Compos 2000;27(2):305–311.
76. Ma C-CM, Lin J-M, Chang W-C, Ko T-H. Carbon/carbon nanocomposites derived from phenolic resin–silica hybrid ceramers: microstructure, physical and morphological properties. Carbon 2002;40:977–984.
77. Wang Q-H, Zhang X-R, Pei X. Study on the friction and wear behavior of basalt fabric composites filled with graphite and nano-SiO_2. Mater Des 2010;31:1403–1409.
78. Hossain F, Dean D, Haque A, Shamsuzzoha M. S2 glass/vinylester polymer nanocomposites: manufacturing, structures, thermal and mechanical properties. J Adv Mater 2005;37(1):16–27.
79. Yuan L, Ma X, Liang G, Yan H. Fibre reinforced organic rectorite/unsaturated polyester composites. Compos Sci Technol 2007;67:2311–2322.
80. Zhou G, Movva S, Lee LJ. Preparation and properties of nanoparticle and long-fiber-reinforced unsaturated polyester composites. Polym Compos 2009;30:861–865.
81. Monti M, Terenzi A, Natali M, Gaztelumendi I, Markaide N, Kenny JM, Torre L. Development of unsaturated polyester matrix—carbon nanofibers nanocomposites with improved electrical properties. J Appl Polym Sci 2010;117:1658–1666.
82. Vera-Aguillo J, Gloria-Pereira A, Varela-Rizo H, Gonzalez JL, Martin-Guillon I. Comparative study of the dispersion and functional properties of multiwall carbon nanotubes and helical-ribbon carbon nanofibers in polyester nanocomposites. Compos Sci Technol 2009;69(10):1521–1532.
83. Oh J, Oh K, Kim C, Hong C. Design of radar absorbing structures using glass/epoxy composite containing carbon black in X-band frequency ranges. Compos Part B 2004;35:49–56.
84. Chin W, Lee D. Development of the composite RAS (radar absorbing structure) for the X-band frequency range. Compos Struct 2007;77:457–465.
85. Lee S, Kang J, Kim C. Fabrication and design of multi-layered radar absorbing structures of MWNT-filled glass/epoxy plain-weave composites. Compos Struct 2006;76:397–405.
86. Kim J, Lee S, Kim C. Comparison study on the effect of carbon nano materials for single-layer microwave absorbers in X-band. Compos Sci Technol 2008;68:2909–2916.
87. Das NC, Khastgir D, Chaki TK, Chakraborty A. Electromagnetic interference shielding effectiveness of carbon black and carbon fibre filled EVA and NR based composites. Compos Part A 2000;31:1069–1081.
88. Annadurai P, Mallick AK, Tripathy DK. Studies on microwave shielding materials based on ferrite and carbon black-filled EPDM rubber in the X-band frequency. J Appl Polym Sci 2002;83:145–150.
89. Park K, Lee S, Kim C, Han J. Application of MWNT-added glass fabric/epoxy composites to electromagnetic wave shielding enclosures. Compos Struct 2007;81:401–406.
90. Wang S, Chung DDL. Piezoresitivity in continuous carbon fibre polymer-matrix composite. Polym Compos 2000;21:13–19.
91. Schulte K, Baron Ch. Load and failure analyses of CFRP laminates by means of electrical resistivity measurements. Compos Sci Technol 1989;36:63–76.
92. Todoroki A, Yoshida J. Electrical resistance change of unidirectional CFRP due to applied load. JSME Int J, Ser A 2004;47:357–364.
93. Ogi K, Takao Y. Characterization of piezoresitance behaviour in a CFRP unidirectional laminate. Compos Sci Technol 2005;65:231–239.
94. Ceysson O, Salvia M, Vincent L. Damage mechanisms characterization of carbon fiber/epoxy composite laminates by both electrical resistance measurements and acoustic emission analysis. Scr Mater 1996;34:1273–1280.
95. Wang S, Chung DDL, Chung JH. Impact damage of carbon fiber polymer–matrix composites, studied by electrical resistance measurement. Compos Part A 2005;36:1707–1715.
96. Angelidis N, Irving PE. Detection of impact damage in CFRP laminates by means of electrical potential techniques. Compos Sci Technol 2007;67:594–604.
97. Kupke M, Wentzel H-P, Schulte K. Electrically conductive glass fibre reinforced epoxy resin. Mater Res Innovat 1998;2:164–169.
98. Kupke M, Schulte K, Schüler R. Non-destructive testing of FRP by d.c. and a.c. electrical methods. Compos Sci Technol 2001;61:837–847.
99. Fiedler B, Gojny FH, Wichmann MHG, Bauhofer W, Schulte K. Can carbon nanotubes be used to sense damage in composites? Ann Chim Sci Mat 2004;29:81–94.
100. Böger L, Wichmann MHG, Meyer LO, Schulte K. Load and health monitoring in glass fibre reinforced composites with an electrically conductive nanocomposite epoxy matrix. Compos Sci Technol 2008;68:1886–1894.
101. Fernberg SP, Joffe R. Piezoresistive performance of long-fiber composites with carbon nanotube doped matrix. J Intell Mater Syst Struct 2009;20:1017–1023.
102. Park J, Kim D, Kim S, Kim P, Yoon D, DeVries KL. Inherent sensing and interfacial evaluation of carbon nanofiber and nanotube/epoxy composites using electrical resistance measurement and micromechanical technique. Compos Part B 2007;38:847–861.
103. Chou TW, Gao L, Thostenson ET, Zhang Z, Byun J. An assessment of the science and technology of carbon nanotube-based fibers and composites. Compos Sci Technol 2010;70:1–19.
104. Zhang R, Baxendale M, Peijs T. Universal resistivity–strain dependence of carbon nanotube/polymer composites. Phys Rev B 2007;76:195433.
105. Fernberg P, Nilsson G, Roberts J. Piezoresistive performance of long-fiber composites with carbon nanotube doped matrix. J Intell Mater Syst Struct 2009;20:1017–1023.
106. Gao L, Thostenson ET, Zhang Z, Chou T. Coupled carbon nanotube network and acoustic emission monitoring for sensing of damage development in composites. Carbon 2009;4(7):1381–1388.
107. Berber S, Kwon Y-K, Tománek D. Unusually high thermal conductivity of carbon nanotubes. Phys Rev Lett 2000;84:4613–4616.
108. Choi TY, Poulikakos D, Tharian J, Sennhauser U. Measurement of thermal conductivity of individual multiwalled carbon nanotubes by the 3-omega method. Appl Phys Lett 2005;87:013108.
109. Kim YA, Kamio S, Tajiri T, Hayashi T, Song SM, Endo M, Terrones M, Dresselhaus MS. Enhanced thermal conductivity of carbon fiber/phenolic resin composites by the introduction of carbon nanotubes. Appl Phys Lett 2007;90:093125.
110. Wang S, Qiu J. Enhancing thermal conductivity of glass fiber/polymer composites through carbon nanotubes incorporation. Compos Part B 2010;41:533–536.

111. Chang LN, Chow WS. Accelerated weathering on glass fiber/epoxy/organo-montmorillonite nanocomposites. J Compos Mater 2010;44:1421–1434.
112. Levchik SV, Camino G, Luda MP, Costa L, Muller G, Costes B, Henry Y. Epoxy resins cured with aminophenylmethylphosphine oxide 1: combustion performance. Polym Adv Technol 1996;7:823.
113. Ho SM, Lee YJ. MRL Bull Res Dev 1998;2:27. Q10
114. Shaw SJ. Chemistry and technology of epoxy resins. Glasgow, NZ: Chapman and Hall; 1993. p. 117.
115. Tanaka Y. Epoxy resins chemistry and technology. New York: Dekker; 1988. p. 719.
116. Camino G, Lomakin S. Fire retardant materials. England: Woodhead Publishing Limited, Cambridge CB1 6 AH; 2001. p. 318.
117. Halpern Y, Mott DM, Niswander RH. Ind Eng Chem Prod Res Dev 1984;23:233.
118. Lomakin S, Zaikov GE. Ecological aspects of flame retardancy. Zeis, Netherlands: V S P International Science Publishers; 1999. p. 170.
119. Pilato LA, Koo JH, Wissler GE, Lao S. A review-phenolic and related resins and their nanomodification into phenolic resin FRP systems. J Adv Mater 2008;40(3):5–16.
120. Schartel B, Bartholmai M, Knoll U. Some comments on the use of cone calorimeter data. Polym Degrad Stab 2005;88:540–547.
121. Laoutid F, Bonnaud L, Alexandre M, Lopez-Cuesta JM, Dubois P. New prospects in flame retardant polymer materials: from fundamental to nanocomposites. Mater Sci Eng 2009;63:100–125.
122. Morgan AB, Gagliardi NA, Price WA, Galaska ML. Cone calorimeter testing of S2 glass reinforced polymer composites. Fire Mater 2009;33:323–344.
123. Camino G, Tartaglione G, Frache A, Manferti C, Costa G. Thermal and combustion behaviour of layered silicateeepoxy nanocomposites. Polym Degrad Stab 2005;90:354–362.
124. Zanetti M, Camino G, Mülhaupt R. Combustion behavior of EVA/flourohectorite nanocomposites. Polym Degrad Stab 2001;74:413–417.
125. Gilman JW, Kashiwagi T, Lichtenhan JD. Nanocomposites: a revolutionary new flame retardant approach. SAMPE Journal 1997;33(4):40–46.
126. Gilman JW, Kashiwagi T, Nyden M, Brown JET, Jackson CL, Lomakin S, *et al*. Chemistry and technology of polymer additives. In: Ak-Malaika S, Golovoy A, Wilkie CA, editors. Oxford: Blackwell Science Ltd; 1999. p. 249.
127. Eckel T, Ooms P, Wittmann D, Buysch H-J. German patent DE 42 31 774 A 1. 1994.
128. Klatt M, Grutke S, Heitz T, Rauschenberger V, Plesnivy T, Wolf P, Jwünsch JR, Fischer M. German patent 197 05 998 A1. 1998.
129. Klatt M, Grutke S, Heitz T, Rauschenberger V, Plesnivy T, Wolf P, Jwünsch JR, Fischer M. German patent 197 14 900 A1. 1998.
130. Eckel T, Zobel M, Wittmann D. German patent DE 198 28 536 A 1. 1999.
131. Schall N, Engelhardt T, Simmler- Hübenthal H, Beyer G. German patent DE 199 21 472 A 1. 2000.
132. Gilman JW, Kashiwagi T. Polymer-layered silicate nanocomposites with conventional flame retardants. In: Pinnavaia TJ, Beall GW, editors. Polymer-clay nanocomposites. Chichester: John Wiley & Sons, Inc.; 2000. pp. 193–206, Chapter 10.
133. Beyer G. Flame retardant properties of EVA-nanocomposites and improvements by combination of nanofillers with aluminium trihydrate. Fire Mater 2001;25:193–197.
134. Chigwada G, Wilkie CA. Synergy between conventional phosphorus fire retardants and organically-modified clays can lead to fire retardancy of styrenics. Polym Degrad Stab 2003;81:551–557.
135. Le Bras M, Bourbigot S. Mineral fillers in intumescent fire retardant formulations—criteria for the choice of a natural clay filler for the ammonium polyphosphate/pentaerythritol/polypropylene system. Fire Mater 1996;20:39–49.
136. Bourbigot S, LeBras M, Dabrowski F, Gilman JW, Kashiwagi T. PA-6 clay nanocomposite hybrid as char forming agent in intumescent formulations. Fire Mater 2000;24(4):201–208.
137. Bourbigot S, Duquesne S, Jama C. Polymer nanocomposites: how to reach low flammability? Macromol Sympos 2006;233(1):180–190.
138. Morgan AB. Flame retarded polymer layered silicate nanocomposites: A review of commercial and open literature systems. Polym Adv Technol 2006;17:206–217.
139. Schartel B, Knoll U, Hartwig A, Pütz D. Phosphonium-modified layered silicate epoxy resins nanocomposites and their combinations with ATH and organo-phosphorus fire retardants. Polym Adv Technol 2006;17:281–293.
140. Zanetti M, Lomakin LS, Camino G. Polymer layered silicate nanocomposites. Macromol Mater Eng 2000;279:1.
141. Torre L, Frulloni E, Kenny JM, Manferti C, Camino G. Processing and characterization of epoxy–anhydride-based intercalated nanocomposites. J Appl Polym Sci 2003;90:2532.
142. Zanetti M, Camino G, Reichert P, Moulhaupt R. Thermal behaviour of poly(propylene) layered silicate nanocomposites. Macromol Rapid Comm 2001;22:176.
143. Zanetti M, Camino G, Canavese D, Morgan AB, Lamelas FJ, Wilkie CA. Fire retardant halogen-antimony-clay synergism in polypropylene layered silicate nanocomposites. Chem Mater 2002;14:189–193.
144. Zanetti M, Kashiwagi T, Falqui L, Camino G. Cone calorimeter combustion and gasification studies of polymer layered silicate nanocomposites. Chem Mater 2002;14:881–887.
145. Schartel B, Weir A, Sturm H, Kleemeier M, Hartwig A, Vogt C, Fischer RX. Layered silicate epoxy nanocomposites: formation of the inorganic-carbonaceous fire protection layer. Polym Adv Technol 2010. DOI: 10.1002/pat.1644.
146. Duquesne S, Jama C, Bras ML, Delobel R, Recourt P, Gloaguen JM. Elaboration of EVA-nanoclay systems-characterization, thermal behaviour and fire performance. Compos Sci Technol 2003;63:1141–1148.
147. Gilman JW, Jackson CL, Morgan AB, Harris R, Manias E, Giannelis EP, Wuthenow M, Hilton D, Phillips SH. Flammability properties of polymer layered silicate nanocomposites. Polypropylene and polystyrene nanocomposites. Chem Mater 2000;12:1866–1873.
148. Gilman JW. Flammability and thermal stability studies of polymer-layered silicate clay nanocomposites. Appl Clay Sci 1999;15:31–49.
149. Kashiwagi T, Harris RH Jr, Zhang X, Briber RM, Cipriano BH, Raghavan SR, Awada WH, Shields JR. Flame retardant mechanism of polyamide 6–clay nanocomposites. Polymer 2004;45:881–891.

150. Boerdiger M, Eckel T, Wittmann D, Alberts H. German patent DE 195 30 200 A 1. 1997.
151. Gilman JW, Kashiwagi T, Giannelis EP, Manias E, Lomakin S, Lichtenham JD, Jones P. Nanocomposites: radiative gasification and vinyl polymer flammability. In: Le Bras M, Camino G, Bourbigot S, Delobel R, editors. Fire retardancy of polymers: the use of intumescence. Cambridge: Royal Society of Chemistry; 1998. pp. 203–221.
152. Pastore HO, Frache A, Boccaleri E, Marchese L, Camino G. Heat induced structure modifications in polymer-layered silicate nanocomposites. Macromol Mater Eng 2004;289(9):783–786.
153. M Lewin, Some comments on the modes of action of nanocomposites in the flame retardancy of polymers, Fire Mater 2003;27:1–7.
154. Lewin M. Reflections on migration of clay and structural changes in nanocompositesy. Polym Adv Technol 2006;17:758–763.
155. Kashiwagi T, Du F, Winey KI, Groth KM, Shields JR, Bellayer SP, Kim H, Douglas JF. Flammability properties of polymer nanocomposites with single-walled carbon nanotubes: effects of nanotube dispersion and concentration. Polymer 2005;46:471–481.
156. Kashiwagi T, Du F, Douglas JF, Winey KI, Harris RH, Shields JR. Nanoparticle networks reduced the flammability of polymer nanocomposites. Nat Mater 2005;4:928–933.
157. Cipiriano BH, Kashiwagi T, Raghavan SR, Yang Y, Grulke EA, Yamamoto K, Shields JR, Douglas JF. Effects of aspect ratio of MWNT on the flammability properties of polymer nanocomposites. Polymer 2007;48:6086–6096.
158. Kashiwagi T, Mu M, Winey K, Cipriano B, Raghavan SR, Pack S, Rafailovich M, Yang Y, Grulke E, Shields J, Harris R, Douglas J. Relation between the viscoelastic and flammability properties of polymer nanocomposites. Polymer 2008;49:4358–4368.
159. Zhao Z, Gou J. Improved fire retardancy of thermoset composites modified with carbon nanofibers. Sci Technol Adv Mater 2009;10:015005.
160. Rahatekara SS, Zammarano M, Matko S, Koziol KK, Windle AH, Nyden M, Kashiwagi T, Gilman JW. Effect of carbon nanotubes and montmorillonite on the flammability of epoxy nanocomposites. Polym Degrad Stab 2010;95:870–879.
161. Steurer P, Wissert R, Thomann R, Mülhaupt R. Functionalized graphenes and thermoplastic nanocomposites based upon expanded graphite oxide. Macromol Rapid Commun 2009;30:316–327.
162. Zhang R, Hu Y, Xu J, Fan W, Chen Z. Flammability and thermal stability studies of styrene-butyl acrylate copolymer/graphite oxide nanocomposite. Polym Degrad Stab 2004;85:583–588.
163. Zhang R, Hu Y, Xu J, Fan W, Chen Z, Wang Q. Preparation and combustion properties of flame retardant styrene-butyl acrylate copolymer/graphite oxide nanocomposites. Macromol Mater Eng 2004;289:355–359.
164. Tang Y, Zhuge J, Gou J, Chen R-H, Ibeh C, Hu Y. Morphology, thermal stability, and flammability of polymer matrix composites coated with hybrid nanopapers. Polym Adv Technol. DOI: 10.1002/pat.1621.
165. Zhuge J, Tang Y, Gou J, Chen R-H, Ibeh C, Hu Y. Flammability of carbon nanofiber–clay nanopaper based polymer composites. Polym Adv Technol 2010. DOI: 10.1002/pat.1753.
166. Zhao ZF, Gou JH, Bietto S, Ibeh C, Hui D. Fire retardancy of clay/carbon nanofiber hybrid sheet in fiber reinforced polymer composites. Compos Sci Technol 2009;69:2081–2087.
167. Pilato L. Phenolic resins: a century of progress. Springer; 2010. p. 600. ISBN:3642047130. Q11
168. Stephen GK, Hiltz JA, Waitkus PA. Impact performance of phenolic composites following thermal exposure. J Appl Polym Sci 1998;67:349–361.
169. Firouzmanesh MR, Aref Azar A. Study of thermal stability and ablation behavior of carbon/epoxy-novolac composites. J Appl Polym Sci 2003;88:2455–2461.
170. Patel K, Pappas J, Nauman EB. Structure and properties of phenolic resin/nanoclay composites synthesized by *in situ* polymerization. J Appl Poly Sci 2005;95(5):1169.
171. Natali M, Kenny J, Torre L. Phenolic matrix nanocomposites based on commercial grade resols: synthesis and characterization. Compos Sci Technol 2010;70(4):571–577.
172. Natali M, Monti M, Kenny J, Torre L. Synthesis and thermal characterization of phenolic resin/silica nanocomposites prepared with high shear rate-mixing technique. J Appl Poly Sci. DOI: 10.1002/app.33494.
173. Wu Z, Zhou C, Qi R. The preparation of phenolic resin/montmorillonite nanocomposite by suspension condensation polymerization and their morphology. Poly Compos 2002;23(4):634.
174. Chiang CL, Ma CCM, Wu DL, Kuan HC. Preparation, characterization and properties of novolac type phenolic/SiO2 hybrid organic/inorganic nano-composite materials by sol–gel method. J Polym Sci A Polym Chem 2003;41:905–913.
175. Wang H, Zhao T, Yan Y. Synthesis of resol–layered silicate nanocomposites by reaction exfoliation with acid-modified montmorillonite. J Appl Polym Sci 2004;92:791–797.
176. Kato M, Tsukigase A, Usuki A, Shimo T, Yazawa H. Preparation and thermal properties of resole-type phenol resin-clay nanocomposites. J Appl Poly Sci 2006;99:3236–3240.
177. Jiang W, Chen S-H, Chen Y. Nanocomposites from phenolic resin and various organo-modified montmorillonite: preparation and thermal stability, ibid. J Appl Polym Sci 2006;102:5336.
178. Kaynak C, Tasan C. Effects of production parameters on the structure of resol type phenolic resin/layered silicate nanocomposites. Eur Polym J 2006;42:1908–1921.
179. Srikantha I, Daniela A, Padmavathib SKN, Singhb V, Ghosal P. Nano silica modified carbon–phenolic composites for enhanced ablation resistance. Scr Mater 2010;63(2):200–203.
180. Koo JH, Chow WK, Stretz H, Cheng AC-K, Bray A, Weispfenning J. Flammability properties of polymer nanostructured materials. Proceedings SAMPE 2003 International Symposium, SAMPE, Covina, CA, May 2003.
181. Tate JS, Kabakov D, Koo JH, Lao SC. Nanomodified phenolic/E-glass composites. Proceedings SAMPE 2009, Baltimore, MD, May 2009.
182. Bahramian AR, Kokabi1 M, Beheshty MH, Famili MHN. Thermal degradation process of resol type phenolic matrix/kaolinite layered silicate nanocomposite. Iran Polym J 2007;16(6):375–387.

FURTHER READING

Alexandre M, Beyer G, Henrist C, Cloots R, Rulmont A, Jerome R. Preparation and properties of layered silicate nanocomposites based on ethylene vinyl acetate copolymers. Macromol Rapid Commun 2001;22:643–646.

Bartholmai M, Schartel B. Layered silicate polymer nanocomposites: new approach or illusion for fire retardancy? Investigations of the potentials and the tasks using a model system. Polym Adv Technol 2004;15:355–364.

Q12 Beyer G. Polym News 2001;26:334–342.

Gilman JW, Jackson CL, Morgan AB, Harris R, Manias E, Giannelis EP. Chem Mater 2000;12:1866.

Gilman JW, Kashiwagi T, Giannelis EP, Manias E, Lomakin S, Lichtenhan JD, *et al*. Fire retardancy of polymers: the use of intumescence. In: Camino G, Le Bras M, Bourbigot S, DeLobel R, editors. The royal society of chemistry. Cambridge; 1998. p. 203. Q13

Kojima Y, Usuki A, Kawasumi M, Okada A, Fukushima Y, Kamigaito O. Mechanical properties of nylon 6-clay hybrid. J Mater Res 1993;8:1185.

Wang Z, Pinnavaia T. Hybrid organic-inorganic nanocomposites: exfoliation of magadiite nanolayers in an elastomeric epoxy polymer. J Chem Mater 1998;10:1820.

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Q14

Keywords: polymer nanocomposites; mechanical properties; electrical properties; carbon fibers; carbon nanotubes