

Phenylethynyl-terminated polyimide, exfoliated graphite nanoplatelets, and the composites: an overview

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Article Info

Received 21 December 2015

Accepted 21 June 2016

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Open Access

DOI: <http://dx.doi.org/10.5714/CL.2016.19.001>

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Abstract

In efforts to characterize and understand the properties and processing of phenylethynyl-terminated imide (LaRC PETI-5, simply referred to as PETI-5) oligomers and polymers as a high-temperature sizing material for carbon fiber-reinforced polymer matrix composites, PETI-5 imidization and thermal curing behaviors have been extensively investigated based on the phenylethynyl end-group reaction. These studies are reviewed here. In addition, the use of PETI-5 to enhance interfacial adhesion between carbon fibers and a bismaleimide (BMI) matrix, as well as the dynamic mechanical properties of carbon/BMI composites, are discussed. Reports on the thermal expansion behavior of intercalated graphite flake, and the effects of exfoliated graphite nanoplatelets (xGnP) on the properties of PETI-5 matrix composites are also reviewed. The dynamic mechanical and thermal properties and the electrical resistivity of xGnP/PETI-5 composites are characterized. The effect of liquid rubber amine-terminated poly(butadiene-*co*-acrylonitrile) (ATBN)-coated xGnP particles incorporated into epoxy resin on the toughness of xGnP/epoxy composites is examined in terms of its impact on Izod strength. This paper provides an extensive overview from fundamental studies on PETI-5 and xGnP, as well as applied studies on relevant composite materials.

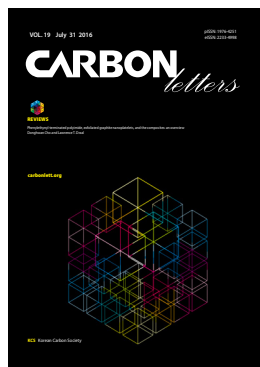
Key words: polyimide, exfoliated graphite nanoplatelets, carbon fiber, composite, properties

1. Phenylethynyl-Terminated Imide Polymer

Polyimides have been extensively used in the electronics industry [1] as coatings, films, or adhesives and also in composite applications [2] as a primary or secondary structural material. When incorporated with organic or inorganic fibers, including carbon fibers and glass fibers, they can potentially be applied as a sizing material for high-temperature uses. In advanced applications, one of the most desirable advantages of polyimides, especially the aromatic polyimides, is their excellent high-temperature performance. Their thermal characteristics, including high temperature stability and cure behavior, are critical to successful processing and to the final properties of the resulting polyimide. For aerospace and aircraft applications, advanced polymer materials must successfully maintain their properties at high service temperatures over a long exposure time [3-5].

The important parameters influencing the heat resistance of a polymeric material are its glass transition temperature (T_g), melting point (T_m), thermal stability, and etc., which may depend on its thermal history. Accordingly, polymers that are used to fulfill such high temperature performance should exhibit a high T_g or T_m and have excellent thermal stability. Even though some polyimides meet the high temperature requirement, their uses have been limited due to processing difficulties, such as poor solubility in common solvents, the release of volatiles, brittleness, and high processing temperature [6,7].

Aromatic polyimides, especially acetylene or ethynyl-terminated polyimides, have been extensively studied over the past two decades as candidate resins for advanced applications due to their unique combination of properties [8-12]. In the 1990s a variety of phenylethynyl-



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pISSN: 1976-4251

eISSN: 2233-4998

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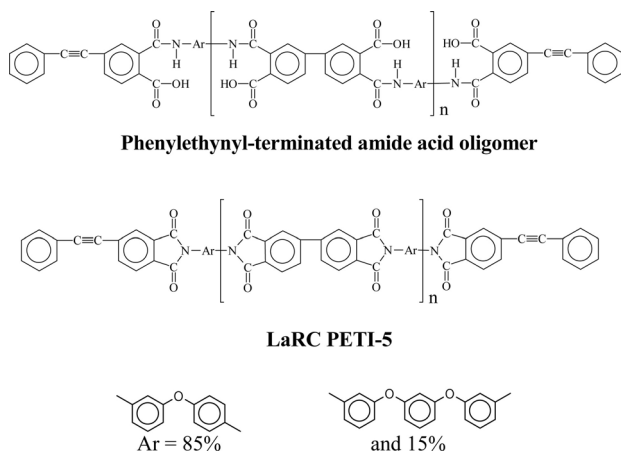


Fig. 1. Chemical structures of phenylethynyl-terminated amide acid oligomer and polymer, simply referred to as LaRC PETI-5.

terminated imide oligomers for high-temperature aerospace and aircraft applications, known as phenylethynyl-terminated imide (LaRC PETI), were developed at the National Aeronautics and Space Administration (NASA) Langley Research Center, USA [13-19]. These materials have broader processing windows and thermal oxidative stability than simple ethynyl-terminated materials, and consequently have many practical advantages as a potential material for coatings, adhesives, films, and composite matrix resins [20,21].

Among the LaRC PETI series, it was found that a PETI-5 version with a molecular weight of 2500 g/mol exhibits an excellent combination of processing, toughness, thermal, mechanical, physical, and chemical performances at elevated temperature [22].

Phenylethynyl-terminated polyimides require high temperature treatment to completely remove solvents, and also to convert the oligomeric precursor into cured polyimide. The LaRC PETI-5 amide acid oligomer is imidized via cyclodehydration between the amide and carboxylic acid groups to form the corresponding LaRC PETI-5 polyimide on heating, as indicated in Fig. 1 (hereinafter, LaRC PETI-5 will simply be referred to as PETI-5). During thermal cure this material undergoes a complex reaction involving crosslinking and chain extension of the phenylethynyl groups located on the imide polymer chain ends, without releasing volatiles [21-23].

The neat PETI-5 resin is very viscous and may be applied to the surface of various substrates as a sizing, coating, matrix prepreg, or adhesive. Because processing generally requires the resin to be exposed to a prescheduled temperature and time cycle, to optimize resin processing and properties it is necessary to understand the chemical changes that occur in the PETI-5 during imidization, curing, and consolidation.

2. Phenylethynyl End-Group Reaction Behavior of PETI-5 [24]

Fourier transform infrared (FTIR) spectroscopy is a powerful tool used to monitor chemical changes that occur during thermal treatment. The FTIR method has also been successfully used

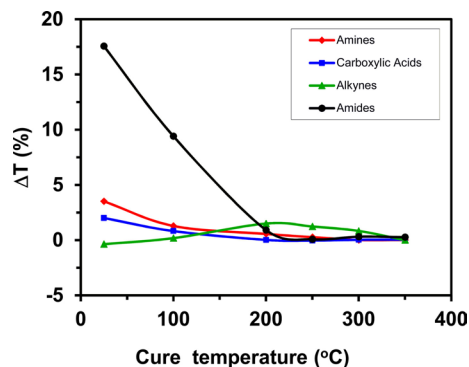


Fig. 2. Variations of characteristic infrared absorption peaks resulting from some chemical groups in phenylethynyl-terminated amide acid oligomer during cure at different temperatures [24].

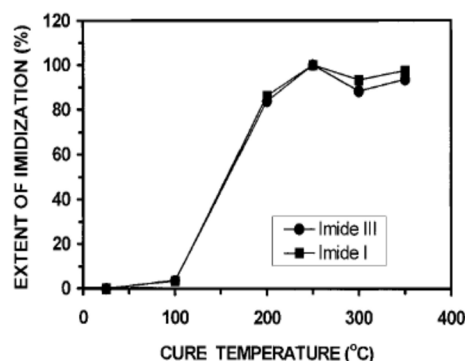


Fig. 3. The extent of imidization as a function of cure temperature determined from the absorption peaks of imides I and III [24].

in many research areas to study the curing [25], thermal aging [26], crosslinking reaction [5], semi-interpenetrating networks [27,28], as well as structure identification [29,30] of polyimides.

The imidization of PETI-5 has been monitored by examining the disappearance and appearance of the most characteristic infrared absorption bands, and by monitoring the variation of representative amide acid and imide peaks observed via imidization, during cure of PETI-5 at different temperatures. In Fig. 2, the ΔT (%) values determined from amide, amine, and carboxylic acid groups are shown to decrease with increasing temperature, and are constant above 250°C. The ΔT (%) values were calculated from the difference in transmittance values between the absorption maximum and the minimum in close proximity to the characteristic absorption peak. All the values are close to zero at 350°C. This indicates that the conversion of the phenylethynyl-terminated amide acid oligomer into the corresponding imide polymer proceeds rapidly at around 200°C, becomes less reactive with temperature, and is complete around 250°C. The reduction of the ΔT value for the amide group is remarkable and the value approaches close to zero around 220°C. The amide groups in the oligomer are substantially consumed first during the imidization reaction.

FTIR analysis also provides useful information on the extent of conversion of poly(amide acid) into polyimide through imidization [31,32]. The extent of imidization can be determined from the heights of the absorption bands for imides I and III,

normalized to the height of the absorption band for 'as-received' PETI-5, at 1374 and 1777 cm^{-1} , respectively. In Fig. 3, the imidization reaction initiates around 100°C, increases linearly up to about 200°C, and then proceeds slowly to 250°C. This can be explained by the fact that below 200°C the solvent in the neat resin does not play an important role in the reaction but still contributes to stabilizing the conformation of amide acid.

The values of the extent of imidization determined for PETI-5 at various temperatures are similar to a polyimide system with different monomers, studied by Ishida et al. [33]. A small decrease in the extent of reaction after 250°C is probably due to a lack of sensitivity in detecting the vibrational segmental motion in the fully imidized molecular chains using FTIR spectroscopy, resulting from an increase in the local viscosity in the sample.

In summary, the phenylethynyl end-group reaction of PETI-5 can be well monitored by inspecting the disappearance and appearance of FTIR absorption bands of characteristic chemical groups, and it was found that the phenylethynyl-terminated amide acid was completely converted to polyimide at about 250°C.

3. Curing Behavior of PETI-5 [23]

The extent of cure of thermosetting resins can often be determined from differential scanning calorimetry (DSC) data, in terms of the heat of reaction. Fig. 4 exhibits the variation in the extent of cure of PETI-5 exposed to two different thermal histories, individual and cumulative cure conditions, and as a function of temperature, respectively. The extent of cure can be calculated from the changes in the exothermic peak areas. The cumulatively cured material exhibits a higher extent of cure than the one cured individually over the entire temperature range up to complete cure, with the exception of those cured at 300°C. It should also be noted that the material starts to cure slowly and partially at a temperature lower than the imidization temperature. The cure accelerates around the imidization temperature. The extent of cure of the cumulatively cured sample in the imidization temperature re-

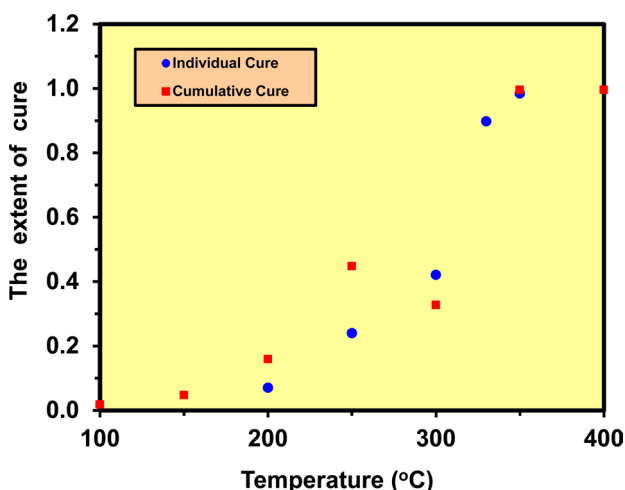


Fig. 4. Variations in the extent of cure as a function of temperature for LaRC PETI-5 with different cure histories [23]. LaRC PETI-5, phenylethynyl-terminated imide.

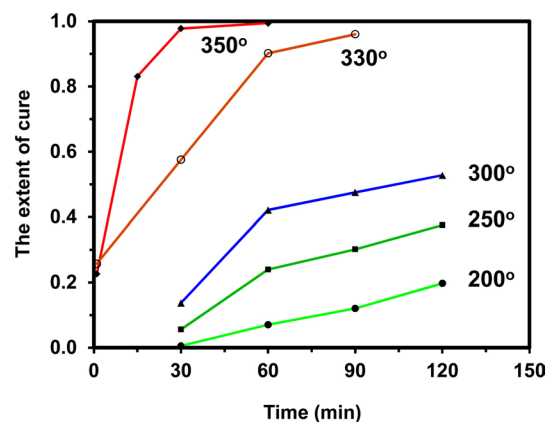


Fig. 5. Effect of isothermal cure at different temperatures on the extent of cure [23].

gion (200°C–250°C) is about twice that of the individually cured sample. The thermal history of the imidization reaction may significantly influence the extent of cure of the partially cured resin. The extent of cure increases most in the range of 300°C–350°C, where the reaction of the phenylethynyl end-group predominates.

The T_g increases very slowly with increasing cure time below 300°C. This indicates that such temperatures do not significantly influence the chain stiffness of the polymer even after an extended period of time. However, the T_g increases rapidly with time above 330°C, showing that the T_g already has reached a higher temperature (about 280°C) than the temperature required for full imidization. Similar to the tendency of the T_g change, the extent of cure increases gradually with temperature up to 300°C after 60 min isothermal cure, as seen in Fig. 5. Such a large increase between 300°C and 350°C in the isothermally cured sample is consistent with the result obtained from the cumulatively cured sample. Upon thermal cure, temperatures greater than the imidization temperature lead to a higher T_g and extent of cure. Therefore, a cure temperature of around 350°C in air produces a fully cured PETI-5 within an hour.

In summary, the curing behavior of PETI can be monitored either by a dynamic heating method (individual or cumulative cure) or by an isothermal method. It is concluded that the T_g of PETI-5 increases with increasing cure time as well as cure temperature, and heat treatment of PETI-5 at 350°C for 1 h in air is sufficient for full curing.

4. Imidization and Cure Reaction of PETI-5 Impregnated Glass Fabrics [34]

Many investigators have utilized a variety of analytical methods to examine the imidization and/or cure of ethynyl- or phenylethynyl-terminated imide polymers, including, for example, FTIR [19,24,35], DSC [19,23,36], thermogravimetric analysis (TGA) [23], high performance liquid chromatography (HPLC) [4], and solid-state ^{13}C nuclear magnetic resonance (NMR) [37] methods. Nonetheless, each of the approaches has limitations. FTIR measurement may restrict further monitoring of the cure behavior of PETI-5 occurring

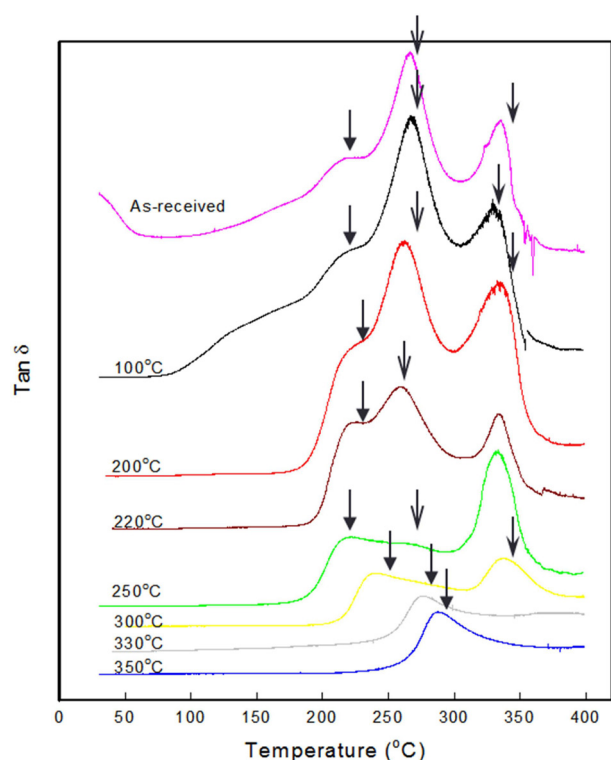


Fig. 6. Variations of $\tan \delta$ as a function of temperature in PETI-5/braided glass fabric specimens cured at different temperatures. The arrows on the left designate glass transition peaks, the arrows in the middle designate imidization peaks, and the arrows on the right designate cure reaction peaks [34]. PETI-5, phenylethynyl-terminated imide.

above the full imidization temperature, even though the presence and absence of the FTIR absorption band of the phenylethynyl end group can be successfully detected, depending on the thermal cure history. This is because the glass transition temperature and chain stiffness of the imide polymer increase with increasing degree of cure and the local mobility of the chain segments is largely restricted while being consolidated [24]. DSC may also limit further understanding of the imidization behavior occurring in the early stage, during consolidation, even though it provides useful information on cure behavior [23]. Solid-state ^{13}C NMR can provide chemical identification of the molecular structure of cured polyimides, but it cannot give detailed information for monitoring imidization and cure [37].

Dynamic mechanical analysis (DMA) is a very powerful technique for obtaining information on the thermo-mechanical behavior of polymers, and is based on the temperature dependence of storage modulus, loss modulus and $\tan \delta$. The glass transition temperature and other physical transition temperatures can be determined from the peak of the $\tan \delta$ or loss modulus, which are sensitive to molecular mobility, stiffness behavior, phase transformation and morphological change [38]. Owing to its analytical advantage in providing molecular information and ease of use, the DMA technique has been widely used to explore the thermal mechanical behavior of not only viscoelastic polymer materials [5], blends

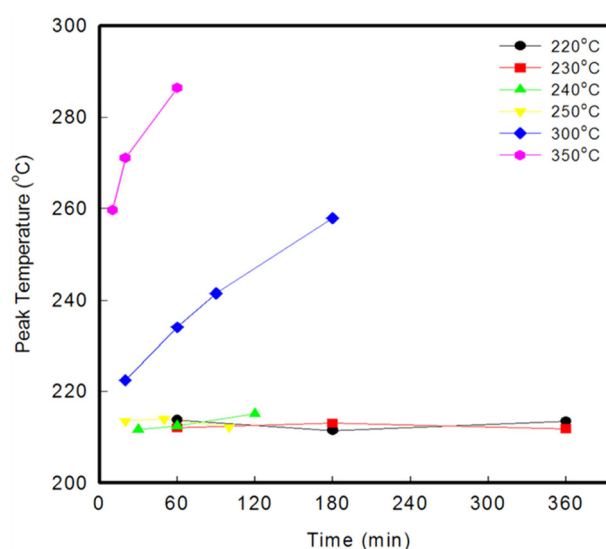


Fig. 7. Effect of isothermal cure at various temperatures on the $\tan \delta$ peak temperature as a function of time in PETI-5/braided glass fabric specimens [34]. PETI-5, phenylethynyl-terminated imide.

[39] and polymeric composites [40,41] but also at the interface or sizing interphase [42-44] between fiber and matrix in a composite system. Also, the reaction behavior can be observed using this method, because changing thermal conditions can change molecular states during the transformation from amide acid to fully cured polyimide.

Imidization and cure reaction behaviors have been simultaneously monitored during cumulative and isothermal cure processes, based on the dynamic mechanical behavior of a phenylethynyl imide oligomer material impregnated in a glass fabric composite system, using DMA. The chain stiffness, and the corresponding storage modulus of PETI-5, increases with increasing cure temperature as the amide acid transforms into imide oligomer and then polyimide. The dynamic mechanical property of PETI-5 strongly depends on thermal history, especially above 300°C.

The three distinguishable peaks in the $\tan \delta$ curves, as shown in Fig. 6, indicate the glass transition temperature, the imidization temperature, and the cure reaction temperature from each peak, respectively. The completion and incompleteness of the imidization or cure reaction occurring during cumulative and isothermal cure processes is demonstrated by the absence and presence of an imidization peak, or a cure reaction peak. The degree of cure increases with a higher rate, above 250°C, and then greatly increases near full cure temperature due to the rapid development of a three dimensionally crosslinked network structure. With the cumulative or isothermal curing process, the PETI-5 imide oligomer can be converted to a fully cured polyimide at 350°C for 1 h, as indicated in Fig. 7.

In summary, it was found that impregnating PETI-5 in a glass fabric, and its thermal cure history, significantly influenced the dynamic mechanical properties of the fiber sizing material and accordingly, the fiber-reinforced composite material.

5. Improvement in Adhesion of Carbon Fiber/BMI Composites Using a High Temperature Sizing Material, PETI-5 [45]

Carbon fiber/bismaleimide (BMI) composite materials are currently utilized for commercial and military aircraft and aerospace applications [46]. However, these materials have some critical issues, such as brittleness and loss of properties due to microcracking and thermal degradation. The level of fiber-matrix adhesion for carbon/BMI composites has been measured using a variety of adhesion tests, and it has been found that in general the adhesion is very low [47]. Therefore, achieving better adhesion in carbon/BMI composites has become an important research objective [48].

Adhesion, or the interfacial strength between fibers and matrix, is critically important in a carbon/polymer composite material because the ultimate mechanical properties and performance of the material strongly depend on it [49]. There have been considerable efforts to improve the interfacial properties of carbon fiber-reinforced polymer matrix composites. They include changes in fiber surface energy [50], surface morphology [51], surface chemistry [52] and resin chemistry [53], and fiber sizing [54]. Sizing is normally used to provide better adhesion between fibers and matrix in a composite system [55] as well as to improve the handleability and reduce fiber damage during fabrication of the prepreg and composite [56]. The proper sizing material has high thermal stability and durability, and these properties are desirable because a beneficial interphase may be created if there is appropriate miscibility between the sized material and matrix resin. Optimizing the sizing interphase and sizing process is, of course, necessary to obtain the desired ultimate properties of a composite.

In general, the experimental methods used to characterize the fiber-matrix interphase have been based on single fiber-matrix interfacial measurements, such as the single fiber fragmentation test, single fiber pull-out test and microbonding test; or they have been based on direct interfacial measurements of the actual composite laminate, such as the transverse tensile test, short-beam shear test, and micro-indentation test. Excellent review articles describing these experimental methods and the measurement of fiber-matrix adhesion in composites have been published elsewhere [49,57-59].

PETI-5 oligomer has been applied as a sizing material onto the surfaces of polyacrylonitrile (PAN)-based carbon fiber tows and woven carbon fabrics, to introduce an interphase between the fibers and matrix in carbon/BMI composites. The adhesion between the fibers and matrix was largely enhanced by the PETI-5 interphase. For evaluating the fiber-matrix adhesion of fiber-reinforced plastics, interfacial shear strength and/or interlaminar shear strength (ILSS) tests can often provide very useful information [60-62]. Short-beam shear test results have indicated that when PETI-5 was sized at 150°C, the ILSS of a 2-directional carbon/BMI composite was markedly improved, by about 35% and 66%, respectively, in comparison to an unsized counterpart, as seen in Fig. 8. The adhesion enhancement strongly depends not only on the presence and absence of the PETI-5 sizing interphase, but also on sizing temperature, because both factors critically influence the physical and chemical state of the sizing

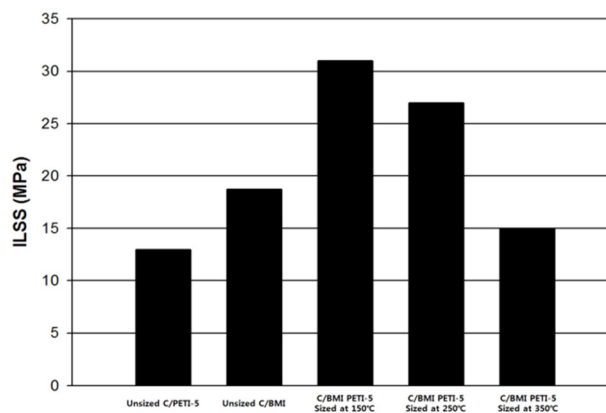


Fig. 8. A comparison of the interlaminar shear strengths for carbon/BMI composites with unsized and sized PETI-5 at different temperatures, and an unsized carbon/PETI-5 [46]. ILSS, interlaminar shear strength; BMI, bismaleimide; PETI-5, phenylethynyl-terminated imide.

material.

In summary, sizing the PET-5 at 150°C prior to composite processing is appropriate to increase the interfacial and ILSSs of carbon fiber reinforced BMI composites.

6. Expansion Behavior of Graphite Flake [63]

Like layered silicates, graphite is a layered mineral having a large aspect ratio. It consists of a huge number of graphene layers held together by weak van der Waals forces. Theoretically, single crystal graphite has an elastic modulus of over 1 TPa, which is many times greater than nanoclay. Unlike clay, graphite is thermally and electrically conductive. Expandable graphite, which is composed of natural graphite flake intercalated with acid, can be expanded up to hundreds of times its initial volume at high temperature, resulting in separation of the graphene sheets at the nanoscopic level along the c axis of the graphene layers [64-67]. The extent of expansion may depend on the heat-treatment temperature, processing method, the amount of intercalant, and the stage index of intercalant [67,68]. The intercalated graphite flake material is also referred to as a graphite intercalation compound [68,69].

Fig. 9 shows the thermal expansion behavior of a single intercalated graphite flake as a function of temperature, as studied by thermomechanical analysis (TMA) [63]. The result reveals that the onset temperature of expansion is about 160°C–170°C. The expansion takes place most rapidly in the range of 220°C–240°C, and the expansion ratio is approximately 20–35, which is much less than expected. The following three reasons explain why. First, during the measurement the flake is substantially loaded by the TMA probe itself, by a minimum normal force of 0.005 N in the direction opposite to the expansion. Therefore, the expansion is significantly suppressed under the probe during the measurement. Second, the expansion proceeds in a twisting and bending configuration, not in a single straightforward direction. Third, the TMA instrument normally cannot successfully monitor extremely rapid expansion, meaning it is measuring just a partial range of the expansion, not the full range.

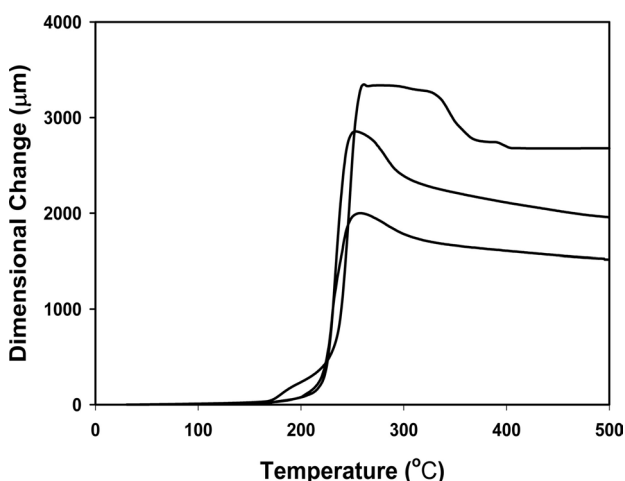


Fig. 9. Thermomechanical analysis curves monitoring the expansion behavior of a single intercalated graphite flake as a function of temperature [64].

Much attention has been paid to carbon nanoparticle-based polymer materials with high performance and/or functionality, for the purpose of improving the polymer properties and extending their applications [70-72]. By utilizing layered reinforcements with a large aspect ratio, such as graphite flake, which can be exfoliated and dispersed in a polymer matrix as nanoplatelets, polymer nanocomposites have exhibited improved mechanical, thermal and barrier properties, depending upon the type of nanoplatelets [73-75].

7. Dynamic Mechanical and Thermal Properties of PETI-5/xGnP Composites [76]

One approach to further improving polymer properties involves preparing polymer composites that are composed of a thermally stable polymer matrix reinforced with exfoliated graphite nanoplatelets (xGnP) [77-79]. Nano-sized graphite

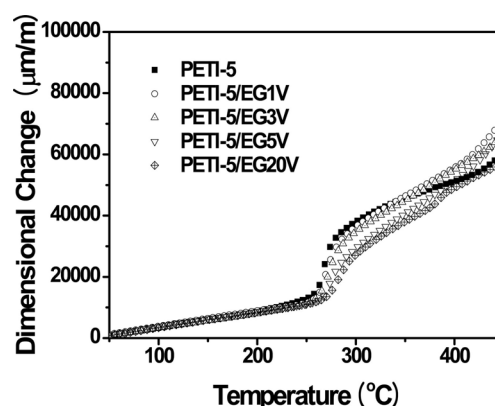


Fig. 10. TMA curves showing the thermal expansion behavior for cured PETI-5 resin and PETI-5/xGnP composites with various vibratory ball-milled xGnP contents (EG#V) [77]. PETI-5, phenylethynyl-terminated imide; xGnP, exfoliated graphite nanoplatelets.

flakes can be expanded and exfoliated and then pulverized to produce reinforcement with pristine characteristics.

The dynamic mechanical and thermal properties of PETI-5 composites reinforced with three types of xGnP having an average particle size of 1 μm , 7 μm , and 19 μm have been studied. The xGnP samples were prepared by ultrasonication and vibratory ball-milling techniques, respectively. As listed in Table 1, the DMA results demonstrate that reinforcing the PETI-5 resin with the xGnP particles increased its storage modulus, both through a composite reinforcing mechanism, and by decreasing the flexibility of the PETI-5 molecular chain in the composite. The storage modulus of cured PETI-5 polymer was significantly enhanced by the incorporation of xGnP in the matrix. The storage modulus of PETI-5/xGnP composites increases with increasing xGnP content, and also by decreasing the average particle size from 19 μm to 7 μm and to 1 μm . The improvement in storage modulus is also greater in the temperature range above the T_g than below the T_g .

Table 1. A summary of the storage moduli of PETI-5/xGnP composites at 100°C and 200°C [12]

Composite specimen	Storage modulus at 100°C (GPa)	Improvement from control (%)	Storage modulus at 200°C (GPa)	Improvement from control (%)
PETI-5 Control	0.897	0	0.716	0
PETI-5/EG1U	1.133	26.3	0.944	31.8
PETI-5/EG3U	1.193	33.0	0.981	37.0
PETI-5/EG5U	1.255	39.9	1.070	49.4
PETI-5/EG10U	1.276	42.3	1.116	55.9
PETI-5/EG1V	0.939	4.7	0.768	7.3
PETI-5/EG3V	0.902	0.6	0.746	4.2
PETI-5/EG5V	1.295	44.4	1.095	52.9
PETI-5/EG20V	1.604	78.8	1.375	92.0

PETI-5, phenylethynyl-terminated imide; xGnP, exfoliated graphite nanoplatelets.

The coefficient of thermal expansion (CTE) of PETI-5/xGnP composites is slightly lower than that of cured PETI-5 in the temperature region below the glass transition, as indicated in Fig. 10. In the glass transition region where enhanced thermal expansion takes place, the thermal expansion of the composites significantly decreases with increasing xGnP content. A lower CTE value was obtained with smaller average particle size xGnP, because it allowed better dispersion of the xGnP in the composite matrix.

In summary, the dynamic mechanical properties, the T_g and the CTE of xGnP-incorporated polymer composites all depend on the particle size, pulverization method, and concentration of PETI-5.

8. Effect of xGnP on the Electrical Resistivity of PETI-5 [80]

In recent years, many research efforts have been devoted to studying the effect of carbon nanoparticles, such as xGnP and carbon nanotubes, on the mechanical, thermal, and/or electrical properties of various polymers [80-88].

Fig. 11 displays the variations in the electrical resistivity of PETI-5 and PETI-5/xGnP composites as a function of xGnP content. Resistivity is gradually decreased by increasing xGnP. It seems that the percolation threshold occurs at 5 wt%. This result is consistent with an earlier study on xGnP-polypropylene composites processed by injection molding and compression molding, as reported by Kalaitzidou et al. [82]. Also, the incorporation of small sized (1 μm) xGnP into PETI-5 helps to reduce the amount of xGnP needed to reach the percolation threshold, because the presence of small xGnP particles increases the number of xGnP-PETI-5 interfaces, increasing the number of contact points between the xGnP and PETI-5. At 20 wt%, the electrical resistivity was decreased to about $3 \times 10^3 \text{ ohm}\cdot\text{cm}$.

In summary, the incorporation of xGnP into PETI-5 has a significant effect on decreasing electrical resistivity, suggesting that an optimal concentration of xGnP should be determined.

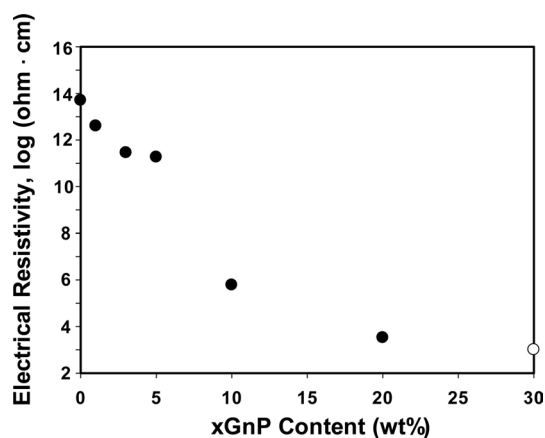


Fig. 11. Variations in the electrical resistivity of PETI-5/xGnP composites as a function of xGnP loading [81]. PETI-5, phenylethynyl-terminated imide; xGnP, exfoliated graphite nanoplatelets.

9. Coating of xGnP with ATBN and an Epoxy Composite [89]

Recently, a large number of papers have reported studies to modify carbon nanoparticles in efforts to improve their dispersibility in polymer, as well as in solutions, and ultimately to increase targeted properties of polymers [91,92]. The modification of carbon nanoparticles has often focused on chemical modification or functionalization, to covalently attach specific functional groups to their surfaces and edges [93-96].

Amine-terminated poly(butadiene-*co*-acrylonitrile) (ATBN) is a liquid rubber with amine groups at the ends, and butadiene and acrylonitrile groups in the repeating unit. Due to their many advantages, liquid rubbers, including ATBN or carboxyl-terminated poly(butadiene-*co*-acrylonitrile) (CTBN), have been utilized to make brittle polymers more ductile, and in particular to toughen thermosetting polymers such as epoxy, unsaturated polyester, vinyl ester, and phenolic resins [97-99].

Epoxy resins have versatile applications due to their excellent mechanical, thermal, and electrical, and adhesive properties. However, their brittleness restricts other potential uses. ATBN has been utilized as an impact modifier of epoxy for this reason [97,100,101]. In many cases, a relatively large amount of ATBN, higher than 10 wt%, has been used to toughen epoxy, resulting in a considerable decrease in mechanical and thermal properties [101,102].

Other work has been motivated by the hypothesis that incorporating a small amount of xGnP particles coated with ATBN into a thermosetting polymer would contribute to toughening the thermosetting polymer, if the elastomeric coating performed well. Fig. 12 shows the effect of ATBN coating concentration on the impact strength of uncoated and ATBN-coated xGnP/epoxy composites. The xGnP (here referred to as EGN) content was fixed at 1 wt% of the epoxy content. The impact strength of the cured epoxy composites was gradually increased by increasing the ATBN coating concentration, indicating a toughening effect. The maximum impact strength was obtained when the xGnP

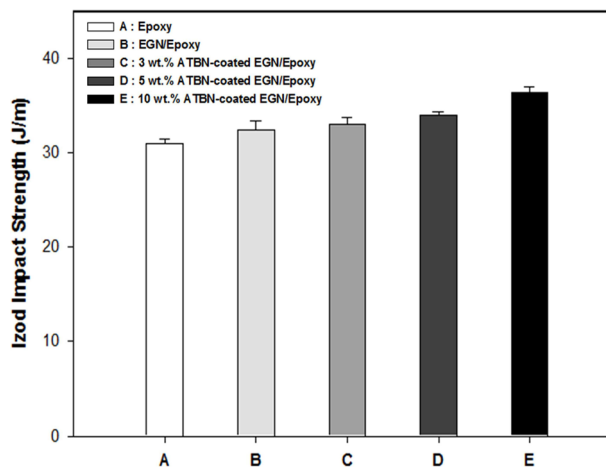


Fig. 12. Izod Impact strengths of epoxy and xGnP/epoxy and ATBN-coated xGnP/epoxy composites [90]. xGnP, exfoliated graphite nanoplatelets; ATBN, Amine-terminated poly(butadiene-*co*-acrylonitrile).

was coated with 10 wt% ATBN, which resulted in an improvement of 18% compared to epoxy. 10 wt% ATBN coated onto 1 wt% xGnP corresponds to only 0.1 wt% ATBN against the epoxy amount. The result indicates that a very small amount of rubber component used in the xGnP/epoxy system can play a considerable role in increasing the toughness of the epoxy resin.

In summary, xGnP nanoparticles can be physically modified by coating with a liquid rubber ATBN, and the effect of the coating is well demonstrated by multiple analytical approaches. In particular, incorporating the ATBN coated nanoparticles into epoxy resin considerably enhances the impact toughness of xGnP/epoxy composites, with only a small ATBN coating concentration.

10. Concluding Remarks

This paper provides an extensive overview of fundamental studies on PETI-5 and xGnP, and applied studies on relevant composite materials.

The paper described imidization and thermal curing behaviors based on phenylethynyl end-group reactions, using thermal analyses and FTIR spectroscopy, to review the characterization, properties, and processing of PETI-5 as a high-temperature sizing material for carbon fiber-reinforced polymer matrix composites. Simultaneous monitoring of the imidization and cure reactions of PETI-5 impregnated on a glass fabric composite was studied using DMA. The role of PETI-5 in enhancing the interfacial adhesion between carbon fibers and the BMI matrix, as well as the dynamic mechanical properties of carbon/BMI composites, were discussed.

The effect of incorporated xGnP on the properties of PETI-5 matrix composites was also stressed. The thermal expansion behavior of intercalated graphite flake, preliminarily monitored using the TMA technique, was reported. The dynamic mechanical and thermal properties, the fracture surface topography, and the electrical resistivity of PETI-5 composites reinforced with xGnP were described. It was noted that physically modifying xGnP particles by coating the carbon nanoparticles with ATBN liquid rubber, and then incorporating the coated xGnP into epoxy resin, significantly influenced the Izod impact strength of the xGnP/epoxy composites.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

References

- [1] Rabilloud G. High-Performance Polymers: Chemistry and Applications-Polyimides in Electronics, Institut Français du Pétrole Publication, Paris (2000).
- [2] Jang BZ. Advanced Polymer Composites: Principles and Applications, ASM International, Materials Park, Chapter 2 (1994).
- [3] Ghosh MK, Mittal MT. Polyimides: Fundamentals and Applications. Marcel Dekker, New York, Chapter 13 (1996).
- [4] Takekoshi T, Terry JM. High-temperature thermoset polyimides containing disubstituted acetylene end groups. *Polymer*, **35**, 4874 (1994). [http://dx.doi.org/10.1016/0032-3861\(94\)90746-3](http://dx.doi.org/10.1016/0032-3861(94)90746-3).
- [5] Russell JD, Kardos JL. Crosslinking characterization of a polyimide: AFR700B. *Polym Compos*, **18**, 595 (1997). <http://dx.doi.org/10.1002/pc.10311>.
- [6] Southcott M, Amone M, Senger J, Wang A, Polio A, Sheppards CH. The development of processable, fully imidized, polyimides for high-temperature applications. *High Perform Polym*, **6**, 1 (1994). <http://dx.doi.org/10.1088/0954-0083/6/1/001>.
- [7] Scola DA, Vontell JH. High temperature polyimides, chemistry and properties. *Polym Compos*, **9**, 443 (1988). <http://dx.doi.org/10.1002/pc.750090611>.
- [8] Pater RH. Thermosetting polyimides: a review. *SAMPE J*, **30**, 29 (1994).
- [9] Hergenrother PM. In: Mark HF, Bikales NM, Overberger CG, Menges G, Kroschwitz JI, eds. *Encyclopedia of Polymer Science and Engineering*, Vol. 1, Wiley, New York, 61 (1988).
- [10] Capo DJ, Schoenberg JE. Acetylenic-terminated fluorinated polyimide, properties and applications. *SAMPE J*, **23**, 35 (1987).
- [11] Sastri SB, Keller TM, Jones KM, Armistead JP. Studies on cure chemistry of new acetylenic resins. *Macromolecules*, **26**, 6171 (1993). <http://dx.doi.org/10.1021/ma00075a005>.
- [12] Rossi RD. In: Dostal CA, ed. *Engineered Materials Handbook*, Vol. 3: Adhesives and Sealants, ASM International, Materials Park, 151 (1990).
- [13] Hergenrother PM, Smith JG Jr. Chemistry and properties of imide oligomers end-capped with phenylethynylphthalic anhydrides. *Polymer*, **35**, 4857 (1994). [http://dx.doi.org/10.1016/0032-3861\(94\)90744-7](http://dx.doi.org/10.1016/0032-3861(94)90744-7).
- [14] Hergenrother PM, Bryant RG, Jensen BJ, Havens SJ. Phenylethynyl-terminated imide oligomers and polymers therefrom. *J Polym Sci Part A Polym Chem*, **32**, 3061 (1994). <http://dx.doi.org/10.1002/pola.1994.080321607>.
- [15] Hou TH, Jensen BJ, Hergenrother PM. Processing and properties of IM7/PETI composites. *J Compos Mater*, **30**, 109 (1996). <http://dx.doi.org/10.1177/002199839603000107>.
- [16] Bryant RG, Jensen BJ, Hergenrother PM. Chemistry and properties of a phenylethynyl-terminated polyimide. *J Appl Polym Sci*, **59**, 1249 (1996). [http://dx.doi.org/10.1002/\(sici\)1097-4628\(19960222\)59:8<1249::aid-app7>3.0.co;2-c](http://dx.doi.org/10.1002/(sici)1097-4628(19960222)59:8<1249::aid-app7>3.0.co;2-c).
- [17] Rommel ML, Konopka L, Hergenrother PM. Proceedings of 28th International SAMPE Technical Conference, Society for the Advancement of Materials and Processing, Baltimore, MD, 1 (1996).
- [18] Cano RJ, Jensen BJ. Effect of molecular weight on processing and adhesive properties of the phenylethynyl-terminated polyimide LARC™-PETI-5. *J Adhes*, **60**, 113 (1997). <http://dx.doi.org/10.1080/00218469708014413>.
- [19] Hergenrother PM, Rommel ML. Proceedings of 41st International SAMPE Symposium, Society for Advancement of Material and Process Engineering, Anaheim, CA, 1061 (1996).
- [20] Jensen BJ. Copolyimides prepared from 3,4'-oxydianiline and 1,3-bis(3-aminophenoxy) benzene with 3,3'-4,4'-biphenylcarboxylic dianhydride having reactive end groups. US Patent 5,644,022 (1997).
- [21] Cho D, Choi Y, Chang JH, Drzal LT. Interphase sizing temperature effect of LARC PETI-5 on the dynamic mechanical thermal properties of carbon fiber/BMI composites. *Compos Interfaces*, **13**, 215 (2006). <http://dx.doi.org/10.1163/156855406775997105>.

- [22] Smith JG JR, Connell JW, Hergenrother PM. Proceedings of 43rd International SAMPE Symposium, Advancement of Material and Process Engineering, Anaheim, CA, 93 (1998).
- [23] Cho D, Drzal LT. Characterization, properties, and processing of LaRC PETI-5 as a high-temperature sizing material: II. thermal characterization. *J Appl Polym Sci*, **75**, 1278 (2000). [http://dx.doi.org/10.1002/\(sici\)1097-4628\(20000307\)75:10<1278::aid-app9>3.0.co;2-m](http://dx.doi.org/10.1002/(sici)1097-4628(20000307)75:10<1278::aid-app9>3.0.co;2-m).
- [24] Cho D, Drzal LT. Characterization, properties, and processing of LaRC PETI-5 as a high-temperature sizing material: I. FTIR studies on imidization and phenylethynyl end-group reaction behavior. *J Appl Polym Sci*, **76**, 190 (2000). [http://dx.doi.org/10.1002/\(sici\)1097-4628\(20000411\)76:2<190::aid-app8>3.0.co;2-8](http://dx.doi.org/10.1002/(sici)1097-4628(20000411)76:2<190::aid-app8>3.0.co;2-8).
- [25] Rich DC, Sichel EK, Cebe P. Curing study of a preimidized photosensitive polyimide. *Polym Eng Sci*, **36**, 2179 (1996). <http://dx.doi.org/10.1002/pen.10615>.
- [26] Jordan K, Iroh JO. Effect of isothermal aging on the imidization of PMR-15. *Polym Eng Sci*, **36**, 2550 (1996). <http://dx.doi.org/10.1002/pen.10654>.
- [27] Pater RH, Morgan CD. Interpenetrating polymer network approach to tougher and more microcracking resistant high temperature polymers: I. LaRC-RP40. *SAMPE J*, **24**, 25 (1988).
- [28] Tai HJ, Jang BZ, Wang JB. Synthesis and processing of PMR-15/LaRC-TPI semi-IPN systems. *J Appl Polym Sci*, **58**, 2293 (1995). <http://dx.doi.org/10.1002/app.1995.070581217>.
- [29] Clemenson PI, Pandiman D, Pearson JT, Lavery AJ. Synthesis and characterization of new water-soluble precursors of polyimides. *Polym Eng Sci*, **37**, 966 (1997). <http://dx.doi.org/10.1002/pen.11741>.
- [30] Kim DS, Lee JR. Characterization and properties of carbon/PMR-15 composites. *Polym Adv Technol*, **6**, 711 (1995). <http://dx.doi.org/10.1002/pat.1995.220061106>.
- [31] Pryde CA. IR studies of polyimides: I. effects of chemical and physical changes during cure. *J Polym Sci Part A Polym Chem*, **27**, 711 (1989). <http://dx.doi.org/10.1002/pola.1989.080270229>.
- [32] Coburn JC, Pottiger MT. Thermal Curing in Polyimide Films and Coatings. In: Ghosh MK, Mittal KL, eds. *Polyimides: Fundamentals and Applications*, Marcel Dekker, New York, 207 (1996).
- [33] Ishida H, Wellinghoff ST, Baer E, Koenig JL. Spectroscopic studies of poly[N,N'-bis(phenoxyphenyl)pyromellitimide]: I. structures of the polyimide and three model compounds. *Macromolecules*, **13**, 826 (1980). <http://dx.doi.org/10.1021/ma60076a011>.
- [34] Cho D, Choi Y, Drzal LT. Simultaneous monitoring of the imidization and cure reactions of LaRC PETI-5 sized on a braided glass fabric substrate by dynamic mechanical analysis. *Polymer*, **42**, 4611 (2001). [http://dx.doi.org/10.1016/s0032-3861\(00\)00863-6](http://dx.doi.org/10.1016/s0032-3861(00)00863-6).
- [35] Johnston JA, Li FM, Harris FW, Takekoshi T. Synthesis and characterization of imide oligomers end-capped with 4-(phenylethynyl)phthalic anhydrides. *Polymer*, **35**, 4865 (1994). [http://dx.doi.org/10.1016/0032-3861\(94\)90745-5](http://dx.doi.org/10.1016/0032-3861(94)90745-5).
- [36] Fang X, Rogers DF, Scola DA, Stevens MP. A study of the thermal cure of a phenylethynyl-terminated imide model compound and a phenylethynyl-terminated imide oligomer (PETI-5). *J Polym Sci Part A Polym Chem*, **36**, 461 (1998). [http://dx.doi.org/10.1002/\(sici\)1099-0518\(199802\)36:3<461::aid-pola10>3.3.co;2-l](http://dx.doi.org/10.1002/(sici)1099-0518(199802)36:3<461::aid-pola10>3.3.co;2-l).
- [37] Meyer GW, Glass TE, Grubbs HJ, McGrath JE. Synthesis and characterization of polyimides endcapped with phenylethynylphthalic anhydride. *J Polym Sci Part A Polym Chem*, **33**, 2141 (1995). <http://dx.doi.org/10.1002/pola.1995.080331307>.
- [38] Hunt BJ, James MI. *Polymer Characterisation*, Chapman & Hall, London, Chapter 7 (1993).
- [39] Pascal T, Mercier R, Sillion B. New semi-interpenetrating polymeric networks from linear polyimides and thermosetting bismaleimides: 2. mechanical and thermal properties of the blends. *Polymer*, **31**, 78 (1990). [http://dx.doi.org/10.1016/0032-3861\(90\)90353-z](http://dx.doi.org/10.1016/0032-3861(90)90353-z).
- [40] Labronici M, Ishida H. Dynamic mechanical characterization of PMR polyimide/carbon fiber composites modified by fiber coating with silicones. *Compos Interfaces*, **5**, 257 (1997). <http://dx.doi.org/10.1163/156855498x00180>.
- [41] Kuzak SG, Shanmugam A. Dynamic mechanical analysis of fiber-reinforced phenolics. *J Appl Polym Sci*, **73**, 649 (1999). [http://dx.doi.org/10.1002/\(sici\)1097-4628\(19990801\)73:5<649::aid-app5>3.0.co;2-b](http://dx.doi.org/10.1002/(sici)1097-4628(19990801)73:5<649::aid-app5>3.0.co;2-b).
- [42] Thomason JL. Investigation of composite interphase using dynamic mechanical analysis: artifacts and reality. *Polym Compos*, **11**, 105 (1990). <http://dx.doi.org/10.1002/pc.750110206>.
- [43] Dong S, Gauvin R. Application of dynamic mechanical analysis for the study of the interfacial region in carbon fiber/epoxy composite materials. *Polym Compos*, **14**, 414 (1993). <http://dx.doi.org/10.1002/pc.750140508>.
- [44] Elmore JS, Stinchcomb WW. Proceedings of the 7th Annual Meeting Adhesion Society, Jacksonville, FL, 150 (1994).
- [45] Cho D, Choi Y, Drzal LT. Characterization, properties, and processing of LaRC PETI-5 as a high-temperature sizing material: III. adhesion enhancement of carbon/BMI composites. *J Adhes*, **79**, 1 (2003). <http://dx.doi.org/10.1080/00218460309559>.
- [46] Lincoln JE, Morgan RJ, Shin EE. Moisture absorption-network structure correlations in BMPM/DABPA bismaleimide composite matrices. *J Adv Mater*, **32**, 24 (2000).
- [47] Wilenski MS. The Improvement of the Hygrothermal and Mechanical Properties of Bismaleimide and K3B/IM7 Carbon Fiber Composites through a Systematic Study of the Interphase, Michigan State University, East Lansing, MI, PhD Thesis (1997).
- [48] Heisey CL, Wood PA, McGrath JE, Wightmany JP. Measurement of adhesion between carbon fibers and bismaleimide resins. *J Adhes*, **53**, 117 (1995). <http://dx.doi.org/10.1080/00218469508014375>.
- [49] Herrera-Franco PJ, Drzal LT. Comparison of methods for the measurement of fibre/matrix adhesion in composites. *Composites*, **23**, 2 (1992). [http://dx.doi.org/10.1016/0010-4361\(92\)90282-y](http://dx.doi.org/10.1016/0010-4361(92)90282-y).
- [50] Nardin M, Asloun EM, Schultz J. Study of the carbon fiber-poly(ether-ether-ketone) (PEEK) interfaces, 2: relationship between interfacial shear strength and adhesion energy. *Polym Adv Technol*, **2**, 115 (1991). <http://dx.doi.org/10.1002/pat.1991.220020302>.
- [51] Jangchud I, Eby RK, Serrano AM, Meador MA. Studies of PAN-based carbon fiber surfaces: their influence on interfacial bonding with PMR-15 polyimide and composite thermo-oxidative stability. *J Adv Mater*, **28**, 19 (1996).
- [52] Donnet JB, Wang TK, Peng JCM, Rebouillat S. *Carbon Fibers*. 3rd ed., Marcel Dekker, New York (1998).
- [53] Wilkinson SP, Ward TC, McGrath JE. Effect of thermoplastic modifier variables on toughening a bismaleimide matrix resin for high-performance composite materials. *Polymer*, **34**, 870 (1993). [http://dx.doi.org/10.1016/0032-3861\(93\)90376-l](http://dx.doi.org/10.1016/0032-3861(93)90376-l).
- [54] Drzal LT. The role of the fiber-matrix interphase on composite properties. *Vacuum*, **41**, 1615 (1990). [http://dx.doi.org/10.1016/0042-207x\(90\)94034-n](http://dx.doi.org/10.1016/0042-207x(90)94034-n).

- [55] Drzal LT, Rich MJ, Koenig MF, Lloyd PF. Adhesion of graphite fibers to epoxy matrices: II. the effect of fiber finish. *J Adhes*, **16**, 133 (1983). <http://dx.doi.org/10.1080/00218468308074911>.
- [56] Blackketter DM, Upadhyaya D, King TR, King JA. Evaluation of fiber surfaces treatment and sizing on the shear and transverse tensile strengths of carbon fiber-reinforced thermoset and thermoplastic matrix composites. *Polym Compos*, **14**, 430 (1993). <http://dx.doi.org/10.1002/pc.750140510>.
- [57] Kim JK, Mai YW. *Engineered Interfaces in Fiber Reinforced Composites*, Science Ltd., Amsterdam, Chapter 3 (1998).
- [58] Drzal LT, Herrera-Franco PJ, Ho H. Fiber-Matrix Interface Tests. In: Kelly A, Zweben C, eds. *Comprehensive Composite Materials*, Elsevier Science Ltd., Amsterdam, Chapter 5 (2000).
- [59] Cho D, Kim HJ, Drzal LT. Surface Treatment and Characterization of Natural Fiber: Effects on the Properties of Biocomposites. In: Thomas S, Joseph K, Malhotra SK, Goda K, Sreekala MS, eds. *Polymer Composites, Biocomposites*, Wiley-VCH Verlag GmbH & Co, Weinheim, Chapter 4 (2013).
- [60] Pang Y, Cho D, Han SO, Park WH. Interfacial shear strength and thermal properties of electron beam-treated henequen fiber reinforced unsaturated polyester composites. *Macromol Res*, **13**, 453 (2005). <http://dx.doi.org/10.1007/bf03218480>.
- [61] Han SO, Cho D, Park WH, Drzal LT. Henequen/poly(butylene succinate) biocomposites: electron beam irradiation effects on henequen fiber and the interfacial properties of biocomposites. *Compos Interfaces*, **13**, 231 (2006). <http://dx.doi.org/10.1163/156855406775997123>.
- [62] Seo JM, Cho D, Park WH, Han SO, Hwang TW, Choi CH, Jung SJ. Fiber surface treatments for improvement of the interfacial adhesion and flexural and thermal properties of jute/poly (lactic acid) biocomposites. *J Biobased Mater Bioenergy*, **1**, 331 (2007). <http://dx.doi.org/10.1166/jbmb.2007.007>.
- [63] Lee S, Cho D, Drzal LT. Real-time observation of the expansion behavior of intercalated graphite flake. *J Mater Sci*, **40**, 231 (2005). <http://dx.doi.org/10.1007/s10853-005-5715-0>.
- [64] Chung DDL. Exfoliation of graphite. *J Mater Sci*, **22**, 4190 (1987). <http://dx.doi.org/10.1007/bf01132008>.
- [65] Drzal LT, Fukushima H. Graphite nanoplatelets as reinforcements for polymers. *Polym Prepr*, **42**, 42 (2001).
- [66] Chen GH, Wu DJ, Weng WG, YAN WL. Preparation of polymer/graphite conducting nanocomposite by intercalation polymerization. *J Appl Polym Sci*, **82**, 2506 (2001). <http://dx.doi.org/10.1002/app.2101>.
- [67] Kang F, Zheng YP, Wang HN, Nishi Y, Inagaki M. Effect of preparation conditions on the characteristics of exfoliated graphite. *Carbon*, **40**, 1575 (2002). [http://dx.doi.org/10.1016/s0008-6223\(02\)00023-4](http://dx.doi.org/10.1016/s0008-6223(02)00023-4).
- [68] Dresselhaus MS. Modifying materials by intercalation. *Phys Today*, **37**, 60 (1984). <http://dx.doi.org/10.1063/1.2916162>.
- [69] Shioyama H. The interactions of two chemical species in the interlayer spacing of graphite. *Synth Met*, **114**, 1 (2000). [http://dx.doi.org/10.1016/s0379-6779\(00\)00222-8](http://dx.doi.org/10.1016/s0379-6779(00)00222-8).
- [70] Park SB, Lee MS, Park M. Study on lowering the percolation threshold of carbon nanotube-filled conductive polypropylene composites. *Carbon Lett*, **15**, 117 (2014). <http://dx.doi.org/10.5714/cl.2014.15.2.117>.
- [71] Zou JF, Yu ZZ, Pan YX, Fang XP, OU YC. Conductive mechanism of polymer/graphite conducting composites with low percolation threshold. *J Polym Sci Part B Polym Phys*, **40**, 954 (2002). <http://dx.doi.org/10.1002/polb.10141>.
- [72] Koo MY, Shin HC, Kim WS, Lee GW. Properties of multi-walled carbon nanotube reinforced epoxy composites fabricated by using sonication and shear mixing. *Carbon Lett*, **15**, 255 (2014). <http://dx.doi.org/10.5714/cl.2014.15.4.255>.
- [73] Kim M, Kim Y, Baeck SH, Shim SE. Effect of surface treatment of graphene nanoplatelets for improvement of thermal and electrical properties of epoxy composites. *Carbon Lett*, **16**, 34 (2015). <http://dx.doi.org/10.5714/cl.2015.16.1.034>.
- [74] Magaraphan R, Lilayuthalert W, Sirivat A, Schwank JW. Preparation, structure, properties and thermal behavior of rigid-rod polyimide/montmorillonite nanocomposites. *Compos Sci Technol*, **61**, 1253 (2001). [http://dx.doi.org/10.1016/s0266-3538\(01\)00026-4](http://dx.doi.org/10.1016/s0266-3538(01)00026-4).
- [75] Cho D, Lee S, Yang G, Fukushima H, Drzal LT. Proceedings of the 14th International Conference on Composite Materials (ICCM-14), San Diego, CA, 471 (2003).
- [76] Cho D, Lee S, Yang G, Fukushima H, Drzal LT. Dynamic mechanical and thermal properties of phenylethynyl-terminated polyimide composites reinforced with expanded graphite nanoplatelets. *Macromol Mater Eng*, **290**, 179 (2005).
- [77] Jin FL, Park SJ. Recent advances in carbon-nanotube-based epoxy composites. *Carbon Lett*, **14**, 1 (2013). <http://dx.doi.org/10.5714/cl.2012.14.1.001>.
- [78] Karevan M, Pucha RV, Bhuiyan MA, Kalaitzidou K. Effect of interphase modulus and nanofiller agglomeration on the tensile modulus of graphite nanoplatelets and carbon nanotube reinforced polypropylene nanocomposites. *Carbon Lett*, **11**, 325 (2010). <http://dx.doi.org/10.5714/cl.2010.11.4.325>.
- [79] Park JK, Lee JY, Drzal LT, Cho D. Flexural properties, interlaminar shear strength and morphology of phenolic matrix composites reinforced with xGnP-coated carbon fibers. *Carbon Lett*, **17**, 33 (2016). <http://dx.doi.org/10.5714/cl.2016.17.1.033>.
- [80] Cho D, Fukushima H, Drzal LT. Effect of exfoliated graphite nanoplatelets on the fracture surface morphology and the electrical resistivity of phenylethynyl-terminated polyimide. *Carbon Lett*, **13**, 121 (2012). <http://dx.doi.org/10.5714/cl.2012.13.2.121>.
- [81] Kim S, Seo J, Drzal LT. Improvement of electric conductivity of LLDPE based nanocomposite by paraffin coating on exfoliated graphite nanoplatelets. *Compos Part A Appl Sci Manuf*, **41**, 581 (2010). <http://dx.doi.org/10.1016/j.compositesa.2009.05.002>.
- [82] Kalaitzidou K, Fukushima H, Askeland P, Drzal LT. The nucleating effect of exfoliated graphite nanoplatelets and their influence on the crystal structure and electrical conductivity of polypropylene nanocomposites. *J Mater Sci*, **43**, 2895 (2008). <http://dx.doi.org/10.1007/s10853-007-1876-3>.
- [83] Li J, Vaisman L, Marom, G, Kim JK. Br treat graphite nanoplatelets for improved electrical conductivity of polymer composites. *Carbon*, **45**, 744 (2007). <http://dx.doi.org/10.1016/j.carbon.2006.11.031>.
- [84] Ma PC, Liu MY, Zhang H, Wang SQ, Wang R, Wang K, Wong YK, Tang BZ, Hong SH, Paik KW, Kim JK. Enhanced electrical conductivity of nanocomposite containing hybrid fillers of carbon nanotubes and carbon black. *ACS Appl Mater Interfaces*, **1**, 1090 (2009). <http://dx.doi.org/10.1021/am9000503>.
- [85] Kim S, Do I, Drzal LT. Multifunctional xGnP/LLDPE nanocomposites prepared by solution compounding using various screw rotating systems. *Macromol Mater Eng*, **294**, 196 (2009). <http://dx.doi.org/10.1002/mame.200800319>.
- [86] Kalaitzidou K, Fukushima H, Drzal LT. A route for polymer nano-

- composites with engineered electrical conductivity and percolation threshold. *Materials*, **3**, 1089 (2010). <http://dx.doi.org/10.3390/ma3021089>.
- [87] Liu W, Do I, Fukushima H, Drzal LT. Influence of processing on morphology, electrical conductivity and flexural properties of exfoliated graphite nanoplatelets-polyamide nanocomposites. *Carbon Lett*, **11**, 279 (2010). <http://dx.doi.org/10.5714/cl.2010.11.4.279>.
- [88] Li J, Wong PS, Kim JK. Hybrid nanocomposites containing carbon nanotubes and graphite nanoplatelets. *Mater Sci Eng A*, **483-484**, 660 (2008). <http://dx.doi.org/10.1016/j.msea.2006.08.145>.
- [89] Cho D, Hwang JH. Elastomeric coating of exfoliated graphite nanoplatelets with amine-terminated poly(butadiene-co-acrylonitrile): characterization and its epoxy toughening effect. *Adv Polym Technol*, **32**, 21366 (2013). <http://dx.doi.org/10.1002/adv.21366>.
- [90] Hwang JH, Cho D. Simultaneous enhancement of impact toughness, mechanical properties and thermo-dimensional stability of epoxy composites by rubber-coated exfoliated graphite nanoplatelets. *Fibers Polym*, **14**, 1947 (2013). <http://dx.doi.org/10.1007/s12221-013-1947-9>.
- [91] Najafi E, Kim JY, Han SH, Shin K. UV-ozone treatment of multi-walled carbon nanotubes for enhanced organic solvent dispersion. *Colloids Surf A Physicochem Eng Asp*, **284-285**, 373 (2006). <http://dx.doi.org/10.1016/j.colsurfa.2005.11.074>.
- [92] Chen X, Wang J, Lin M, Zhong W, Feng T, Chen X, Chen J, Xue F. Mechanical and thermal properties of epoxy nanocomposites reinforced with amino-functionalized multi-walled carbon nanotubes. *Mater Sci Eng A*, **492**, 236 (2008). <http://dx.doi.org/10.1016/j.msea.2008.04.044>.
- [93] Okpalugo TIT, Papakonstantinou P, Murphy H, McLaughlin J, Brown NMD. High resolution XPS characterization of chemical functionalised MWCNTs and SWCNTs. *Carbon*, **43**, 153 (2005). <http://dx.doi.org/10.1016/j.carbon.2004.08.033>.
- [94] Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, Wu Y, Nguyen ST, Ruoff RS. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, **45**, 1558 (2007). <http://dx.doi.org/10.1016/j.carbon.2007.02.034>.
- [95] Bose S, Drzal LT. Functionalization of graphene nanoplatelets using sugar azide for graphene/epoxy nanocomposites. *Carbon Lett*, **16**, 101 (2015). <http://dx.doi.org/10.5714/cl.2015.16.2.101>.
- [96] Peng BX, Wong SS. Functional covalent chemistry of carbon nanotube surfaces. *Adv Mater*, **21**, 625 (2009). <http://dx.doi.org/10.1002/adma.200801464>.
- [97] Chikhi N, Fellahi S, Bakar M. Modification of epoxy resin using reactive liquid (ATBN) rubber. *Eur Polym J*, **38**, 251 (2002). [http://dx.doi.org/10.1016/s0014-3057\(01\)00194-x](http://dx.doi.org/10.1016/s0014-3057(01)00194-x).
- [98] Robinette EJ, Ziaee S, Palmese GR. Toughening of vinyl ester resin using butadiene-acrylonitrile rubber modifiers. *Polymer*, **45**, 6143 (2004). <http://dx.doi.org/10.1016/j.polymer.2004.07.003>.
- [99] Chen S, Wang Q, Wang T. Hydroxy-terminated liquid nitrile rubber modified castor oil based polyurethane/epoxy IPN composites: damping, thermal and mechanical properties. *Polym Test*, **30**, 726 (2011). <http://dx.doi.org/10.1016/j.polymertesting.2011.06.011>.
- [100] Choi SY, Chu JM, Lee EK. Influences of liquid rubber on the surfacial and mechanical properties of epoxy composites. *Elastomers Compos*, **43**, 113 (2008).
- [101] Ramos VD, da Costa HM, Soares VLP, Nascimento RSV. Modification of epoxy resin: a comparison of different types of elastomer. *Polym Test*, **24**, 387 (2005). <http://dx.doi.org/10.1016/j.polymertesting.2004.09.010>.
- [102] Ratna D, Banthia AK. Reactive acrylic liquid rubber with terminal and pendant carboxyl groups as a modifier for epoxy resin. *Polym Eng Sci*, **47**, 26 (2007). <http://dx.doi.org/10.1002/pen.20633>.