

# Highly Processable Ternary Systems Based on Benzoxazine, Epoxy, and Phenolic Resins for Carbon Fiber Composite Processing

Sarawut Rimdusit,<sup>1</sup> Passarin Jongvisuttisun,<sup>1</sup> Chanchira Jubsilp,<sup>1</sup> Wiwut Tanthapanichakoon<sup>2</sup>

<sup>1</sup>Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand

<sup>2</sup>National Nanotechnology Center, 111 Thailand Science Park, Klong Luang, Pathumthani 12120, Thailand

Received 22 November 2007; accepted 8 July 2008

DOI 10.1002/app.29085

Published online 22 October 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Effects of resin compositions in ternary systems of benzoxazine, epoxy, and phenolic novolac resins on processability, and thermomechanical properties of their carbon fiber-reinforced composites are investigated. At suitable range of resin mass ratios, the ternary mixtures can provide a relatively wide processing window ranging from 50 to 200°C by maintaining their low A-stage viscosity for a relatively long time which is crucial in the fiber preimpregnating process. Furthermore, relatively long shelf-life of the ternary mixtures stored at room tempera-

ture (~ 30°C) up to 270 days is obtained with minimal effect on their processability. The optimum mass ratio of B : E : P was determined to be 3 : 6 : 2, i.e., BEP362 resin. Finally, the carbon fiber composite based on BEP362 was found to exhibit substantial enhancement in its mechanical properties. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1225–1234, 2009

**Key words:** composites; curing of polymers; gelation; thermosets; reinforcement

## INTRODUCTION

Advanced composites such as fiber-reinforced polymer composites have been extensively used in many high performance applications that require excellent mechanical properties especially in structural utilizations because of their outstanding specific modulus and specific strength.<sup>1–9</sup> One important group of polymeric composites is based on carbon fiber reinforcing systems which is often used in weight reduction and high specific strength requirement, i.e., aerospace, ballistic armor, or extreme sport applications. In the production of carbon fiber-reinforced composites, the materials are typically preformed as prepregs for easy handling and processing.<sup>10–16</sup>

Good prepreg characteristics include not only specific end-properties but also processability of the materials such as shelf life of the matrices, pot life of the systems at various temperatures, and suitable

curing condition.<sup>11–18</sup> At present, there are two major prepregging methods used industrially, i.e., solution impregnation and hot melt impregnation methods. Each method is depending on the processability of matrix resins to provide an appropriate resin viscosity to coat the reinforcing fiber. Since the composite quality is partly controlled by (1) resin-fiber interfacial wetting and (2) uniform resin content, the low viscosity resins are typically required. In addition, at the prepregging temperature, the matrix resins are recommended to retain their low viscosity which is usually in a range of 1–3 Pa.s to provide desirable end-products.<sup>11,13</sup> However, a time period for “B-staging” step of the resins should also be minimized, i.e., 1–15 min at temperatures of 90–200°C.<sup>13,14</sup> The various currently used matrices, however, contain some shortcomings such as narrow processing window, short storage life, need of curing agent, required refrigeration for storage, as well as complicated processing methods. These make their utilization less user-friendly. In the past decades, epoxy resins have been widely used in fiber-reinforced polymer composites which required thermosetting characteristics<sup>7,8,15</sup> because the resins possess relatively high modulus and strength values, high thermal stability, and outstanding adhesive properties to various types of surfaces. In addition, the resins also show good corrosion resistance with relatively low water absorption. However, most

Correspondence to: S. Rimdusit (sarawut.r@chula.ac.th).

Contract grant sponsors: Industry-University Joint Research Fund of Center of Excellence in Particle Technology, Chulalongkorn University; Research Grant for TRF Research Scholar of the Thailand Research Fund and the Hitachi Scholarship Foundation; The Affair of Commission for Higher Education-CU Graduate Thesis Grant of Chulalongkorn University.

curing agents of epoxy resins, including amines and anhydrides, have some drawbacks such as high toxicity or low storage stability. Therefore, the development of user-friendly, highly processable, and more stable matrices is still necessary in the composite industries.

Polybenzoxazine, a novel class of phenolic resins, has been developed with a wide range of mechanical and physical properties that can be tailored to specific needs. Polybenzoxazine can be synthesized using a patented solventless technology to yield a relatively clean precursor, without the need of solvent elimination or monomer purification. The polymer can undergo ring-polymerization of its aromatic oxazines upon heating without the aid of a curing agent (strong acid and alkaline); therefore, no condensation by-products are released during a fabrication process as well as no corrosion of processing equipments.<sup>19</sup> The property balance of the material, including good thermal, chemical, and electrical properties, makes polybenzoxazine attractive as an alternative candidate for existing applications.<sup>20–33</sup> Moreover, polybenzoxazine possesses several outstanding properties such as very low A-stage viscosity, near-zero shrinkage, fast development of mechanical properties as a function of curing conversion, high thermal stability, and low water absorption. Hence, polybenzoxazine was chosen as a major component for the high performance and high processability matrix of carbon fiber composites.

As aforementioned, high performance fiber-reinforced composites with the excellent mechanical properties are normally required. Although polybenzoxazine shows many remarkable properties, one shortcoming of this resin is its relatively high rigidity, particularly in the basic-typed polybenzoxazine such as bisphenol A-aniline species (namely BA-a). In addition, some recent researches have also been conducted to enhance an adhesion between carbon fiber and polybenzoxazine including by fiber surface modification, or incorporation of rubber interlayer to yield improved mechanical properties of the resulting composites.<sup>3–7</sup> An ability of benzoxazine resin to form alloys with various other resins or polymers has been reported to render novel classes of resin systems with broader range of properties such as with a monofunctional benzoxazine diluent (Ph-a),<sup>25</sup> epoxy resins,<sup>34–37</sup> urethane resins,<sup>38,39</sup> and polyimide.<sup>40</sup> Jubsilp et al.<sup>25</sup> reported that the BA-a/Ph-a mixtures are miscible in nature rendering the properties highly dependent on their compositions. The viscosity of the BA-a resin can be reduced to one third using only about 10% by weight the Ph-a diluent and the addition of the Ph-a resin into the BA-a resin can also lower the liquefying temperature of the resin mixtures whereas the gel point is marginally decreased. Ishida and Allen<sup>31</sup> demonstrated that

alloying between benzoxazine resin (BA-a) and bisphenol A-typed epoxy (EPON825) greatly increases the crosslinked density, thus raising their glass transition temperature (141°C of neat polybenzoxazine to 155°C at 30% by weight of epoxy), flexural stress, and flexural strain at break over those of the BA-a homopolymer. Kimura et al.<sup>34,35</sup> examined the use of benzoxazine resin as a hardener of epoxy resin and reported greater heat resistance, water resistance, electrical insulation, and mechanical properties of the cured materials compared with the epoxy resin cured by bisphenol-A type novolac.

Furthermore, toughness of polybenzoxazine enhanced by alloying with flexible epoxy (EPO732) has been reported by Rimdusit et al.<sup>38</sup> The experimental results from flexural testing and dynamic mechanical analysis reveal that the toughness of the miscible alloys of the rigid polybenzoxazine and the EPO732 systematically increases with the amount of the epoxy toughener due to the addition of more flexible molecular segments in the polymer hybrids. Ishida and Ohba<sup>41</sup> reported that the toughness and glass transition temperature by incorporating epoxy into maleimide functionality benzoxazine monomer were found to improve when compared with those of the neat maleimide-functionalized benzoxazine (MIB).

Rimdusit and Ishida<sup>38,42–45</sup> have studied the ternary systems based on benzoxazine (B), liquid epoxy (E), and phenolic novolac (P) and concluded that epoxy not only acted as a reactive diluent in the BEP systems but also contributed to higher crosslinked density and flexibility compared with the neat benzoxazine resin. Moreover, the addition of small amount of phenolic resin into the BE systems resulted in a mixture to be cured at lower temperature when compared with curing reaction of the BE systems. Synergism in glass transition temperature was also observed in these ternary mixtures with great variety of resin properties, particularly their processing ability and mechanical characteristics.

In this study, suitable compositions of the ternary systems of benzoxazine, epoxy, and phenolic resins for utilizing as a matrix of carbon fiber prepregs are evaluated. The characteristics of the ternary resin systems such as viscosity, gelation time, shelf-life, and curing properties as well as the mechanical and thermal properties of their fully cured polymers and their carbon fiber composites will also be investigated.

## EXPERIMENTAL

### Materials

The 2,2'-(3-phenyl-4-dihydro-1,3,2-benzoxazine)propane designated as BA-a based on bisphenol-A, formaldehyde, and aniline was synthesized by a patented solvent-less method.<sup>19</sup> Bisphenol-A was

kindly supplied by Thai Polycarbonate Co., Ltd. (TPCC). Para-formaldehyde (AR grade) and aniline (AR grade) were purchased from Merck Ltd. and Asia Pacific Specialty Chemicals Ltd., respectively. The obtained benzoxazine monomer is clear-yellowish solid at room temperature. Phenolic novolac resin is prepared following the method explained in Ref. <sup>32</sup> by reacting phenol, 37% by weight of aqueous formaldehyde from Apec Chemical Co., Ltd. and oxalic acid (AR grade, from Suksapanpanit, Thailand). Both resins can be ground into fine powder and kept in a refrigerator for future-use. The DGEBA-based epoxy resin (Epikote 828-EL) from East Asiatic (Thailand) Public Co., Ltd. was used as-received. The resin is a clear viscous liquid at room temperature.

Carbon fiber plain fabric (KN #C100) in 3k-tows with a fiber areal weight of 165 g/m<sup>2</sup> was purchased from Asia Kangnam Co., Ltd. The fiber diameter was 8 μm, with the density of 1.78 g/cm<sup>3</sup>. The tensile strength and modulus of the fiber were 4.2 GPa and 235 GPa, respectively. It was used as-received without any additional surface modification.

### Monomer preparation

The ternary systems based on benzoxazine, epoxy, and phenolic novolac resins to be investigated are BEP361, BEP362, BEP363, and BEP364. In the nomenclature of the mixtures, B stands for the BA-a type benzoxazine resin, E is an epoxy resin, and P is the phenolic novolac resin, respectively. The numbers after letters are the mass ratio of the three monomers in the respective order. Each resin was first measured at the desirable mass fraction. The resin mixture was then heated to about 90°C in an aluminum container and was mixed thoroughly for a few minutes to obtain a homogeneous and a transparent resin mixture. All resin mixtures were kept in a refrigerator for future-use.

### Prepreg and composite manufacture

The prepreg material was made using a solvent impregnation method. Carbon fiber plain fabric prepreg was prepared by brushing ternary mixture solution (50 wt % solution in THF). After brushing, the prepreg was removed and cut to appropriate sizes followed by conditioning at 45°C for 10 h in a vacuum oven to ensure that no solvent remained. The composite laminates were cured at 180°C for 3 h in the hydraulic press using a pressure of 10.0 MPa followed by postcuring in an air-circulating oven at 200°C for 2 h.

### Differential scanning calorimetry (DSC)

Curing temperature of each matrix resin was examined using a DSC (model 2910) from TA Instruments

in a temperature range of 30–300°C. A 5–10 mg sample was placed in an aluminum pan with lid. The experiment was performed at a heating rate of 10°C/min in a constant flow of nitrogen of 50 mL/min.

### Chemorheological characterization

Dynamic shear viscosity measurements of the ternary mixtures were performed on a parallel plate rheometer using HAAKE RheoStress model RS600. Disposable aluminum plates with 60 mm in diameter were preheated with the gap zeroed at the testing temperature. The void-free monomer mixture, which was liquefied at 80°C, was then poured onto the lower plate and the gap was set to 0.5 mm. The temperature was immediately equilibrated at the set point for about 60 s and the test was then started.

### Thermogravimetric analysis (TGA)

Degradation temperature ( $T_d$ ) and char yield of the ternary systems and their composites were studied using a TGA apparatus (model TGA/SDTA 851<sup>e</sup>, Mettler-Toledo). Sample mass of 15–20 mg was heated using a linear heating rate of 20°C/min from room temperature to 800°C under dried nitrogen atmosphere.

### Bending test

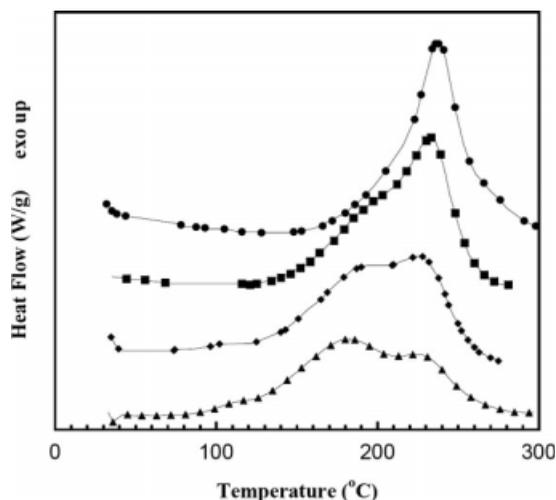
The flexural behaviors of the cured copolymers were determined using a universal testing machine (Instron Instrument, model 5567) at room temperature. The samples were tested according to ASTM D790M-93 (Method I) with a support span of 32 mm at the crosshead speed of 0.85 mm/min. Three samples from each copolymer composition were tested and the average values were reported.

### Dynamic mechanical analysis

Dynamic mechanical properties of the samples were obtained using a dynamic viscoelastic analyzer model DMA 242 C from Netzsch Inc. The test was performed under a three-point bending mode. The strain amplitude used is 30 μm at the frequency of 1 Hz. The sample was heated at a rate of 2°C/min from 30 to 270°C. The sample dimension is 52 × 10 × 2.5 mm<sup>3</sup>. Glass transition temperature of each sample was taken from the temperature at the maximum point on the loss modulus curve.

### Scanning electron microscopy (SEM)

The fractured surface of a tested sample was investigated using a scanning electron microscope (JEOL,



**Figure 1** DSC thermograms of BEP mixtures: (●) BEP361, (■) BEP362, (◆) BEP363, (▲) BEP364.

model JSM-5800LV) at an acceleration voltage of 15 kV. Samples were coated with thin film of gold using a ion sputtering device (Balzers, model SCD040) for 4 min to obtain a thickness of approximately  $\sim 30$  nm and the micrographs of the fracture surfaces of each sample were taken.

## RESULTS AND DISCUSSION

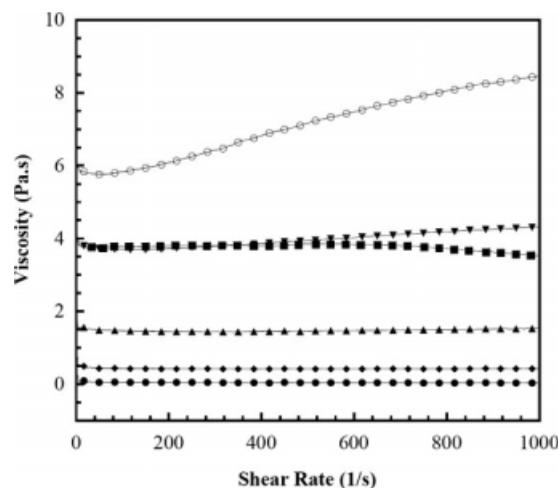
### Processability of ternary resin mixtures

Processability of ternary mixtures based on benzoxazine, epoxy, and phenolic resins was evaluated based on variation of their viscosity with temperature, i.e., the processing window as well as their curing temperature. Regarding the processability of prepreps, the matrices must be capable of wetting and penetrating into the bundle of reinforcing fibers. The higher wettability can lead to the greater mechanical performance of the composites. Additionally, resin proportions added to the fibers in the prepregging will be readily controlled with low viscosity and suitable processing window systems. Figure 1 illustrates the curing behaviors of the series of ternary mixtures under this investigation. In this case, the composition of benzoxazine and epoxy in the ternary mixtures was fixed at 1 : 2 mass ratios and the amount of phenolic novolac was systematically varied. The fixed 1 : 2 mass ratio was selected as it provided the BEP resin mixtures with high processability characteristics, i.e., melt viscosity as low as 0.3 Pa.s at 100°C, with relatively low curing temperature.<sup>42</sup>

As reported by Rimdusit and Ishida,<sup>44</sup> the recommended fraction of epoxy resin in the ternary mixtures should be in the range of 30–60% by weight to provide a suitable time window for mixing or compounding due to the appropriate viscosity and che-

morheological properties obtained. In this work, the investigated ternary compositions are BEP361, BEP362, BEP363, and BEP364. As evidently seen in Figure 1, the increase in phenolic novolac content in the BEP resin mixtures tends to lower the curing exotherm peaks in DSC thermograms, i.e., from 240°C in BEP 361 to 225°C in BEP364. Moreover, we can see that the curing reaction of the BEP363 and BEP364 compositions can be initiated at relatively lower temperature, i.e., as low as 100°C, with the amount of the phenolic resin. The appearance of the second peak in the thermograms was also observed more clearly with the increasing mass fraction of the phenolic novolac. From the thermograms, the peak situated at 225–240°C was assigned to the interaction between the benzoxazine resin and the epoxy whereas the second peak at lower temperature was attributed to the ring-opening reaction of the benzoxazine resin catalyzed by the presence of the phenolic novolac.

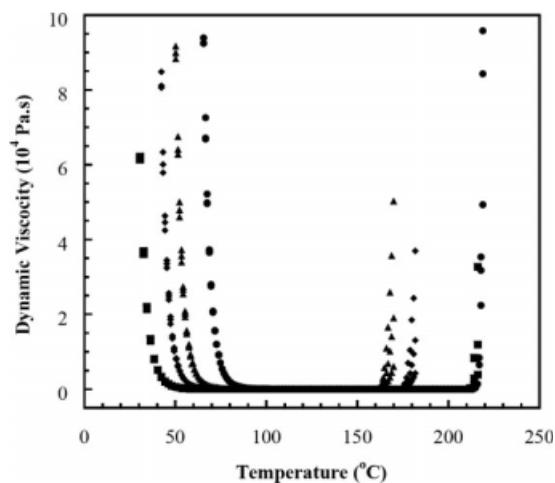
In the prepregging process such as a hot melt method, low and fairly constant viscosity is required as the low melt viscosity provides better resin wetting prepreps as well as void-free final product while constant viscosity renders enough time for prepreps processing.<sup>15</sup> The viscosity of the four different ternary mixture compositions compared with that of neat BA-a and neat epoxy resins is presented in Figure 2. The measurement was performed under shear rate sweep mode at 100°C within the shear rate range of 0.001–1000  $\text{s}^{-1}$  and experimental time of 600 s. From the curves, almost all resin mixtures show constant viscosity in a shear rate range mentioned. This implies Newtonian flow behavior of the resin mixtures as they can maintain their low-molecular weight nature in the investigated period of time. From the figure, the melt viscosity values of



**Figure 2** Viscosity of ternary systems measured at 100°C: (●) Epikote828-EL, (■) Polybenzoxazine, (◆) BEP361, (▲) BEP362, (▼) BEP363, (○) BEP364.

the ternary mixtures increase with increasing the amount of phenolic novolac. The viscosity values are ranging from 0.4 Pa.s of BEP361, 1.3 Pa.s of BEP362, and 3.8 Pa.s of BEP363 compared with about 3.8 Pa.s of the BA-a resin and 0.06 Pa.s of the liquid epoxy. Additionally, the viscosity of BEP364 was found to significantly increase with the shear rate because the curing reaction of BEP364 can proceed even at the relatively low testing temperature, i.e., 100°C. This behavior also confirmed the DSC experiment of the same resin mixture described previously. However, those viscosity values remain low enough for the preimpregnation process.

In the fabrication process of prepregs or composites, it is also important to identify the temperature limit or window for product processing where the resin should be molten and impregnated with fiber or fully cured to final composite products. The effect of the phenolic novolac on chemorheology of the BEP resin mixtures compared with that of the BA-a resin is shown in Figure 3. In this figure, the processing window of each ternary system was determined under an oscillatory shear mode. The evaluating waveform was obtained by the superposition of mechanical waves with four different frequencies, i.e., 1 rad/s, 3 rad/s, 10 rad/s, and 31 rad/s. The testing strain amplitude was kept constant at 2.5% for each frequency. The temperature of the resin mixtures was ramped from about 30°C up to the temperature beyond the gel point of each sample using a heating rate of 2°C/min and the dynamic viscosity was recorded. In this experiment, the uncured resin mixture characteristics at room temperature are varied from semisolid in BEP361 to solid in BEP363. BEP364 was not evaluated in this experiment due to its rather reactive nature with heat. On the left hand side of Figure 3, we can see that the liquefying temperature of the resin mixtures as indicated by the lowest temperature that the viscosity rapidly approaches its minimum value significantly decreases with increasing the mass fraction of the phenolic novolac. For consistency, the temperature at the viscosity value of 1,000 Pa.s was used as a liquefying temperature of each resin. Based on this convention, the liquefying temperatures of BEP361, BEP362, and BEP363 mixtures were determined to be 56°C, 60°C, and 67°C, respectively. However, the liquefying temperatures of these ternary mixtures are still lower than that of the unmodified BA-a resin which possesses the liquefying temperature of about 73°C as determined using the same convention. These liquefying behaviors are attributed to the presence of the epoxy diluent, which is a liquid at room temperature, while benzoxazine resin and phenolic novolac resin are solids at room temperature. In practice, lowering the resin liquefying temperature obviously enables the use of lower processing

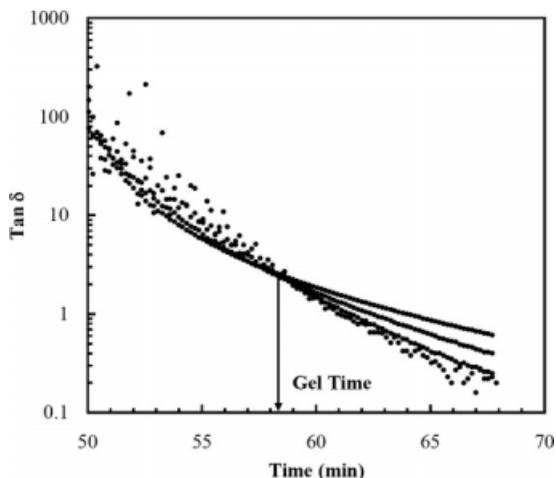


**Figure 3** Processing window of ternary mixtures at heating rate of 2°C/min: (●) BA-a resin, (■) BEP361, (◆) BEP362, (▲) BEP363.

temperature and less energy for a compounding process which is desirable in general composite applications.

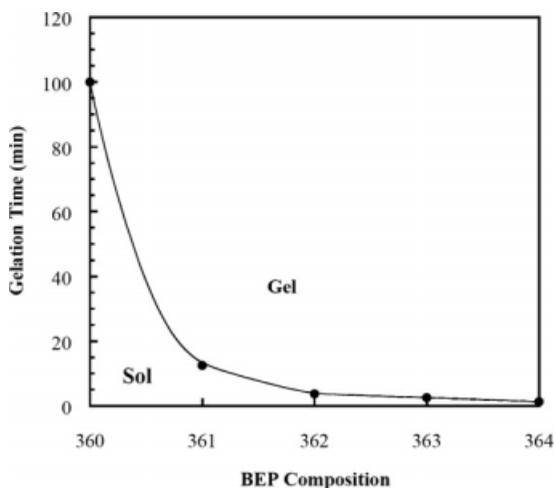
On the contrary, the gel point of these ternary mixtures tends to decrease with increasing the amount of the phenolic novolac resin. In this case, the maximum temperature at which the viscosity was rapidly raised above 1000 Pa.s was used as gel temperature of each resin. From the graph, the BA-a resin shows gel point at a temperature of 215°C while those of BEP361, BEP362, and BEP363 are 218°C, 177°C, and 163°C, respectively. This characteristic corresponds to the DSC results that phenolic novolac resin can substantially reduce the curing temperature of the resin mixtures between benzoxazine and epoxy resins. As a result, BEP363 exhibits the narrowest processing window among the three ternary systems due to the most phenolic novolac mass fraction in the systems.

As aforementioned, gelation time of each resin mixture which is in the B-staging step should be carried out within 1–15 min in the prepreg processing. Holly et al.<sup>46</sup> proposed the use of loss angle ( $\delta$ ) to determine gel point of the network forming materials. The proposed criterion is that at the gel point,  $\tan \delta$  becomes frequency independent. Therefore, the exact gel point is determined by the intersection of the various curves in a plot of  $\tan \delta$  versus time at various frequencies. As an exemplification, Figure 4 exhibits the  $\tan \delta$  crossover of BEP362 cured isothermally at 100°C and at different frequencies, i.e., 1 rad/s, 3 rad/s, 10 rad/s, and 31 rad/s. A minimum constant stress at 20 Pa is used for gel point determination to ensure both linear viscoelastic relationship as well as minimum gel network rupturing. From the plot, the values of  $\tan \delta$  intersect at a time of about 58.3 min corresponding to the gel time of

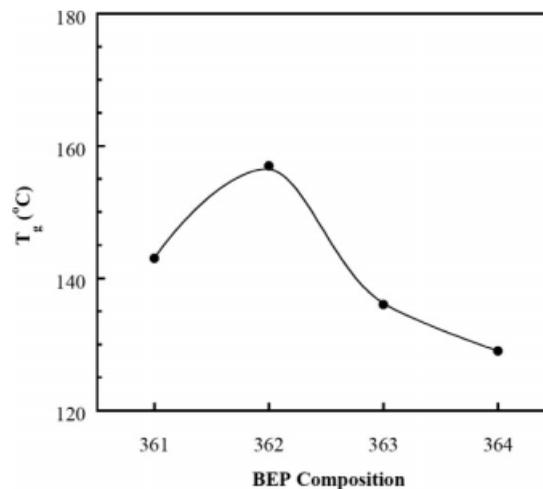


**Figure 4** Gelation time of BEP362 at 120°C using frequency independent of loss tangent to define a gel point.

BEP362 at that temperature. The conversion of the BEP362 mixture at the gel point was determined to be 35%. This result is in good agreement with other resin systems, i.e., BEP121 = 34%,<sup>44</sup> and some epoxy molding compound 22–35%.<sup>47</sup> Figure 5 illustrates the effect of phenolic novolac mass fraction, which was varied systematically from BEP360, BEP361 to BEP364, on the gelation behavior of the ternary mixtures at 180°C. Gelation time of the ternary mixtures is obtained from the point that  $\tan \delta$  is frequency independent as explained previously. From the plot, a systematic increase in phenolic novolac mass fraction was found to lower the gelation time of the ternary mixtures in an exponential decay manner. The gelation time of the ternary mixtures is ranging from more than 100 min in BEP360 (i.e., binary mixture between B and E) to about 1 min in BEP364.



**Figure 5** Gelation time as a function of BEP compositions at gel temperature of 180°C.

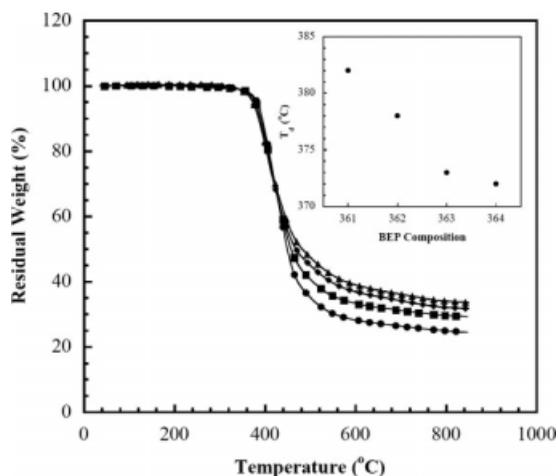


**Figure 6** Glass transition temperature from DSC of fully cured BEP systems.

#### Properties of the fully cured ternary alloy systems

The effect of the presence of epoxy and phenolic novolac resins on the glass transition temperature ( $T_g$ ) of the ternary systems have been investigated in Figure 6. From the figure,  $T_g$ s of the ternary alloys were found to strongly depend on the mixed composition of benzoxazine, epoxy, and phenolic novolac resins. In addition, it is clearly seen that the optimum in  $T_g$  of the ternary alloys under this investigation is observed. BEP362 exhibits the highest  $T_g$  among the four ternary alloys evaluated with the value of approximately 158°C. The slight increase in  $T_g$  of BEP362 compared with BEP361 is possibly due to the more perfect network structure formed in BEP362. The  $T_g$  values were then found to decrease with further increasing the phenolic novolac fractions, i.e., in BEP363 and BEP364. The primary function of phenolic novolac resin is to lower the curing temperature of the ternary mixtures but excessive amount of the resin renders negative effect of their  $T_g$  due to its limited participation in the network formation.

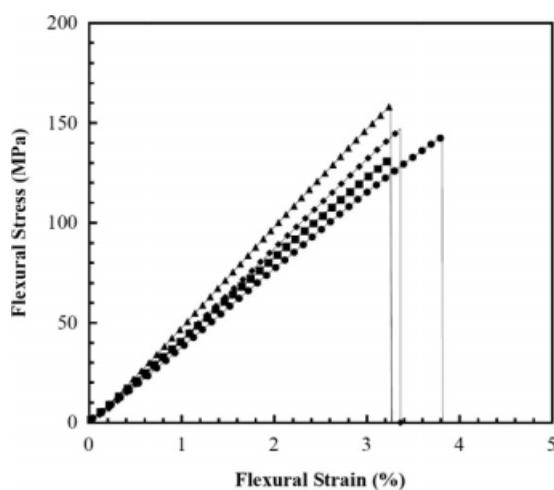
Normally, thermal degradation temperature ( $T_d$ ) is one of the key parameters that need to be considered for high temperature application of materials. The TGA curve of the ternary alloys is presented in Figure 7. From the figure, all alloys exhibit an improvement in their thermal stability over the polybenzoxazine homopolymer. The decomposition temperature at 5% weight loss of the ternary alloys is approximately 372–382°C, as shown in an inset of Figure 7, comparing with 334°C of the polybenzoxazine (BA-a).<sup>25,30</sup> Another interesting feature in the TGA thermogram is the char yield of the alloys reported at 800°C. The char yield of the ternary alloys was found to systematically increase with increasing the phenolic novolac mass fraction. This



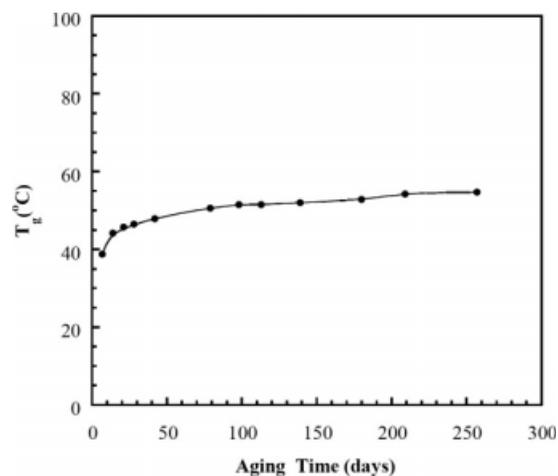
**Figure 7** TGA thermograms of BEP alloys: (●) BEP361, (■) BEP362, (◆) BEP363, (▲) BEP364.

is due to the fact that the phenolic novolac resin possesses the highest char yield (55%) among the three resins used while both benzoxazine resin and epoxy resin render lower char yield, i.e., 30–35%<sup>22</sup> and 15%,<sup>48</sup> respectively.

Flexural properties of the ternary alloys are also depicted in Figure 8. The flexural strength of the ternary alloys was observed to be in the range of 135 to 159 MPa. The results of these showed significantly higher flexural strength value compared with that of the polybenzoxazine (BA-a) reported to be 117 MPa,<sup>38</sup> while the epoxy possesses the strength of about 110–145 MPa depending on the type of the curing agent.<sup>49,50</sup> Furthermore, the increase of the epoxy resin fraction results in the slightly higher flexural strain-at-break of the samples due to the more flexibility in molecular structure of the epoxy resin compared to the other two polymers. The



**Figure 8** Flexural stress-strain curves of BEP alloys at various compositions: (●) BEP361, (■) BEP362, (◆) BEP363, (▲) BEP364.



**Figure 9** Glass transition temperature of BEP362 resin as a function of aging time.

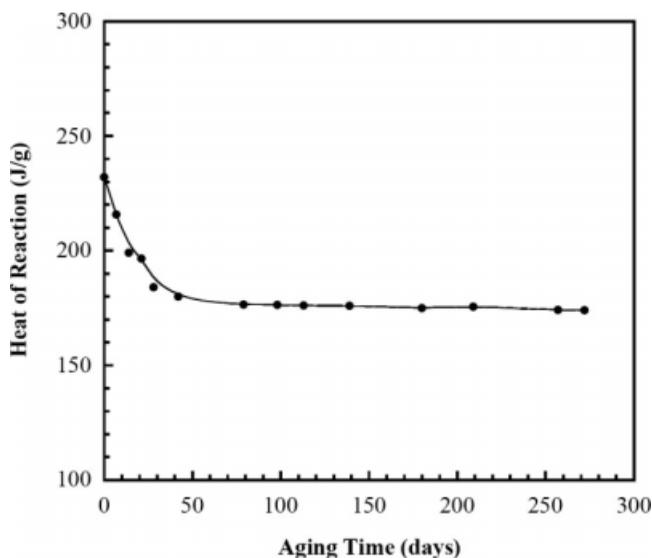
strain at break values are ranging from 3.2% in BEP364 to 3.8% in BEP361. Whereas the flexural modulus of the ternary alloy systems slightly increases when the phenolic novolac mass fraction increases, i.e., 3.8 GPa for BEP361, 4.2 GPa for BEP362, 4.5 GPa for BEP363, and 5.0 GPa for BEP364.

From these property evaluations, the ternary alloy composition to be used for composite processing in this work is BEP362 due to its relatively low curing reaction temperature with wide range of processing window 60–177°C, as well as its ultimate  $T_g$  obtained with good mechanical behaviors comparable to the other ternary systems.

### Reactivity and processability of the aged BEP362 resins

Storing of resin for prolonged time at room temperature has an effect on its final curing characteristics as a result of the so called “chemical aging.” The chemical aging of the resin will lead to permanent changes in its structure and poses some effects such as an increase of viscosity, reduction of reactivity, and more difficult processability. Thus, prepreps are usually stored at low temperatures, often below  $-20^{\circ}\text{C}$ , to ensure that there is no loss in its ability to react up to an appropriate degree of crosslinking.<sup>16</sup> In principle, the degree of crosslinking to ensure processability of the prepreps should be well below the value at its gel point, i.e., corresponding to about 35% conversion in BEP362 or 22–35% conversion in epoxy resin.

The stability of room temperature storage of BEP362 was examined by aging the resin at  $30^{\circ}\text{C}$  in a desiccator for a prolonged time. The resin sample was taken at different times and was analyzed using DSC. Figure 9 illustrates the change in  $T_g$  of BEP362



**Figure 10** Total heat of reaction of BEP362 as a function of aging time.

with the aging time. At an early stage, the  $T_g$  development as a function of aging time was observed to be relatively fast. After approximately 30 days, there was only a slight change in  $T_g$  of the resin up to 270 days. Figure 10 shows the residual heat of reaction as a function of aging time of the same system in Figure 9. From the figure, the heat of reaction of the aged resin decreases significantly in the first 30 days of the aging time and becomes almost unchanged after that. This phenomenon suggested that the cross-linking reaction of this resin mixture can proceed even at room temperature, i.e., 30°C. At this temperature, some resin molecules particularly those of the liquid epoxy may be mobile enough to cause chemical reaction. However, when  $T_g$  of the resin mixture was developed to be 15–20°C greater than its storage temperature, the crosslinking reaction was found to be effectively inhibited. The behavior is clearly in agreement with the development of  $T_g$  of the resin. In other words, increasing degree of conversion of the resin leads to an increase of  $T_g$  from the network formation in the resin. Consequently,  $T_g$ s of the aged samples were somewhat greater than that of the unaged samples, i.e., 39°C versus 53°C of the 270-day aged resin mixtures. The residual heat of reaction of BEP362 after being aged up to 270 days is about 174 J/g whereas that of the unaged resin is 232 J/g. This change corresponds to the conversion degree of BEP362 of about 25% which is well below the conversion degree of 35% at the gel point of this ternary resin mixture. Therefore, it can be inferred at this point that the prolonged time does not significantly affect the processability of BEP362 even after 270 days of room temperature storage although some changes in its  $T_g$  and heat of reaction were observed. As a consequence, the carbon fiber pre-

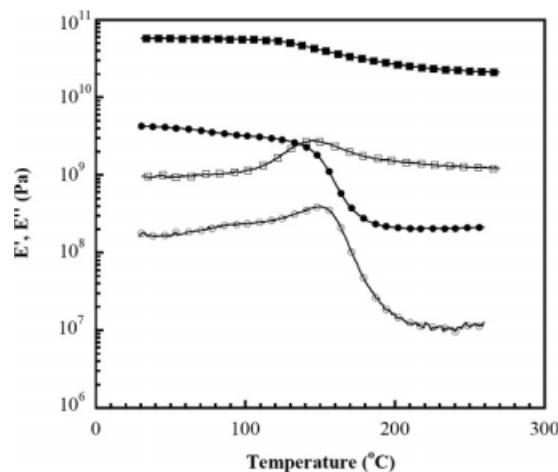
pregs from this resin is highly attractive for composite fabrication if a long shelf-life of the material is of crucial requirement.

### Mechanical properties of carbon fiber-reinforced BEP362 composites

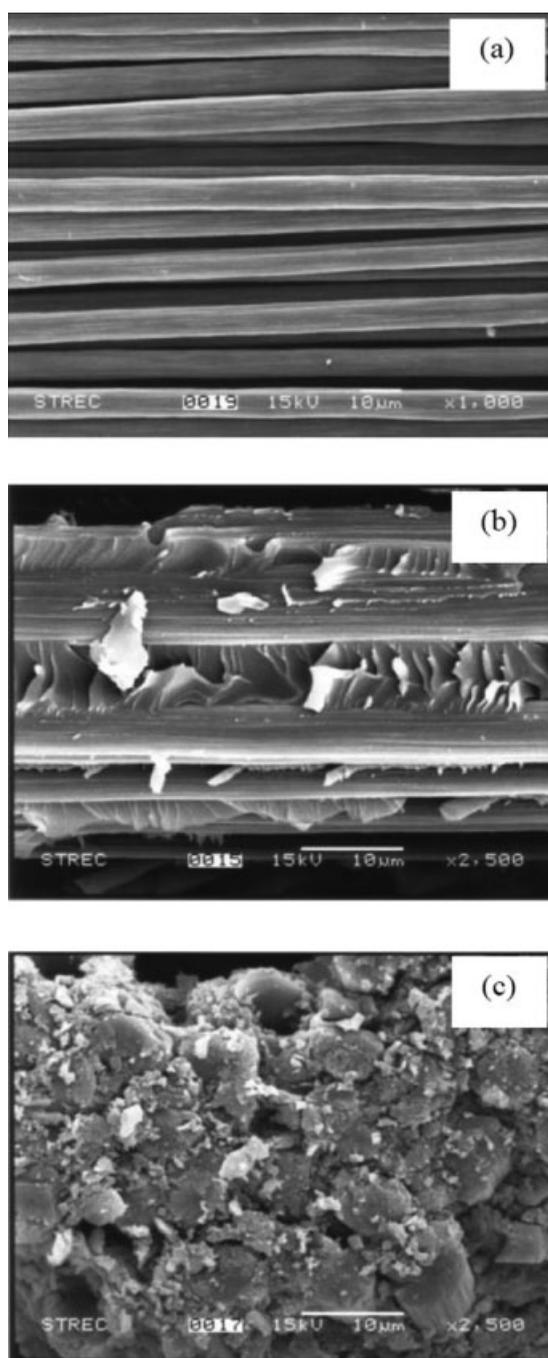
Dynamic mechanical properties of BEP362 alloy and its carbon fiber-reinforced composites are shown in Figure 11. The storage modulus ( $E'$ ), and loss modulus ( $E''$ ) were plotted at varied temperature. Plain type carbon fiber, grade KN #C100, was preimpregnated with BEP362 resin and was compression-molded to yield a fiber content of about 60% by volume. From the thermograms, the room temperature modulus ( $E'$ ) of carbon fiber-reinforced BEP362 composite exhibits a relatively high modulus value of 57.7 GPa comparing with about 4.0 GPa of the neat BEP362 alloy. Moreover, substantial enhancement in the rubbery plateau modulus of the carbon fiber reinforced BEP362 composite was also observed. Moreover, the peak positions of the loss moduli were used to indicate the  $T_g$  of the samples, and the estimated  $T_g$  of BEP362 alloy was approximately 153°C which is similar to its carbon fiber composite having the value of about 150°C. The substantial enhancement in the modulus value is comparable to the carbon fiber composite systems using high performance polybenzoxazine based on biphenyl or benzophenone as a matrix.<sup>5</sup>

### Interfacial characterization

The surface morphology of the carbon fiber and the fracture surface after bending test of the carbon fiber plain-reinforced BEP362 composite was characterized by SEM as shown in Figure 12. From Figure



**Figure 11** Dynamic mechanical properties of BEP362 alloy (●) storage modulus, (○)  $E''$  loss modulus and carbon fiber-reinforced BEP362 composite (■) storage modulus, (□)  $E''$  loss modulus.



**Figure 12** SEM micrographs (a) carbon fiber morphology (b) Fractured surface of carbon fiber plain reinforced BEP362 composite in weft region (c) Fractured surface of carbon fiber plain-reinforced BEP362 composite in warp region.

12(a), the SEM image indicates the relative smooth, defect-free fiber of the carbon fiber fabric without the BEP362 resin coating and also the fibers had cylindrical morphology with a diameter within the range of 8 microns. In addition, the fracture surface in the weft region and in the warp region of the carbon fiber plain-reinforced BEP362 composite was presented in the Figure 12(b) and 12(c), respectively.

In Figure 12(b), the fracture surface is extensively embedded with the BEP362 copolymer. This suggests that cohesive failure occurred in the BEP362 alloy matrix region due to the significant improvement in the interfacial adhesion strength between the carbon fiber and the BEP362 matrix. Moreover, the pull-out length of the carbon fiber is shorter than its full length seen in Figure 12(c). This behavior confirmed that the carbon fibers were potentially adhered by the BEP362 alloy matrix, as can be observed from the pieces of matrix attached to the fiber.

## CONCLUSIONS

The highly processable ternary systems based on benzoxazine (B), epoxy (E), and phenolic novolac (P) resins for carbon fiber composite fabrication was developed. Phenolic novolac fraction in the ternary mixtures was used to effectively lower the curing temperature and control the processing window of the resin mixtures. The mixtures were able to maintain their processing ability even after a prolonged storing time at room temperature. The optimal composition of the ternary mixtures for carbon fiber composite processing consisted of B:E:P at 3 : 6 : 2 mass ratio to yield mixture of very low melt viscosity with ultimate  $T_g$  in the fully cured polymer. The carbon fiber-reinforced BEP362 alloy also showed very high enhancement in its modulus value.

Bisphenol A is kindly supported by Thai Polycarbonate Co. Ltd. (TPCC).

## References

- Lin, P.; Han, J. L.; Yeh, J. T.; Chang, F. C.; Hsieh, K. H. *J Polym Sci* 2007, 104, 655.
- Kurmvanshi, S. K.; Gupta, A. K.; Patel, P. R.; Bajpai, R.; Keller, J. M. *Polym Eng Sci* 2008, 48, 505.
- Jang, J.; Yang, H. *J Mater Sci* 2000, 35, 2297.
- Jang, J.; Yang, H. *Compos Sci Tech* 2000, 60, 457.
- Shen, S.; Ishida, H. *Polym Compos* 1996, 17, 710.
- Ishida, H.; Chaisuwan, T. *Polym Compos* 2003, 24, 597.
- Shin, S.; Jang, J. *J Polym Sci* 2000, 35, 2047.
- Buehler, F. U.; Seferis, J. C. *Compos Part A* 2000, 31, 741.
- Delmonte, J. *Technology of Carbon and Graphite Fiber Composites*; Van Nostrand-Reinhold Company, New York, 1981, p 41–87.
- Gabriella, F. C. *Macromol Symp* 2006, 239, 217.
- Markovitz, M. U. S.; Patent 4,656,090 (1987).
- Zhang, D. U. S.; Patent 6,632,511 (2003).
- Gan, J.; Goodson, A. U.S. Patent 6,645,631 (2003).
- Saitou, T.; Hanawa, A.; Matsuzaki, T.; Sudou, M. U. S.; Patent 6,749,899 (2004).
- Goto, K.; Hayashi, S.; Saito, T.; Kaneko, K.; Mitani, K.; Wakabayashi, K.; Takagi, Y. U. S.; Patent 6,838,176 (2005).
- Frigione, M.; Kenny, J. M. *Polym Comp* 2002, 23, 530.
- Tyberg, C. S.; Bergeron, K.; Sankarapandian, M.; Shih, P.; Loos, A. C.; Dillard, D. A.; McGrath, J. E.; Riffle, J. S.; Sorathia, U. *Polymer* 2000, 41, 5053.
- Gibson, S. L.; Baranaska, V.; Riffle, J. S.; Sorathia, U. *Polymer* 2002, 43, 7389.

19. Ishida, H. U. S.; Patent 5,543,516 (1996).
20. Ning, X.; Ishida, H. *J Polym Sci Part A: Polym Chem* 1994, 32, 1121.
21. Ning, X.; Ishida, H. *J Polym Sci Part B: Polym Phys* 1994, 32, 921.
22. Ishida, H.; Sanders, D. P. *J Polym Sci Part B: Polym Phys* 2000, 38, 3289.
23. Liu, J.; Ishida, H.; *Polymeric Materials Encyclodedia*; Salamon, J. C., Ed.; CRC Press: Florida, 1996, p 484.
24. Shen, S. B.; Ishida H. *J Polym Sci* 1996, 61, 1595.
25. Jubsilp, C.; Takeichi, T.; Rimdusit, S. *J Appl Polym Sci* 2007, 104, 2928.
26. Tiptipakorn, S.; Damrongsakkul, S.; Ando, S.; Hemvichian, K.; Rimdusit, S. *Polym Degrad Stabil* 2007, 92, 1265.
27. Agag, T.; Takeichi, T. *J Appl Polym Sci* 2007, 45, 1878.
28. Ishida, H.; Rimdusit, S. *Thermochim Acta* 1998, 320, 177.
29. Rimdusit, S.; Tanthapanichakoon, W.; Jubsilp, C. *J Appl Polym Sci* 2006, 99, 1240.
30. Rimdusit, S.; Kampangsaeree, N.; Tanthapanichakoon, W.; Suppakarn, N. *Polym Eng Sci* 2007, 47, 140.
31. Rimdusit, S.; Jiraprawatthagool, V.; Tiptipakorn, S.; Covavisaruch, S. *Inter J Polym Anal Ch* 2006, 11, 441.
32. Rimdusit, S.; Jiraprawatthagool, V.; Jubsilp, C.; Tiptipakorn, S.; Kitano, T. *J Appl Polym Sci* 2007, 105, 1968.
33. Chen, Q.; Xu, R.; Yu, D. *J Appl Polym Sci* 2006, 100, 4741.
34. Kimura, H.; Matsumoto, A.; Hawegawa, K.; Ohtsuoka, K.; Fukuda, A. *J Appl Polym Sci* 1998, 68, 1903.
35. Kimura, H.; Murata, Y.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci* 1999, 74, 2266.
36. Ishida, H.; Allen, K. *J Polym Sci Part B: Polym Phys* 1996, 34, 1019.
37. Huang, M. T.; Ishida, H. *Polym Polym Compos* 1999, 7, 233.
38. Rimdusit, S.; Pirstpindvong, S.; Tanthapanichakoon, W.; Damrongsakkul, S. *Polym Eng Sci* 2005, 45, 288.
39. Takeichi, T.; Guo, Y.; Agag, T. *J Polym Sci Part A: Polym Chem* 2000, 38, 4165.
40. Takeichi, T.; Guo, Y.; Rimdusit, S. *Polymer* 2005, 46, 4909.
41. Ishida, H.; Ohba, S. *J Appl Polym Sci* 2006, 101, 1670.
42. Rimdusit, S.; Ishida, H. *Polymer* 2000, 41, 7941.
43. Rimdusit, S.; Ishida, H. *J Polym Sci Part B: Polym Phys* 2000, 38, 1687.
44. Rimdusit, S.; Ishida, H. *Rheol Act* 2002, 41, 1.
45. Ishida, H.; Rimdusit, S. U. S.; Patent 6,207,786 (2001).
46. Holly E. E.; Benkataraman, S. L.; Chambon, F.; Winter, H. H. *J Non-Newtonian Fluid Mech* 1988, 27, 17.
47. Halley, P. *J Appl Polym Sci* 1997, 64, 95.
48. Xing, H. Z.; Shang, C.; Yu, Q. M.; Guo, R. Q. *Polymer* 2006, 47, 1785.
49. Perez, R. M.; Sandler, J. K. W.; Altstädt, V.; Hoffmann, T.; Pospiech, D.; Artner, J.; Ciesielski, M.; Döring, M.; Balabanovich, A. I.; Knoll, U.; Braun, U.; Schartel, B. *J Appl Polym Sci* 2007, 105, 2744.
50. Fu, T.; Zhang, G.; Zhong, S.; Zhao, C.; Shao, K.; Wang, L.; Na, H. *J Appl Polym Sci* 2007, 105, 2611.