



A cyanate ester/microcapsule system with low cure temperature and self-healing capacity

Li Yuan^{1/2*}, Sidi Huang², Aijuan Gu¹, Guozheng Liang¹, Feng Chen¹, Yinghui Hu², Steven Nutt^{2*}

1. Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Materials Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China
2. Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089, United States

Abstract: Microcapsules filled with epoxy resin were blended into cyanate ester resin to produce systems with low cure temperature and self-healing capacity. A 4,4'-diaminodiphenylsulfone (DDS) curing agent was adopted for the systems. The mechanical properties, thermal stability and self-healing ability of the system cured at low temperature were investigated. Cyanate ester systems with 2.5 wt% and 5.0 wt% microcapsules (MCs) demonstrated an 11~43% increase in fracture toughness (KIC) relative to the neat resin cured at high temperature, and exhibited slightly lower thermal stability than the neat resin. The self-healing ability of cyanate ester with MCs was influenced by MC content and healing temperature, although for a formulation with 5.0 wt% MCs, recovery of 85% of the original fracture toughness was achieved by heat treatment of fractured samples for 1 h at 220 °C.

Key words: A. Polymer–matrix composites (PMCs); A. Smart materials; B. Fracture toughness; B. Thermal properties; C. Crack

* Corresponding authors at: Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Materials Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China (L. Yuan). Tel.: +86 512 65880967; fax: +86 512 65880089. E-mail addresses: yuanli@suda.edu.cn (L. Yuan), nutt@usc.edu (S. Nutt).

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



1. Introduction

Text Cyanate ester (CE) resins are important high-temperature thermosetting polymers. The cured CE polymers exhibit high strength, low dielectric constants and dissipation factors, radar transparency, low water absorption, and superior metal adhesion. Because of these characteristics, they are well-suited for use in electrical components, aerospace structures, adhesives and functional materials [1], [2], [3], [4] and [5]. However, the CE polymer is inherently brittle and prone to microcracking under service loads. When subjected to cyclic thermo-mechanical loading, the microcracks compromise the structural integrity of CE-based composites because of fiber/matrix debonding and inter-ply delamination [6], [7], [8], [9], [10] and [11].

Various approaches can be employed to improve the fracture toughness of CE formulations. The approaches include addition of high-thermoplastic tougheners [12], [13] and [14], rubber inclusions [15], [16], [17] and [18], inorganic or organic fillers [19], [20], [21], [22] and [23], thermosetting resins [24] and [25], and flexible molecules [26], [27] and [28]. However, these methods are largely ineffective in restoring strength to cracked or damaged material. In such cases, localized damage is commonly repaired by plug/patch and scarf repairs, bolted plates and injecting resins [29], [30] and [31], although these methods often cause new problems by altering the local stiffness, introducing local stress concentrations (e.g., from mechanical fasteners), and adding weight to the structure.

An alternative approach to repair involves the addition of polymeric microcapsules (MCs) containing a healing agent released when the MCs are ruptured by growing cracks. The addition of appropriate MCs can provide self-healing functionality and increase fracture toughness when the damage is caused by service loads [32], [33] and [34]. Investigations of self-healing thermosetting

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



materials have focused primarily on the effectiveness of self-healing in different polymers or composites fabricated at relatively low temperatures, and these studies have demonstrated benefits to both fracture toughness and the self-healing ability of epoxy resins [32], [33], [34] and [35].

In previous work, we developed systems comprised of CE resin filled with MCs, and showed that judicious additions of MCs improved mechanical properties [36]. However, MCs contents above 5.0 wt% significantly decreased the thermal decomposition temperature of the cured CE, an observation was attributed to the lower thermal stability of the MCs [36]. To design formulations for specific applications, chemists must first optimize the properties of the components of these smart materials. To date, few studies have evaluated the use of poly(urea–formaldehyde) (PUF) microcapsules filled with epoxy resins (PUF/EP MCs) as self-healing agents for high-temperature CE resins.

In this paper, we report the design and characterization of a high performance self-healing CE system with MCs (designated CE/MCs) that can be processed at low temperature (≤ 180 °C). Small amounts of MCs were blended into the CE resin to minimize the influence on the thermal stability of the CE matrix, and 4,4'-diaminodiphenylsulfone (DDS) catalyst was used in the CE formulation to decrease the polymerization reaction temperature, thus ensuring a low cure temperature. The DDS catalyst also served as a curing agent for epoxy resin released from the MCs.



2. Experimental

2.1 Materials

For MC shell materials, a formulation of urea (U) and 37 wt% formaldehyde (F) was selected (Mauinckrodt Chemicals Advantor Performance Materials Inc.), and triethanolamine (TEA) was used to control the solution pH (Alfa Aesar). Analytical grade DDS was selected as catalyst (Alfa Aesar). Industrial grade CE resin (bisphenol A dicyanate (2,2'-bis(4-cyanatophenyl)isopropylidene, 98% pure, molecular weight: 278) were acquired (Zhejiang Shangyu Shengda Biochemical Co. Ltd., China), and bisphenol A epoxy resin (EP) was selected (Henkel). PUF/EP MCs were prepared following a specific protocol [37]. Fig. 1 shows the morphologies of PUF/EP MCs. The MCs are 5~150 μm , and the mean diameter is $\sim 80 \mu\text{m}$. The epoxy content of the MCs was $\sim 82\%$ (by weight), the thermal decomposition temperature (Td: temperature at 5% weight loss) of the MCs was $\sim 213 \text{ }^\circ\text{C}$. Fig. 2 shows the chemical structures of the main materials.

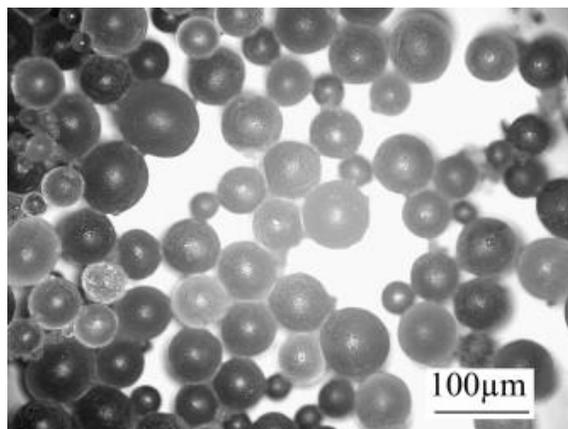


Figure 1: Spherical PUF/EP MCs.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.

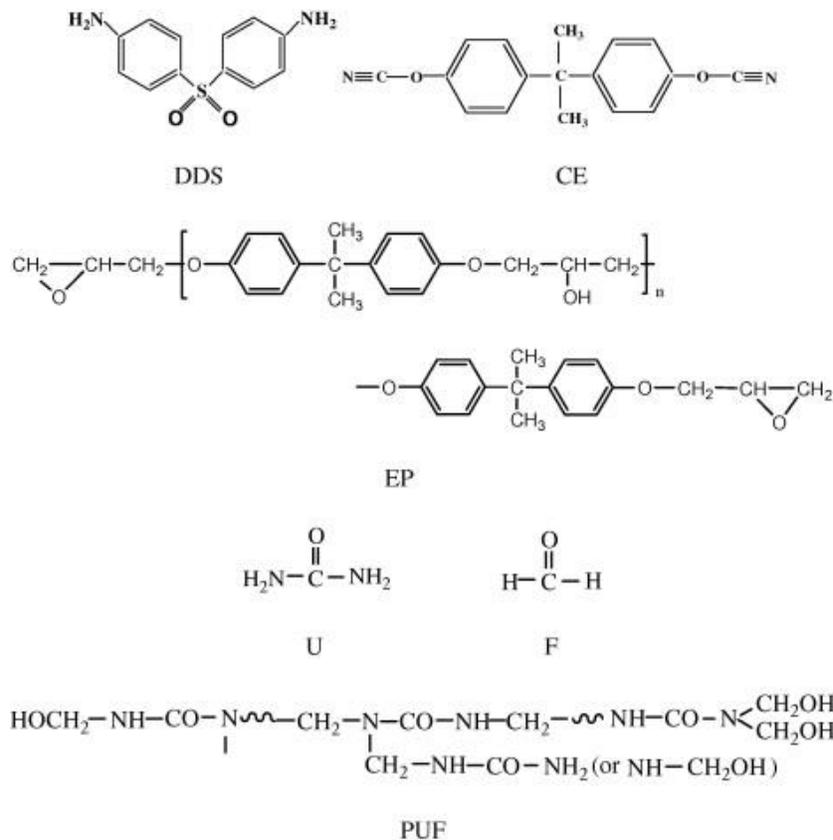


Figure 2: The chemical structures of the main materials..

2.2 Preparation of CE/MCs

To prepare the formulations, the CE resin was heated to 100 °C. After melting to a clear liquid, 1 wt% DDS was added. The temperature was raised to 120 °C and held for 30~40 min while stirring, then PUF/EP MCs (2.5 wt% and 5.0 wt%) were added and the mixture was stirred for an additional 10~20 min. Afterward, the mixture was poured into a pre-heated mold, degassed, and cured according to the following schedule: 130 °C/2 h + 150 °C/2 h + 180 °C/2 h. The cure schedule used for the neat CE was 150 °C/2 h + 180 °C/2 h + 200 °C/2 h, followed by a post-cure at 220 °C for 4 h. After curing, samples were cooled slowly to room temperature.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



2.3 Characterization

Fourier transform infrared (FTIR) spectroscopy was performed by scanning KBr discs of the samples (Nicolet, ThermoScience), and differential scanning calorimetry (DSC) experiments were performed (Q2000, TA Instruments) at a heating rate of 10 °C/min in a nitrogen atmosphere, heating from 30 to 350 °C.

Flexural properties were evaluated using a load frame (Instron 4045). The three-point bend fixture featured contact points with a 5 mm radius of curvature. Tests were conducted at 25 °C using a cross-head speed of 0.5 mm/min, and 10~15 specimens per composition were tested. The flexural strength, σ_f was calculated using following equation:

$$\sigma_f = \frac{3FS}{2wd^2} \quad (1)$$

where F is the applied force at fracture, S the span, and w and d are specimen width and depth.

Fracture toughness (K_{IC}) was measured using standard single-edge notched beam (SENB) specimens under mode I conditions. SENB specimens were loaded to fracture to determine the fracture toughness of the materials. The size and dimension of the specimen is shown in Fig. 3. The notch was introduced by first cutting a notch with a diamond saw, then generating a pre-crack by gently tapping a fresh razor blade at the base of the notch. The size of the original crack was $0.45W < a < 0.7W$. The specimen was tested at a constant 0.5 mm/min displacement rate until fracture, and 10~15 samples for each composition were tested. Fracture toughness (K_{IC}) was calculated using:

$$K_{IC} = Y \frac{3PS\sqrt{a}}{2BW^2} \quad (2)$$

where P is the critical load, B the thickness, W the width, S the span, and Y is defined as:

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



$$Y = 1.93 - 3.07\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.11\left(\frac{a}{W}\right)^3 + 25.80\left(\frac{a}{W}\right)^4 \quad (3)$$

Fractured specimens were examined by light microscopy (Keyence VHX-600). Fractured specimens were rejoined using adhesive tape to ensure mutual contact of the crack surfaces, then heated according to the following schedule: (a) heat to 200 °C and hold for 1 h and (b) heat to 220 °C and hold for 1 h. After heat treatment, the K_{IC} of the specimen was measured using the same test procedure used for the control samples. Then the self-healing efficiency (η) was calculated using Eq. (4) [32]:

$$\eta = \frac{K_{IC \text{ healed}}}{K_{IC \text{ origin}}} \quad (4)$$

where K_{IC origin} is the fracture toughness of the original specimen and K_{IC healed} is the fracture toughness of the specimen after healing.

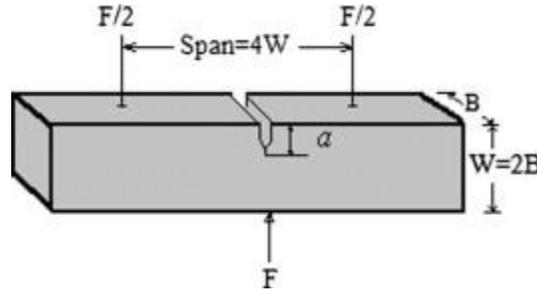


Figure 3: Dimensions of SENB specimen.

The re-bonding area is calculated using an image processing code (MATLAB). The relative re-bonded area (RRBA) is taken as the fraction of the total available fracture surface that is bonded, and is defined as $RRBA = A_b/A_t$, where A_t is the total fracture area available for bonding and A_b is the bonded area.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. “A cyanate ester/microcapsule system with low cure temperature and self-healing” *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



Dynamic mechanical analysis (DMA) was performed using a single cantilever beam clamping setup (TA Q800 DMA) between 30 and 350 °C using a heating rate of 3 °C/min at 1 Hz. Sample dimensions were 35 mm × 10 mm × 2 mm. The glass transition temperature (T_g) was determined from the peak temperature in the $\tan \delta$ -temperature plot.

The thermogravimetric (TGA) analyses were performed from 30 to 800 °C at a heating rate of 10 °C/min using nitrogen flowing at 50 ml/min (TA Instruments SDTQ500).

3. Results and discussion

3.1 Mechanical properties of CE/MCs

The flexural strength and fracture toughness of CE/MCs systems are shown in Fig. 4. Compared to the neat CE cured at high temperature, the CE/MCs systems cured at low temperature show increased flexural strength and fracture toughness (KIC). The strength and fracture toughness increase by 35% and 11% for the system with 2.5 wt% MCs, and by 50% and 43% for the system with 5.0 wt% MCs. The increases in mechanical properties can be understood from considerations of the modified chemistry, as explained below.

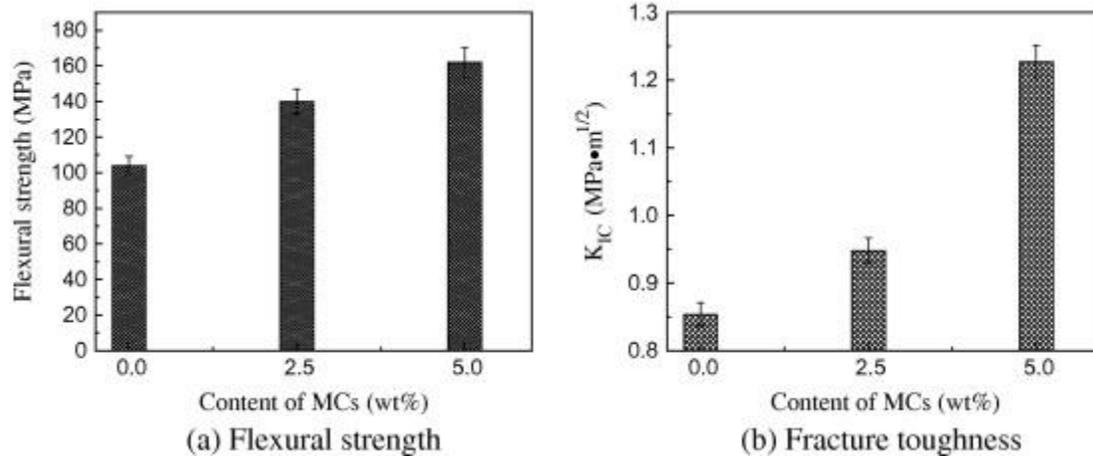


Figure 4: Flexural strength and fracture toughness of CE/MCs systems.

First, the DSC curve of the CE resin (Fig. 5a) shows that the introduction of DDS catalyst reduces the polymerization reaction peak temperature of neat CE from 300 °C to 180 °C, thus the amount of unreacted cyanate ester (single bondOCN) groups decreases at lower temperature, increasing the strength and toughness. Moreover, amine groups in DDS react with single bondOCN groups to form isoureas that contain the flexible chains [21], [38] and [39], improving the impact strength. Secondly, because the PUF shell walls contain single bondOH and amine groups, the MCs catalyze the polymerization reaction of the CE resin [3], [21], [38], [39], [40] and [41] and reduce the unreacted single bondOCN groups, yielding the DSC curve of CE/PUF and CE/MCs system in Fig. 5a. The single bondOH and amine groups react with single bondOCN groups to form iminocarbonate and isoureas, respectively, which can improve the toughness.

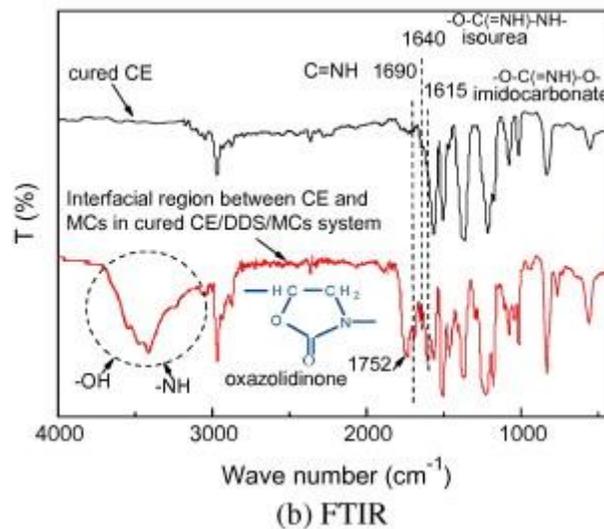
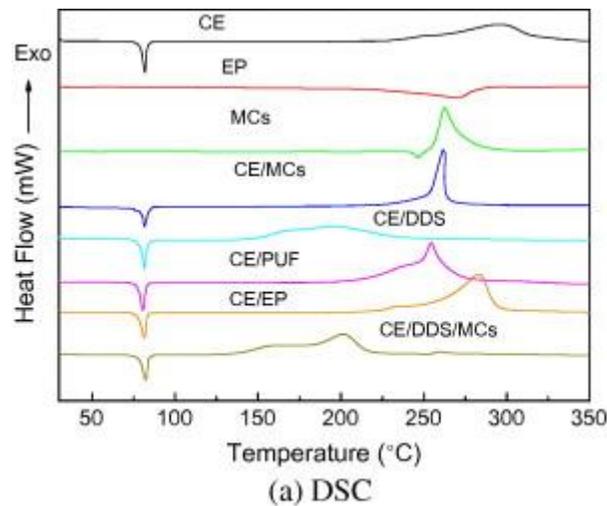


Figure 5: DSC curves of the different CE systems and FTIR spectra of cured CE and the interfacial region between CE and MCs in cured CE/DDS/MCs system.

The formation of iminocarbonate and isoureas is indicated by comparing the FTIR spectra of cured CE and the interfacial region between CE and MCs in cured CE/DDS/MCs (Fig. 5b). For all samples, the absorption peaks at 1564 cm^{-1} and 1367 cm^{-1} in the FTIR spectra are attributed to the triazine ring [3]. For the interfacial region between CE and MCs in cured CE/DDS/MCs, the absorption

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



peaks between 3710 cm^{-1} and 3090 cm^{-1} are attributed to single bondNH and single bondOH, the absorption peak at 1690 cm^{-1} is assigned to the stretching vibration of Cdouble bond; length as m-dashNH in imidocarbonate and isourea [42], the peak at 1640 cm^{-1} is attributed to the isourea [21], and the absorption peak near at 1615 cm^{-1} is attributed to imidocarbonate [40]. The epoxy resins released from MCs catalyze CE and react with single bondOCN group/triazine rings to form aliphatic oxazolidinone rings. This assertion is evidenced by comparing the DSC curves of CE, EP, CE/EP and CE/MCs (Fig. 5a), and by the absorption peak at 1752 cm^{-1} in the FTIR spectrum of the interfacial region between CE and MCs in cured CE/DDS/MCs system (Fig. 5b) [3] and [42]. The oxazolidinone rings can increase fracture toughness [43] and [44].

Thirdly, MCs behave in a visco-elastic manner at small deformations and in a plastic manner at larger deformations [45]. They can also act as stress concentrations under triaxial loading conditions, resulting in localized shear yielding or microcracking in the matrix [46]. As microcracks propagate, MCs arrest propagation, rupture and debond, absorbing energy and stabilizing the crack. Fourthly, due to the reaction between single bondOH, amine, epoxy resin, and single bondOCN groups at the CE/MCs interface, the interfacial adhesion is strong, which improves the mechanical properties. Finally, because CE/MCs systems are cured at low temperature, thermal decomposition of matrix is avoided, then the mechanical property of the systems can be improved. In this study, the CE has the same structure as BADCy reported in Ref. [36], but the DSC curves reported in this work and in Ref. [36] are different, the phenomenon is caused by the different thermal history and mixing processes employed of the sample before DSC experiment, as well as a different batch of CE.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



Fig. 6 shows images of the fracture surface of CE and CE/MCs system after fracture toughness measurements, along with FTIR spectrum of core materials of MCs. Compared to the neat CE, the CE/MCs system exhibit more irregular fracture surface, which is consistent with the higher measured toughness values. Microcracks surrounded the MCs, and ruptured MCs are evident on fracture surfaces of CE/MCs samples, indicating enhanced fracture energy absorption. In addition, the accompanying FTIR spectrum of the released core materials from the region surrounding the fractured MCs shows an absorption peak characteristic of an epoxy group at 910 cm^{-1} (Fig. 6c). Here, the released core material was collected with injection needle under a light microscope and diluted with acetone, then the dilute core material was applied to KBr disc. After the KBr disc dried at $100\text{ }^{\circ}\text{C}$ for 20 min, it was ready for FTIR experiment.

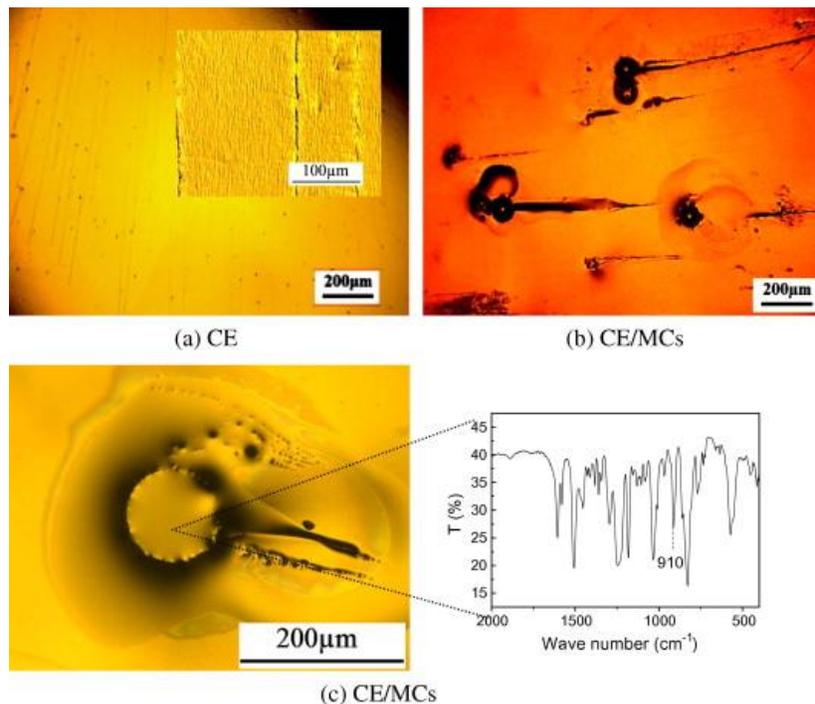


Figure 6: Fracture surfaces of CE and CE/MCs systems along with FTIR spectrum of core materials of MCs.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. “A cyanate ester/microcapsule system with low cure temperature and self-healing” *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



3.2 Thermal stability of CE/MCs

Fig. 7 shows TGA curves of CE/MCs systems. The decomposition temperature (T_d) at 5% weight loss and the temperature of maximum rate of weight loss (T_{max}) for neat CE polymer are 433 °C and 443 °C, respectively. The T_d and T_{max} of CE with 2.5 wt% MCs are 430 °C and 441 °C, and the T_d and T_{max} of CE with 5.0 wt% MCs are 412 °C and 439 °C. In contrast, the T_d for both MC loadings is slightly lower than for the neat CE, while the T_{max} for both MC contents remains roughly unchanged. The decreased T_d for the CE/MCs system is attributed to the lower thermal properties of the MCs and the creation of the molecular networks such as isoureas, iminocarbonate and oxazolidinone rings (Fig. 5b).

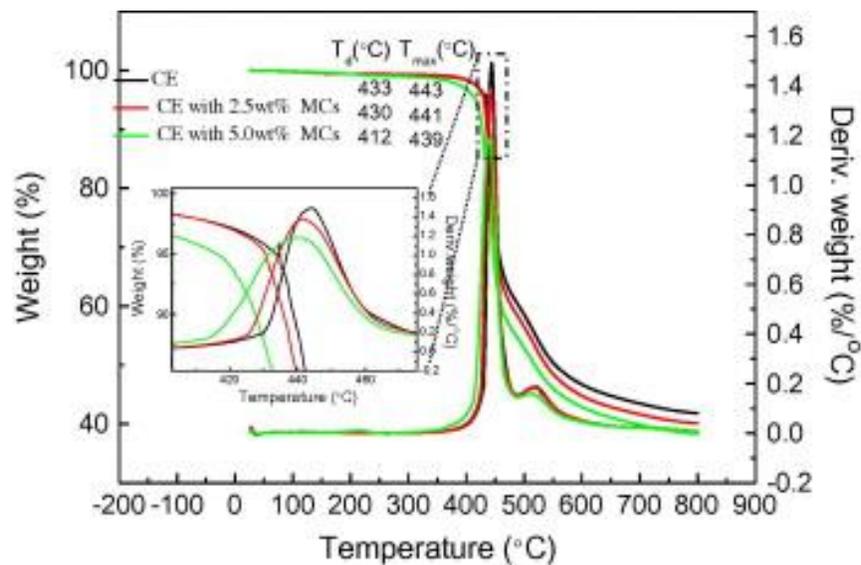


Figure 7: TGA curves of CE/MCs systems.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. “A cyanate ester/microcapsule system with low cure temperature and self-healing” *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



3.3 Thermal dynamic mechanical properties of CE/MCs

Fig. 8 shows DMA curves of CE/MCs systems. The storage moduli in the low temperature range for CE/MCs systems are slightly higher than that of neat CE. As the temperature reaches 170 °C, the storage moduli of the CE/MCs demonstrate a significant drop because of the lower stiffness of the MCs and the low molecular weight epoxy resin core materials. In addition, the drop in storage modulus can also be attributed to the flexible chains in the new networks formed by –OH, amine groups, epoxy groups and single bond OCN [3], [21], [38], [39], [40], [41], [42], [43] and [44], which have lower thermal stability. The two tan delta peaks (Tg1 and Tg2) of CE/MCs systems marked in Fig. 8 indicate multiphase materials. The broadness of the relaxation peak indicates the complexity of the phase morphology of the material. The Tg1 (at 296 °C, 301 °C and 288 °C) is strong and sharp and belongs to the transition of triazine rings. The Tg1 values for the CE/MCs systems are close to the Tg1 value for the neat CE. The small Tg2 at 224 °C is attributed to the MCs and the formation of new networks such as iminocarbonate, isoureas and oxazolidinone rings at the CE/MCs interfaces (Fig. 5b).

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. “A cyanate ester/microcapsule system with low cure temperature and self-healing” *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.

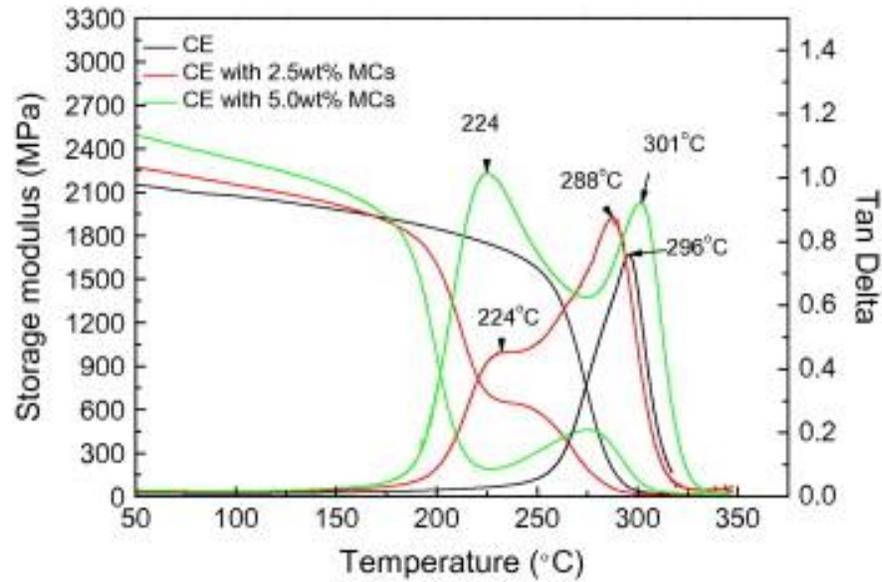


Figure 8: DMA curves of CE/MCs systems.

3.4 Self-healing ability of CE/MCs

Fig. 9 shows the dependence of self-healing efficiency (η) of healed CE/MCs systems on heating schedule. After heat treatment at 200 °C for 1 h, the CE with 2.5 wt% and 5.0 wt% MCs recover ~36% and ~43% of the original fracture toughness. When CE/MCs are healed at 220 °C for 1 h, CE with 2.5 wt% and 5.0 wt% MCs recover even more of the corresponding original fracture toughness, ~56% and ~85%, respectively.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.

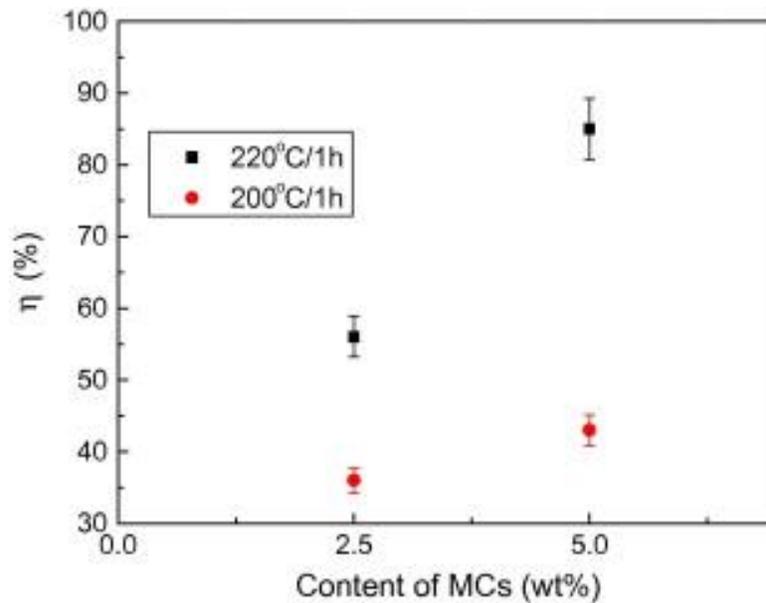


Figure 9: Dependence of self-healing efficiency (η) of healed CE/MCs systems on heating schedule.

The self-healing capacity of CE/MCs systems arises from the release of uncured epoxy from ruptured MCs, and the subsequent reaction with residual amine or amine derivatives within matrix to polymerize and re-bond the crack surfaces [47]. In particular, the released epoxy resin reacts with triazine rings in the matrix to form oxazolidinone rings [43] and [44]. The new network formation significantly increases the bond strength and restores the CE mechanical properties. For a fixed MC loading, higher healing temperatures increase the self-healing efficiency η because of the more complete reaction of epoxy. Also, for a fixed healing temperature, higher MC contents lead to higher η , because the increased amount of epoxy resins leads to more extensive coverage and bonding of crack surfaces.

Fig. 10 shows the fractured surfaces of CE/MCs systems previously fractured and healed at 220 °C for 1 h and FTIR spectrum of polymerized core materials. Adhesion traces near ruptured MCs are

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



visible on the fractured surface in Fig. 10a~c. Fig. 10a shows a microcrack that has intersected and ruptured a MC. The MC is surrounded by a roughened adhesion region caused by the spreading of epoxy resin that subsequently re-bonded to the opposing crack surface. Increasing the MC content provides more healing agent to rebond the crack surfaces (Fig. 10b). The measured values of the relative rebonded areas for CE with 2.5 wt% and 5.0 wt% MCs are 0.20 ± 0.05 and 0.54 ± 0.08 , respectively. The latter value is slightly greater than twice the former value, an observation can be attributed to capillarity effects of interacting pads of resin in close proximity, resulting in coalescence and expansion.

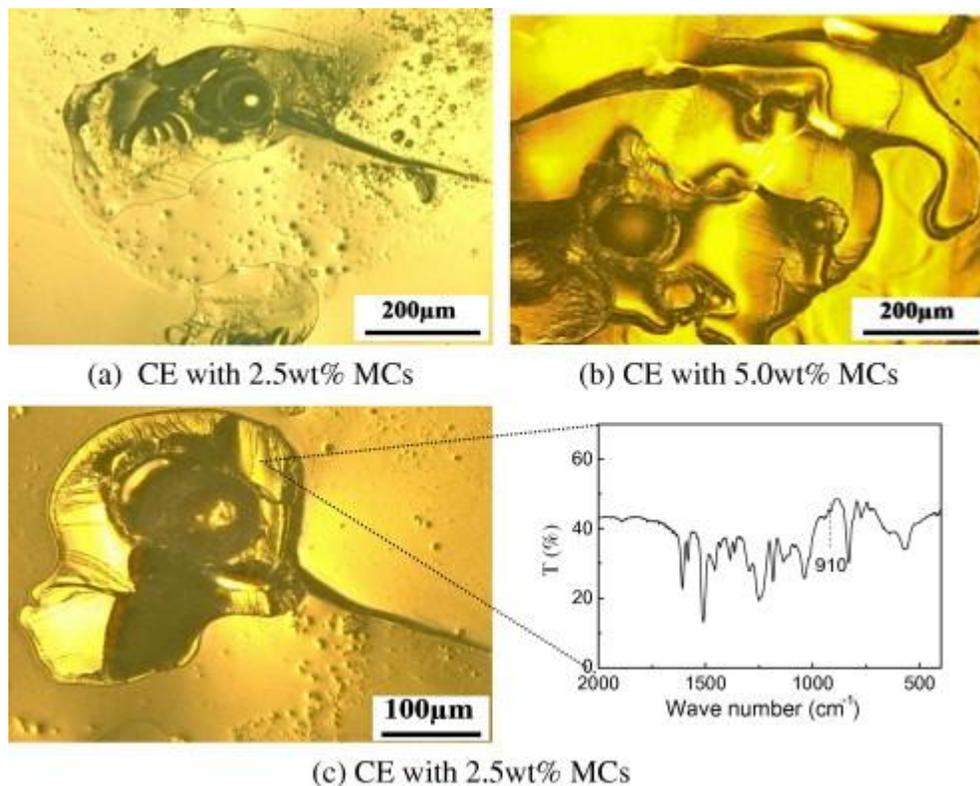


Figure 10: Fractured surfaces of CE/MCs systems previously fractured and healed at 220 °C for 1 h, and FTIR spectrum of polymerized core materials.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



The roughened peripheral regions around the MCs on the re-bonded surface contain epoxy polymers, as confirmed by the disappearance of the epoxy group absorption peak at 910 cm^{-1} in the FTIR spectrum (Fig. 10c). The disappearance of the epoxy group results from the polymerization reaction of the released epoxy resins initiated by the single bondOH, amine group and triazine rings when heated.

4. Conclusions

Self-healing CE/MCs systems with low cure temperature were formulated and mechanical properties were measured before and after healing. The self-healing CE/MCs systems exhibited enhanced mechanical properties and self-healing capacity. The flexural strength of CE loaded with 5.0 wt% MCs was 50% greater than that of neat CE, and the fracture toughness was 43% greater. The CE/MCs systems showed slightly reduced thermal decomposition temperatures due to the MCs and the formation of new networks containing iminocarbonate, isoureas and oxazolidinone rings. When MCs ruptured and released epoxy resin core material to fill cracks, subsequent heating polymerized the epoxy and re-bonded the crack surfaces, thereby restoring as much as 85% of the original fracture toughness. The findings demonstrate the effectiveness of the MC approach for development of self-healing polymer materials, and suggest the potential for extension of a similar approach to fiber-reinforced CE composites.

Acknowledgements: The authors thank the National Natural Science Foundation of China (No. 51273135), the support of the Priority Academic Program Development of Jiangsu Higher Education

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. "A cyanate ester/microcapsule system with low cure temperature and self-healing" *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



Institutions (PAPD), and “Jiangsu Government Scholarship for Overseas Studies” (2011–2012). SN acknowledges support from the M.C. Gill Composites Center.

References:

1. Nair CPR, Mathew D, Ninan KN. Cyanate ester resins recent development. *Adv Polym Sci* 2001;155:1–99.
2. Fink JK. *Reactive polymer fundamentals and applications: a concise guide to industrial polymer*. New York: William Andrew Publishing; 2005.
3. Hamerton I. *Chemistry and technology of cyanate ester resins*. Glasgow: Chapman and Hall; 1994.
4. Yeager GM, Pan YQ. General Electric Company. Cyanate ester based thermoset compositions. US Patent No: 6245841; 2001.
5. Wooster TJ, Abrol S, Hey JM, MacFarlane DR. Thermal, mechanical, and conductivity properties of cyanate ester. *Composites Part A* 2004;35(1):75–82.
6. Wu AS, Coppola AM, Sinnott MJ, Chou TW, Thostenson ET, Byun JH, Kim BS. Sensing of damage and healing in three-dimensional braided composites with vascular channels. *Compos Sci Technol* 2012;72(13):1618–26.
7. Talrega R. *Damage mechanics of composite materials*. New York: Elsevier Science; 1994.
8. Campbell FC. *Manufacturing processes for advanced composites*. New York: Elsevier Science; 2004.
9. Hillermeier RW, Seferis JC. Environmental effects on thermoplastic and elastomer toughened cyanate ester composite systems. *J Appl Polym Sci* 2000;77(3):556–67.
10. Brown TL. *Microcracking of materials for space*. Langley Research Center, NASA; 1998.
11. Imbriale WA, Gao S, Boccia L. *Space antenna handbook*. Chichester: John Wiley & Sons Ltd.; 2012.
12. Kinloch AJ, Taylor AC. The toughening of cyanate-ester polymers Part II chemical modification. *J Mater Sci* 2003;38:65–79.
13. Tao QS, Gan WJ, Yu YF, Wang MH, Tang XL, Li SJ. Viscoelastic effects on the phase separation in thermoplastics modified cyanate ester resin. *Polymer* 2004;45(10):3505–10.
14. Hwang JW, Park SD, Cho K, Kim JK, Park CE, Oh TS. Toughening of cyanate ester resins with cyanated polysulfones. *Polymer* 1997;38(8):1835–43.
15. Feng Y, Fang ZP, Gu AJ. Toughening of cyanate ester resin by carboxyl terminated nitrile rubber. *Polym Adv Technol* 2004;15(10):628–31.
16. Liu J, Ding ND, Xu RF, He QH, Shen J, Hu BX. Cyanate ester resin modified by hydroxyl-terminated polybutadiene: morphology, thermal, and mechanical properties. *Polym Eng Sci* 2011;51(7):1404–8.
17. Zeng MF, Sun XD, Yao XD, Wang Y, Zhang MZ, Wang BY, et al. Modification of cyanate ester resin by hydroxyl-terminated liquid butadiene-acrylonitrile rubber and free volume properties of their composites. *J Appl Polym Sci* 2010;115(1):338–45.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. “A cyanate ester/microcapsule system with low cure temperature and self-healing” *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



18. Hayes BS, Seferis JC, Parker GA. Rubber modification of low temperature cure cyanate ester matrices and the performance in glass composites. *Polym Eng Sci* 2000;40(6):1344–9.
19. Johna B, Nair CPR, Ninan KN. Effect of nanoclay on the mechanical, dynamic mechanical and thermal properties of cyanate ester syntactic foams. *Mater Sci Eng A* 2010;527:5435–43.
20. Yu DH, Wang B, Feng Y, Fang ZP. Investigation of free volume, interfacial, and toughening behavior for cyanate ester/bentonite nanocomposites by positron annihilation. *J Appl Polym Sci* 2006;102(2):1509–15.
21. Pan YZ, Xu Y, An L, Lu HB, Yang YL, Chen W, et al. Hybrid network structure and mechanical properties of rodlike silicate/cyanate ester nanocomposites. *Macromolecules* 2008;41(23):9245–58.
22. Wooster TJ, Abrol S, Hey JM, MacFarlane DR. The effect of particle matrix adhesion on the mechanical properties of silica filled cyanate ester composites. *Macromol Mater Eng* 2004;289(10):872–9.
23. Haman K, Badrinarayanan P, Kessler MR. Effect of a zirconium tungstate filler on the cure behavior of a cyanate ester resin. *ACS Appl Mater Int* 2009;1(6):1190–5.
24. Gu AJ. High performance bismaleimide/cyanate ester hybrid polymer networks with excellent dielectric properties. *Compos Sci Technol* 2006;66(11–12):1749–55.
25. Lin CW, Lin RH, Lu WH. Cure reactions in the blend of cyanate ester with maleimide. *Polymer* 2004;45(13):4423–35.
26. Zhuo DX, Gu AJ, Liang GZ, Hu JT, Yuan L, Ji LF. Novel hyperbranched polyphenylsilsesquioxane-modified cyanate ester resins with improved toughness and stiffness. *Polym Int* 2011;60(8):1277–86.
27. Kumar TP, Sivasankar B. Poly(ether urethane) flexible cyanate ester resins: synthesis, characterization, and performance in commercial epoxy and polyurethane applications. *J Appl Polym Sci* 2008;107(1):193–202.
28. Pazhanikumar T, Sivasankar B, Sugumaran T. Synthesis, characterization and applications of polyurethane aryl cyanate ester resin. *High Perform Polym* 2007;19(1):97–112.
29. Myhre SH, Labor JD. Repair of advanced composites structures. *J Aircr* 1981;18(7):546–52.
30. Roh HS. Repair of composites structure. Purdue University; 2011.
31. Tong LY, Sheppard A, Kelly D. A numerical study of adhesively bonded composite panel-flange joints. *Compos Struct* 1994;28:449–58.
32. White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. Autonomic healing of polymer composites. *Nature* 2001;409:794–7.
33. Yin T, Rong MZ, Zhang MQ, Yang GC. Self-healing epoxy composites preparation and effect of the healant consisting of microencapsulated epoxy and latent curing agent. *Compos Sci Technol* 2007;67(2):201–12.
34. Kessler MR, Scottos NR, White SR. Self-healing structural composite materials. *Composites Part A* 2003;34(8):743–53.
35. Caruso MM, Blaiszik BJ, White SR, Sottos NR, Moore JS. Full recovery of fracture toughness using a nontoxic solvent-based self-healing system. *Adv Funct Mater* 2008;18:1898–904.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. “A cyanate ester/microcapsule system with low cure temperature and self-healing” *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.



36. Yuan L, Gu AJ, Liang GZ. A novel cyanate ester resin/microcapsules system. *Polym compos* 2010;31(1):136–44.
37. Yuan L, Liang GZ, Xie JQ, Lan L, Guo J. Preparation and characterization of poly(urea-formaldehyde) microcapsules filled with epoxy resins. *Polymer* 2006;47(15):5338–49.
38. Wang SK, Sung CSP. Spectroscopic characterization of model urea, urethane compound, and diamine extender for polyurethane–urea. *Macromolecules* 2002;35(3):877–82.
39. Queiroz DP, de Pinho MN, Dias C. ATR-FTIR studies of poly(propylene oxide)/polybutadiene bi-soft segment urethane/urea membranes. *Macromolecules* 2003;36(11):4195–200.
40. Lin Y, Jin J, Song M, Shaw SJ, Stone CA. Curing dynamics and network formation of cyanate ester resin/polyhedral oligomeric silsesquioxane nanocomposites. *Polymer* 2011;52(8):1716–24.
41. Harismendy I, Gomez CM, Río MD, Mondragon I. Cure monitoring of catalysed cyanate ester resins. *Polym Int* 2000;49(7):735–42.
42. Kim BS. Effect of cyanate ester on the cure behavior and thermal stability of epoxy resin. *J Appl Polym Sci* 1997;65(1):85–90.
43. Mathew D, Nair PCR, Ninan KN. Bisphenol a dicyanatenovolac epoxy blend: cure characteristics, physical and mechanical properties, and application in composite. *J Appl Polym Sci* 1999;74(7):1675–85.
44. Lin RH, Hsu JH. FT-IR and DSC investigation on the cure reaction of the dicyanate/diamine system. *Polym Int* 2001;50(10):1073–81.
45. Sun G, Zhang Z. Mechanical strength of microcapsules made of different wall materials. *Int J Pharm* 2002;242(1–2):307–11.
46. Brown EN, White SR, Scottos NR. Microcapsule induced toughening in a selfhealing polymer composite. *J Mater Sci* 2004;39(5):1703–10.
47. Lee H, Neville K. *Epoxy resins: their applications and technology*, Literary Licensing LLC, Whitefish, 2012.

L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hui, and S. Nutt. “A cyanate ester/microcapsule system with low cure temperature and self-healing” *Compos Sci & Tech* 87 (2013) 111-117 DOI<<http://dx.doi.org/10.1016/j.compscitech.2013.08.005>>.