

Available online at www.sciencedirect.com

jmr&t
Journal of Materials Research and Technology
www.jmrt.com.br



Original Article

Modification of cyanate resin by conjugated tri-component interpenetrating polymer networks



Wang Chuang^{a,*}, Jiao Geng-sheng^b, Zhu Bao-lin^b, Peng Lei^a,
He Wen-min^a, Zhao Li-ping^a

^a Shaanxi Province Engineering Laboratory of High Performance Concrete, Shaanxi Railway Institute, Weinan, China

^b School of Life Science and Chemical Engineering, Weinan Teachers University, Weinan, China

ARTICLE INFO

Article history:

Received 22 September 2016

Accepted 29 December 2016

Available online 6 March 2017

Keywords:

Cyanate ester

Interpenetrating polymer networks

Methyl methacrylate

Styrene

ABSTRACT

Cyanate ester (CE) resin was modified in a multi-component way using the technology of conjugated tri-component interpenetrating polymer networks (CTC-IPN). Experimental results showed that the three components in the modified composite existed undependably and they interweaved irregularly in the structure of IPN to form a unique supermolecule structure. The analysis by differential scanning calorimetry (DSC) indicated that the T_g of the modified CE was increased by 22 °C, compared with the T_g prior to modification. When the amount of an initiator was 0.3% or 0.4% and concurrently the ratio of PST/PMMA/CE was 15/15/85, the flexural strength and the impact strength reached the maximum values. Compared with those of pure CE, the flexural strength was increased by 22.65% and the impact strength by 94.99%, respectively.

© 2017 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Interpenetrating polymer networks (IPN) is a kind of interweaved net polymer formed by the interpenetration of two or more than two kinds of cross linked polymers [1–5]. This kind of polymer is different from the usual mechanical blending polymer and the graft copolymer. It is the cross linked interaction of different components, interfingering through the polymer network. In general, IPN is not the cross link at the molecular level, but the interpenetration at the supramolecular level. IPN can improve the compatibility of various molecular chains, enhance the network density, and

micronize the phase microstructure to improve the binding force between phase and phase. Thus, the structural changes and phase structure that a single polymer does not have are achieved. The mechanical properties and other properties are eventually improved [5,6].

In 1960, Millar first proposed the concept of IPN [3,7,8]. Thirty years later, Jia Demin, on the basis of this concept, explained the connotation of the conjugated three-component interpenetrating polymer networks (CTC-IPN) [9–11]. He thought that CTC-IPN is a unique ternary interpenetrating polymer network system, of which one polymer is acted as a public network and two other linear polymers, not interpenetrating but contacting closely, penetrate each

* Corresponding author.

E-mails: wangchuang1961@sina.com, petermullarky@163.com (W. Chuang).

<http://dx.doi.org/10.1016/j.jmrt.2016.12.002>

2238-7854/© 2017 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Table 1 – Comparison of mechanical properties between interfacial conjugated inter-penetrating polymers and pure CE under different formulations.

No.	Formulation	CE/MMA/ST (mass ratio)	Impact strength/KJ m ⁻²	Flexural strength/MPa
1	A	75/25/25	10.621	117.611
2	B	80/20/20	12.084	124.152
3	C	85/15/15	15.307	138.626
4	D	90/10/10	11.489	119.064
5	E	95/5/5	10.435	115.096
6	F	100/0/0	7.85	113.023

other and entangle in the public network. This way, three polymers are closely combined to give CTC-IPN composite a special structure, morphology and properties [12,13]. This special interface structure of CTC-IPN is called the interface conjugated interpenetration [7,11,14].

In this work, cyanate ester resin was modified using a CTC-IPN interface conjugated interpenetrating method. Bisphenol A type isocyanate resin (BADCy) was used as a public network to interpenetrate and entangle each other with methyl methacrylate (PMMA) and polystyrene (PST) to finally prepare an interface conjugated three-component interpenetrating polymer composite. The composite prepared was characterized by infrared spectrometer (IRS) and differential scanning calorimetry (DSC). The mechanical properties of the composite were carefully investigated.

2. Experimental

2.1. Experimental raw materials and pretreatment

Bisphenol A cyanate ester resin (industrial product, 98% in purity, white crystal, melting point 79 °C) was made in Ji'nan, China. Prior to experiment, it was dried for subsequent preparation at the temperature between 50 and 60 °C. Methyl methacrylate (MMA), analytical reagent, was made in Tianjin Chemical Reagent Factory No.6, China. It was washed by alkali (0.1 mol/L NaOH) in atmospheric distillation. Styrene (ST), chemical pure, was from Tianjin Dagang Chemical Plant, China. It was washed by alkali (0.1 mol/L NaOH) at atmospheric distillation. Azobisisobutyronitrile (AIBN), chemical pure, was purchased from Shanghai Four Hervey Chemical Co., Ltd. Epoxy resin, bisphenol A type (two glycerine ether DGEBA), epoxy value 0.52, industrial product, was made in Wuxi Di'aisheng Epoxy Co., Ltd.

2.2. Synthesis of interfacial conjugated interpenetrating polymer network

In the presence of trace evocating agent AIBN, MMA and ST were pre-polymerized, respectively, at the temperature between 60 and 70 °C for 2 h. When the reagent turned slightly thickened, a quantitative BADCy melt was added with the temperature around 60 °C. A homogenizer was employed to stir the mixture evenly. The mixture was transferred into a preheated mold and placed in a thermostat of the constant temperature of 70 °C for 1 h. The box was vacuumed to remove air bubbles. According to the curing process of 120 °C/2 h–150 °C/1 h–180 °C/1 h–200 °C/4 h, the mixture was

polymerized and solidified, cooling naturally to room temperature.

2.3. Testing instruments and characterization of performances

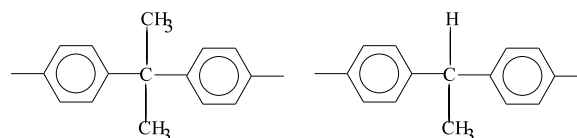
The impact strength and the bending strength were measured, respectively, in German DL-1000B and XCL-40 material testing machines in accordance with the specifications of GB3357-82 and GB3356-82. The deviation was controlled within less than 10%. The sample size was 15 mm × 10 mm × 4 mm. The coating method and the KBr compression method were adopted for infrared spectrum analysis, using a WQF-310 infrared spectrometer made in Beijing Second Optical Instrument Factory. The glass transition temperature was characterized by differential scanning calorimetry in accordance with the national standard GB1634-79. It was measured by a Perkin-Elmer DSC thermal analyzer in nitrogen atmosphere. The starting temperature was 50 °C and the heating rate was increased by 10 °C/min.

3. Results and discussion

3.1. Comparison of mechanical properties of pure CE and interfacial conjugated interpenetrating polymer network

Table 1 indicated the mechanical properties of the modified system under different formulations. As can be seen, except A formula, the impact strength of the PST/PMMA/CE in different mass ratios was all superior to that of pure cyanate ester resin. This is mainly because that cyanate ester resin, methyl methacrylate, and polystyrene interpenetrated each other, entangling to form an interface conjugated interpenetrating network. This network played a role of “forced inclusion” and “synergetic effect” [7,12].

Cyanate ester is a thermosetting resin. Its structural formula is N=C–O–R–C=N, where R stands for



CE was in situ polymerized (curing) into polycyanurate (PCN) at high temperature under the action of catalyst. PCN has many advantages of good toughness, higher glass transition temperature (T_g), lower dielectric constant and loss factor, lower water absorption rate, and inherent flame retardancy. At high temperature (220–270 °C), its molten body is chemically

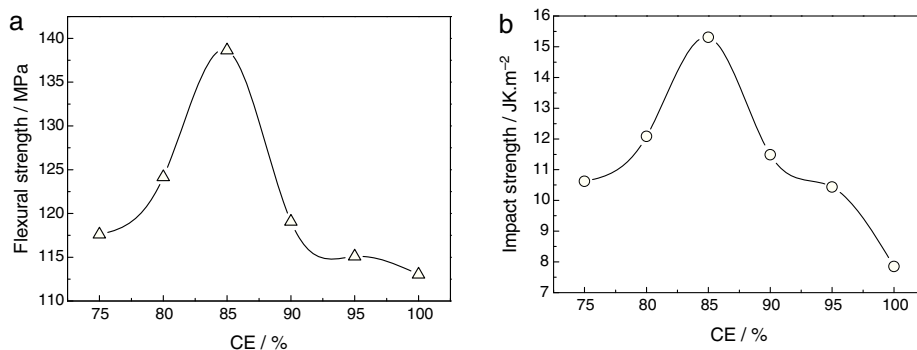


Fig. 1 – Influence of ST/MMA contents on the mechanical properties of IPN.

stable. At the high temperature of 250 °C, it still has excellent bonding on metal conductors [3,7,11].

After physical modification of CE, the so-called semi interpenetrating network (IPN) was formed. This network can also make CE consolidated into PCN. The disadvantage of physical modification is that the achieved PCN is heterogeneous, the regional structure of each phase is difficult to control, and the processing performance is poor. The curing degree of CE depends on the final morphology of the polymer blends.

The main factors that affect the performances of IPN are the interpenetrating degree, component ratio, and cross link density. Due to the enhancement of the interpenetration between the three components and the decrease of the density of the single component such as CE, the impact strength and bending strength of the network polymer are obviously improved, both of which are consistent with the experimental design.

3.2. Influence of MMA/ST contents on the mechanical properties of IPN

Fig. 1 demonstrated the changes of the mechanical properties of IPN with different contents of ST/MMA. Obviously, in the system of different ratios of ST/MMA/CE, both the flexural strength and the impact strength of IPN were increased first and then decreased sharply with the gradually increasing mass ratios of MMA and ST as shown in Fig. 1(a) and (b). The maximum values of both appeared at the content of CE 85%. They reached the optimum state in the mass

ratios of CE/MMA/ST 85/15/15. Compared with the pure CE, the bending strength increased by 22.65%, whereas the impact strength was improved by 94.99%. This is mainly because, with the increase of the contents of MMA and ST, the system transformed gradually from the single CE phase into the miscible system of PMMA and PST assisted phase. The interpenetrating extent of CE with PMMA and PST was gradually increased, improving the rigid dense structure of the pure CE macromolecular network to form a system of interpenetrating interface conjugated supramolecular structure. As a result, the purpose of toughening modification was realized.

However, when the contents of MMA and ST were continuously increased, the compatibility between phase and phase was gradually declined, the self aggregation tendency of each component was enhanced, and the supramolecular structure was gradually weakened. Meanwhile, the main featured structure of CE suffered a greater degree of impact. As a result, both the impact strength and the bending strength were decreased significantly.

3.3. Effect of initiator dosage on the mechanical properties of IPN system

Fig. 2 indicated the effect of AIBN contents on the mechanical properties of the composite. When the amount of initiator (against the mass of cyanate ester resin) was 0.3%, the flexural strength of the composite reached the maximum value as shown in Fig. 2(a). When it was lower or higher than 0.3%, the flexural strength was declined. When the amount of AIBN

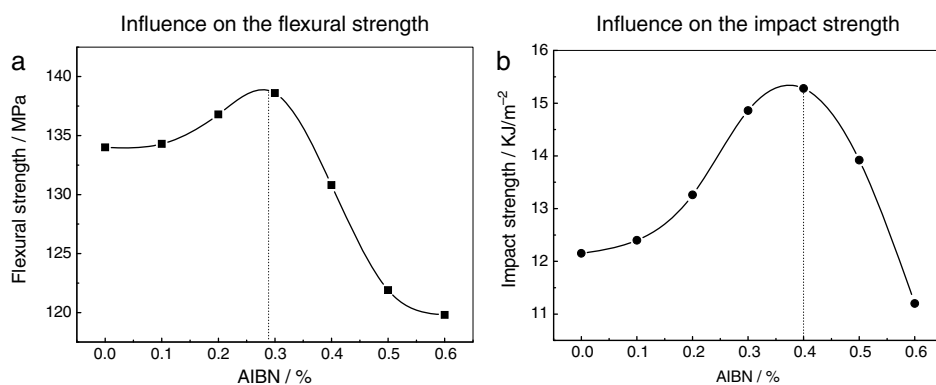


Fig. 2 – Curves of the mechanical properties of the composite varied with the AIBN dosage: (a) Bending strength varies with the amount of AIBN; (b) Impact strength varies with the amount of AIBN.

Table 2 – The characteristic absorption peaks of different groups of cyanate ester (cm^{-1}).

Benzene ring	Ether bond	Poly cyanate	Triazine ring	Isocyanate	Amine (radical) cyanide	Cyanogroup	Methyl	Hydroxyl
830	1120	1369	1565	1696–1457	2210	2270–2235	2960	3400–3600

was 0.4%, the impact strength of the IPN system reached the maximum value seen Fig. 2(b). In the case of the amount of AIBN being below or above that value, the impact strength was reduced. The variations were due to the reason that when the concentration of the initiator was at a certain proper value, the polymer chain formed by the pre-polymerization of MMA and ST was wrapped around the network formed by CE. In this situation, PST and PMMA had larger activity space. The CE macromolecular network structure characteristics were slightly influenced. At this moment, the synergistic effect was dominated. Together with the cyanate resin net, CE shared the impact from the external force, enhancing the strength and toughness of the cyanate ester resin.

When the amount of the initiator was too large, the fast reaction between PMMA and PST took place. Prior to interpenetrating and entanglement, the reaction was completed. Thus, the modification was unable to be realized. But when the amount of the imitator was too small, the reaction speed was too slow. In this case, a linear polymer chain segment of ideal polymerization degree was unable to form within the effective time. The interpenetrating and winding process was impossible to be completed. It was difficult to form the polymer of the interface conjugated supramolecular structure. So, IPN cannot play its normal role, reducing greatly the effect over the toughness of CE [9,13].

3.4. Analysis by infrared spectrum

The wavenumber of the characteristic absorption of each group in the cyanate resin was shown in Table 2. From the infrared spectroscopy in Fig. 3(a), it can be seen that, before and after modification of the cyanate resin, there were

two stronger cyanogen doublets at 2235 cm^{-1} and 2270 cm^{-1} , respectively, indicating that there existed cyanogens in the semi cured product. A weak absorption peak appeared at between 3400 cm^{-1} and 3600 cm^{-1} , showing that there was a small amount of hydroxyl group that was not fully reacted. At 1750 cm^{-1} , a carbonyl absorption peak occurred, signifying that cyanate was reacted partially to generate urethane or imino carbonic acid ester. At 1369 cm^{-1} , the absorption peak was narrowed, demonstrating that there was polycyanate. At 1565 cm^{-1} , a strong absorption peak appeared, which proved the existence of triazine ring. It can be inferred that the system was partially polymerized and the polymerization reaction of forming triazine ring took place.

Comparing Fig. 3(a) with (b), it can be seen clearly that the content of cyanate ester in the IPN system was decreased significantly at 2270 cm^{-1} , whereas the content of triazine ring was increased apparently at 1560 cm^{-1} . This variation showed that at low temperature the self polymerization of cyanate ester occurred mainly to produce the structure of triazine ring. In this case, the characteristic functional groups were still clearly visible in Fig. 3(a) and (b). In terms of pure cyanate resin, there was very slight difference in the two figures. The only small difference lied in the appearance of functional groups of other components, which indicated that, in the curing process, chemical bonds were formed independently in the three components. They interpenetrated and entangled CE through linear polymers, constituting unique CTC-IPN supramolecular structure [7].

3.5. Analysis of differential scanning calorimetry

Fig. 4 showed the T_g spectra of the glass transition temperature, from which it can be seen that the T_g of pure CE was

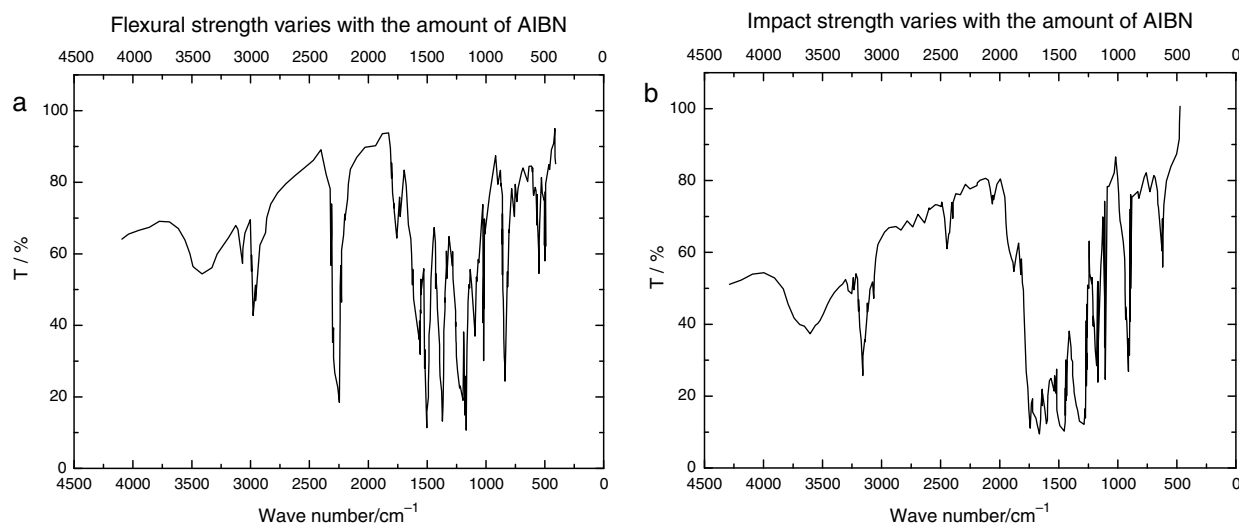
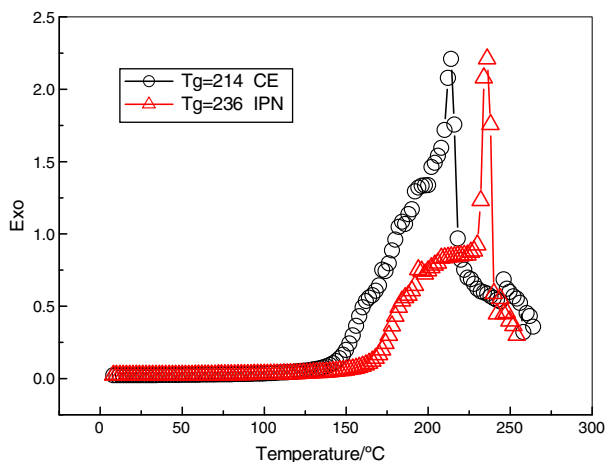


Fig. 3 – IR spectra before and after modification of CE: (a) Pure CE (120 °C, 2 h); (b) Polymer (200 °C, 2 h).

Table 3 – Corrosion rate of H₂SO₄ and NaOH on the curing composite.

Contents of MMA and ST %	0	5	10	15	20	25
Corrosion rate of H ₂ SO ₄ %	0.64	0.61	0.56	0.54	0.53	0.51
Corrosion rate of NaOH %	0.59	0.57	0.56	0.55	0.53	0.51

**Fig. 4 – DMA curves of the vitrification temperature.**

at 214 °C. After modification, the T_g of the PST/PMMA/CE composite was 236 °C, increasing by 22 °C. In addition, the graph after modification was similar to that of pure CE. Only one glass temperature appeared, which showed that a unique interface conjugated IPN system was fully formed through the interpenetrating and entanglement of the three components as well as through the interface conjugation. No phase separation took place.

The characteristics of a single phase always maintained such that the performances of CE modified system were optimized obviously. Eventually, the heat resistance of the composite was greatly improved.

3.6. Corrosion resistance of the composite

The PST/PMMA/CE composite can be used as parts of aviation equipment [1,3,6,7]. In the aerospace environment, the components often suffer from acid, alkali, ultraviolet and other corrosion. Therefore, there are high requirements for the curing material against the chemical resistance and high-light corrosion. To improve the resistance against corrosion, a sample was soaked in 10% HCl solution, 6 mol/L H₂SO₄ solution, and 20% NaOH solution for 18 days. Then, the changes were observed and the amount of losses was measured.

The experimental results showed that 10% HCl solution did not have a corrosive effect on the cured product, while 6 mol/L H₂SO₄ solution and 20% NaOH solution had a certain degree of corrosion. The test results were shown in Table 3.

From the experimental results, it is known that, compared with pure CE, the corrosion degree of the solidified product was gradually reduced with the increase of the contents of ST and MMA. As a whole, the mass loss of the IPN system was less than 1%, which can meet the requirements of the aerospace environment. This result is directly related to the introduction of PMMA/PST. When PMMA/PST was introduced,

two macromolecular chains crossed and entangled to cover and reinforce the local non-aggregation point of the CE network, leading eventually to more complete polymerization degree. As a result, the corrosion resistance of the interpenetrating polymer network composite was enhanced.

4. Conclusions

- (1) After CE was modified by the CTC-IPN interfacial conjugated interpenetrating method, both the mechanical properties and the glass transition temperature of the achieved PST/PMMA/CE composite system were improved significantly. The interface conjugated interpenetrating polymer network that was synthesized in accordance with the process of 120 °C/2 h–150 °C/1 h–180 °C/1 h–200 °C/4 h exhibited the best mechanical property at the ratio of ST/MMA/CE = 15/15/85. Compared with the pure CE, the impact strength was increased by 69.99%, while the bending strength by 12.92%.
- (2) IR analysis and DSC results showed that the three components coexisted independently. Through interpenetrating and entanglement, they were together with CE to form the interface conjugated supramolecular network system. This way, T_g was increased by 22 °C and the IPN system of unique structure was constituted. At the same time, the initiator AIBN exerted a certain influence on the mechanical properties of the system.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

The authors would like to express their gratitude for the financial support by Shaanxi Province Engineering Laboratory of High Performance Concrete with the grant No. G2015-03 and No. G2015-05 as well as by Weinan Basic Research Innovation Talent Project with the grant No. 2015KYJ-3-3. The authors would also like to thank Prof. Li Kezhi of Northwestern Polytechnical University for his experimental support.

REFERENCES

- [1] Zhuo D-X, Gu A-J, Liang G-Z, Hu J-T, Cao L, Li Y. Flame retardancy and flame retarding mechanism of high performance hyperbranched polysiloxane modified bismaleimide/cyanate ester resin. *Polym Degrad Stab* 2011;96(4):505–14.
- [2] Gu X, Zhang Z-J, Yuan L, Liang G-Z, Gu A-J. Developing high performance cyanate ester resin with significantly reduced postcuring temperature while improved toughness, rigidity,

- thermal and dielectric properties based on manganese-Schiff base hybridized graphene oxide. *Chem Eng J* 2016;298(8):214–24.
- [3] Baikova L, Pesina T, Sakseyev D, Fainleib A, Bershtein V. Hybrid cyanate ester resin-based nanocomposites: increased indentation size effect due to anomalous composition of micron subsurface layer. *Polym Test* 2016;53(8):15–8.
- [4] Wang J-L, Wang C, Jiao G-S, Wang Q-Y. Study of SiO₂/PMMA/CE tri-component interpenetrating polymer network composites. *Mater Sci Eng A* 2010;527(7–8):2045–9.
- [5] Zeng M-F, Lu C-Y, Wang B-Y, Qi C-Z. Free volume hole size of cyanate ester resin/Epoxy resin interpenetrating networks and its correlations with physical properties. *Radiat Phys Chem* 2010;79(9):966–75.
- [6] Lin Y, Song M, Stone CA, Shaw SJ. A comprehensive study on the curing kinetics and network formation of cyanate ester resin/clay nanocomposites. *Thermochim Acta* 2013;552(1):77–86.
- [7] Goertzen WK, Kessler MR. Thermal and mechanical evaluation of cyanate ester composites with low-temperature processability. *Compos Part A: Appl Sci Manuf* 2007;38(3):779–84.
- [8] Suman JN, Kathi J, Tammishetti S. Thermoplastic modification of monomeric and partially polymerized Bisphenol A dicyanate ester. *Eur Polym J* 2005;41(12):2963–72.
- [9] Rosu D, Rosu L, Varganici C-D. The thermal stability of some semi-interpenetrated polymer networks based on epoxy resin and aromatic polyurethane. *J Anal Appl Pyrolysis* 2013;100:103–10.
- [10] Wu G, Kou K, Chao M, Zhuo L, Zhang J, Li N. Preparation and characterization of bismaleimide-triazine/epoxy interpenetrating polymer networks. *Thermochim Acta* 2012;537(6):44–50.
- [11] Hu C, Yu J, Huo J, Chen Y, Ma H. Effect of clay and PEO-PPO-PEO block copolymer on the microstructure and properties of cyanate ester/epoxy composite. *Compos Part A: Appl Sci Manuf* 2015;78(11):113–23.
- [12] Kollia E, Loutas T, Fiamegkou E, Vavouliotis A, Kostopoulos V. Degradation behavior of glass fiber reinforced cyanate ester composites under hydrothermal ageing. *Polym Degrad Stabil* 2015;121(11):200–7.
- [13] Harvey BG, Guenther AJ, Yandek GR, Cambrea LR, Meylemans HA, Baldwin LC, et al. Synthesis and characterization of a renewable cyanate ester/polycarbonate network derived from eugenol. *Polymer* 2014;55(20):5073–9.
- [14] Yan H-Q, Wang H-Q, Cheng J. Interpenetrating polymer networks from the novel bismaleimide and cyanate containing naphthalene: cure and thermal characteristics. *Eur Polym J* 2009;45(8):2383–90.