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Fabrication of Functional Waterborne Polyurethane/Montmorillonite Composites by Click Chemistry Method

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Abstract: "Click" chemistry method was used to fabricate novel waterborne polyurethane (WPU)/montmorillonite (MMT) composites based on alkyne-containing WPU and azide-modified montmorillonite. The morphology of these composites was characterized by x-ray diffractometer, scanning electron microscope. The mechanical properties, thermal stability, and flame resistance of the composites were investigated by tensile, thermogravimetry and cone calorimetric experiments, etc. The experimental results show that the tensile strength, water resistance and flame retardancy of the WPU/MMT composites have been reinforced efficiently owing to the linking of MMT by click reaction.

Keywords: Click chemistry, functional polyurethane, montmorillonite, polymer composites.

1. INTRODUCTION

Recently, high performance waterborne polyurethane with low volatile organic compounds has been widely used in coating, adhesive, ink and sealants [1-3]. Because of its unique energy saving, environmental protection and properties tailoring [4-7], WPU has also been applied in aviation, railway and automobile coating [8, 9], textile, glass fiber and military field [10]. However, compared with traditional solvent based polyurethane, WPU confronted with some defects, such as poor water and solvent resistance, less thermal stability and mechanical strength, so it has become one of hot research topics that the development of new and novel hybrid WPU composite [11-13].

MMT with special laminar structure can be exfoliated into clay platelet and its surface activity can be adjusted by organic cation exchange reaction. Compared with conventional filled polymer, the polymer molecules in montmorillonite composites can insert into clay layers to strengthen molecular interactions between polymer and clay. Meanwhile, the mechanical properties of the clay materials, as well as thermal barrier property and solvent resistance could be also improved. During the process of burning, MMT composites can form compact carbon layer to prevent the heat of combustion from spreading. This can decrease the generation of volatile gases and delay the combustion of the materials [14]. However, owing to the intrinsically hydrophilic characteristic, MMT is difficult to disperse in the hydrophobic polymer matrix using traditional methods [15].

"Click" chemistry is a modular approach toward efficient synthesis of organic compounds [16], It has been received wide applications in aspects of functional polymer [17-19], nano materials [20], biological engine [21, 22], supramolecular materials [23], pharmaceutical chemistry [24, 25], surface modification [26], proteomics [27] and self-assembly [28, 29], etc. However, it has never been applied in the fabrication of WPU/MMT flame resistant composite coating. In this work, the stable WPU/MMT composites were prepared by "click" chemistry method with the use of azide-modified clay and alkyne containing waterborne polyurethane. The functional WPU/MMT composites were carefully characterized by FT-IR, x-ray diffractometer (XRD), TGA, elementary analysis, scanning electron microscope (SEM) and cone calorimeter, etc.

2. EXPERIMENTAL

2.1. Materials

Na-MMT purchased from Zhejiang Hongfeng Inc., has a diameter of 250 nm and with a cation exchange capacity of 60~70 mequiv100g^{-1}. Diethyl malonate (BASF Corp), $LiAlH_4$ (Aladdin Co. Ltd.,) sodium azide (Kelon factory), propargyl bromide, sodium ascorbate (Braun Wei Technology Co., Ltd.) and 3-chloropropyltriethoxysilane (Wanda Chemical Co., Ltd., China) were used without treatment.

2.2. The Synthesis of 3-Azidopropyltriethoxysilane

50 ml acetonitrile was added into a three-necked 250 ml round bottom flask under stirring and then 3-chloropropyltriethoxysilane (4.0 g, 16.6 mmol), sodium azide (2.16 g, 33.2 mmol) and tetrabutyl ammonium bromide (1.288 g, 4 mmol) were introduced. The mixture was heated to reflux for 18 hour under nitrogen atmosphere. After the reaction finished, solvent was removed by vacuum distillation, then the mixture was diluted using hexane and filtered in the reduced pressure. After removal of the hexane by a rotary evaporator, colorless liquid was obtained.

2.3. Preparation of Azide-Modified Montmorillonite

200 g ethanol (95%) was charged into a 250 ml flask with a magnetic stirrer. After the pH value was adjusted to 3.5, 5.0 g 3-azidopropyltriethoxysilane was added to hydrolyze for 1 h, then 5.0 g MMT was added into the flask. The reaction was performed at 80^{o}C for 6 h. After completion of the reaction, the solid product was filtered off on a cold glass filter, washed with cold ethanol for four times, and finally dried at 80^{o}C in vacuum.

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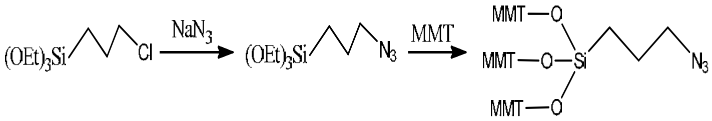

Fig. (1). Procedure for the synthesis of modified MMT by 3-azidopropyltriethaoxysilane.

2.4. Huisgen 1, 3-Dipolar Cycloaddition of WPU/MMT Composites

Alkyne-functionalized WPU (26) (-C≡CH: 1eq) and azide–MMT (N_3: 1.5 eq) were introduced into a three-necked 250 ml flask under stirring. After dispersed for 1h by ultrasonic wave, the mixed solution of $CuSO_4 \cdot 5H_2O$ (0.02eq) and Naasc (0.04 eq) in distilled water and acetone was added into the flask, and the reaction was kept at room temperature for 12 h.

2.5. Characterization

The pure WPU and WPU/clay composites were cast onto Teflon plates, dried at room temperature for 4d, then the films were dried at 70 °C under vacuum for 2d, and stored in a desiccator. FT-IR spectrometer (Germany Brooke Company, VERTEX70) was used to analyze the chemical structure of the modified MMT and WPU/MMT composites prepared by “click” method. Vario EL Ⅲ element analyzer (Germany) was used to analyze the element of C, N contained in azide-Modified MMT. An X-ray diffractometer was used to test the dispersion of clay in the WPU/MMT film. The morphology of WPU/MMT composites was characterized with JEOLJSM-7500F SEM. The TGA of the films were tested in nitrogen atmosphere by means of a Netasch–STA449C thermo balance from 30 to 800 °C at a heating rate of 10 °C/min. The heat release rate (HRR) and mass loss rate (MLR) were measured by Stanton Redcroft cone calorimeter. The testing was performed at an incident heat flux of 35 kwm^{-2}, and the sample size was 10cm×10cm×2mm.

The measurements of elongation at break were measured by LF-Plus Materials Testing Machine (AMETEK Lloyd Instruments Ltd., UK), and the water resistance of the films was measured as follows. Each weighted film of WPU/MMT composite was immersed in DI water for 24 h at RT, and then dried by filter paper. Water absorption (%) was calculated according to the following equation:

$$\text{Water absorption (\%)} = (T - T_0) / T_0 \times 100\%. \quad (1)$$

where T_0 and T represent the weights of dry and immersed films, respectively.

3. RESULT AND DISCUSSION

3.1. Structures of Azide-Modified MMT

The synthesis of azide-modified Montmorillonite was conducted with the assembly of 3-azidopropyltriethoxysilane onto MMT. The schematic presentation is shown in Fig. (**1**).

3.2. The Click Reaction Between Alkyne-WPU and Azido-MMT

Fig. (**2**) show the reaction principle of Huisgen 1,3-dipolar cycloaddition between azide-MMT and alkyne-WPU.

FT-IR spectra of the pristine MMT and azido-MMT are shown in Fig. (**3**). The characteristic peak around 1100 cm^{-1} is due to the Si-O-Si, and the peak at 3415 cm^{-1} corresponds to –OH of MMT. The presence of a broadband between 483 and 600 cm^{-1} peaks contributed to the bending vibration of Si-O, Al-O respectively of MMT. More importantly, compared with pristine MMT, a new absorption peak at around 2100 cm^{-1} appears, which is the characteristic band of the azido bonds from azido-MMT. This indicates that azide group had been grafted onto the surface of MMT successfully.

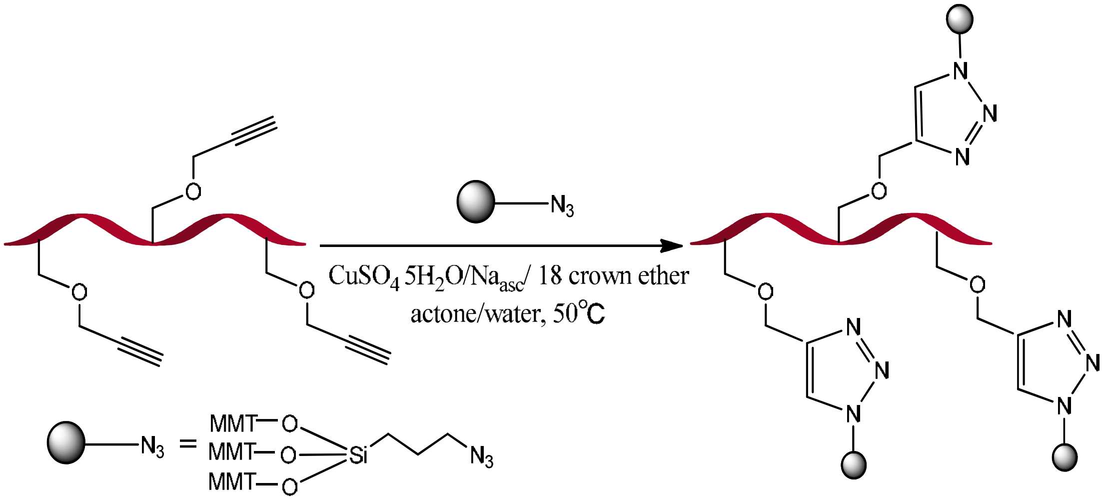

Fig. (2). The click reaction between alkyne-WPU and azido-MMT.

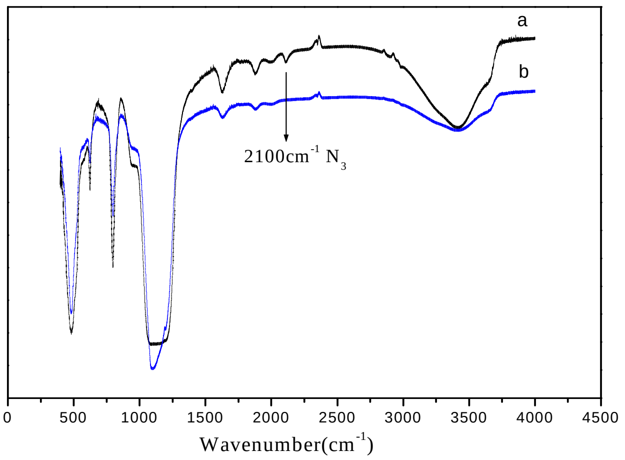

Fig. (3). FT-IR of (**a**) azido-MMT and (**b**) pristine MMT.

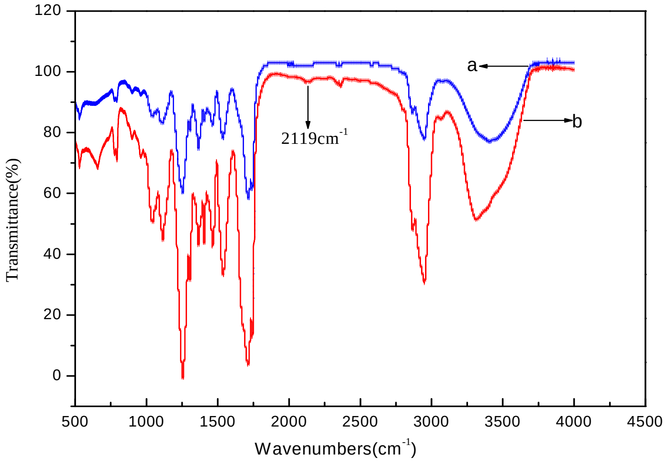

Fig. (4). FTIR spectra of alkyne-functionalized WPU before (**b**) and after "click" reaction (**a**).

Fig. (**4**) clearly shows the IR spectra of alkyne-WPU and the fabricated WPU/MMT composite by "click" method. The 1730 and 1040 cm^{-1} peaks were due to the C=O and the Si-O, and the peaks at 600 and 457 cm^{-1} could be attributed to the Al-O and Si-O stretching vibration, respectively. The peak around 2119 cm^{-1} disappeared in WPU/MMT composites compared to alkyne-WPU indicating that we have successful synthesized WPU/MMT composite by "click" chemistry method.

The elements of C, N contained in azide-MMT were shown in Table **1**, and the grafted density of MMT surface was calculated by the equation (2):

$$G(\text{umolm}^{-2}) = \frac{\%X \times 10^{6}}{(AM)n100(1-\%X(MW)/(AM)n100S} \qquad (2)$$

where AM and %X are the atomic mass and the increase of carbon or nitrogen, respectively, MW is the molecular weight of the bonding species to the MMT surface, n is the number of carbon or nitrogen atoms present in the bonding species, and S is the specific surface area of the MMT (m^{2}g^{-1}). The result presented by grafting ratio (see Table **1**) also proves that azido group has been anchored onto the surface of MMT successfully.

3.3. The XRD Analysis of MMT and WPU/MMT Composites

Fig. (**5**) shows the XRD patterns of pristine MMT and WPU/MMT composites. At low MMT content, the composites show some characteristic broad peaks (at 2θ=19.58°) of WPU amorphous crystals. The characteristic peaks of MMT at 2θ=21.9° and 36°, [27]corresponding to (101) and (004) planes of MMT nanoparticles, respectively are obviously pronounced with the increase of MMT content. This indicates that clay platelet of MMT is covalently modified with WPU by the "click" reaction.

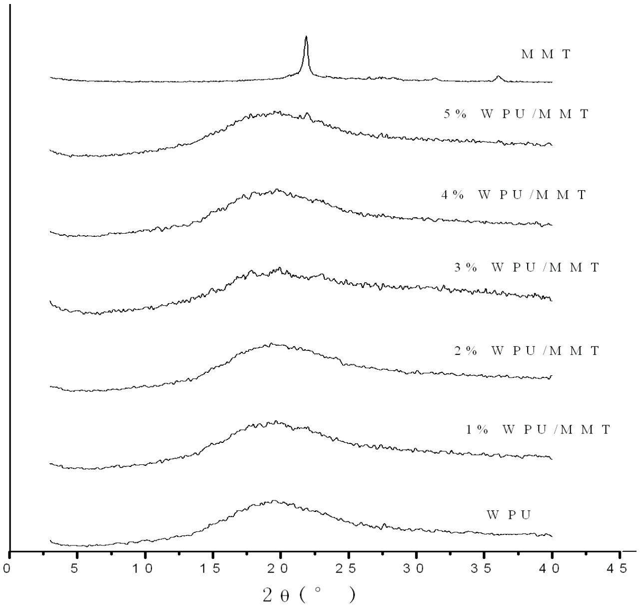

Fig. (5). XRD spectra of WPU and WPU/MMT composite films.

3.4. The SEM Analysis of MMT and WPU/MMT Composites

The fracture surface of the hybrid WPU composites was revealed by the pictures of SEM (Fig. **6**). Due to the "click" reaction, the covalent linking between clay platelet and the WPU permeated into clay platelets occurred and the intercalated structure of exfoliation was formed. The pictures

Table 1. Grafting Density of Azide on MMT

Samples	Carbon Content (%)	Nitrogen Content (%)	The Increase of Nitrogen (%)	Grafting Density of N_3 Groups (umolg^{-1})
Pristine MMT	0.306	0.143		
Modified MMT	2.185	1.036	0.893	220.1

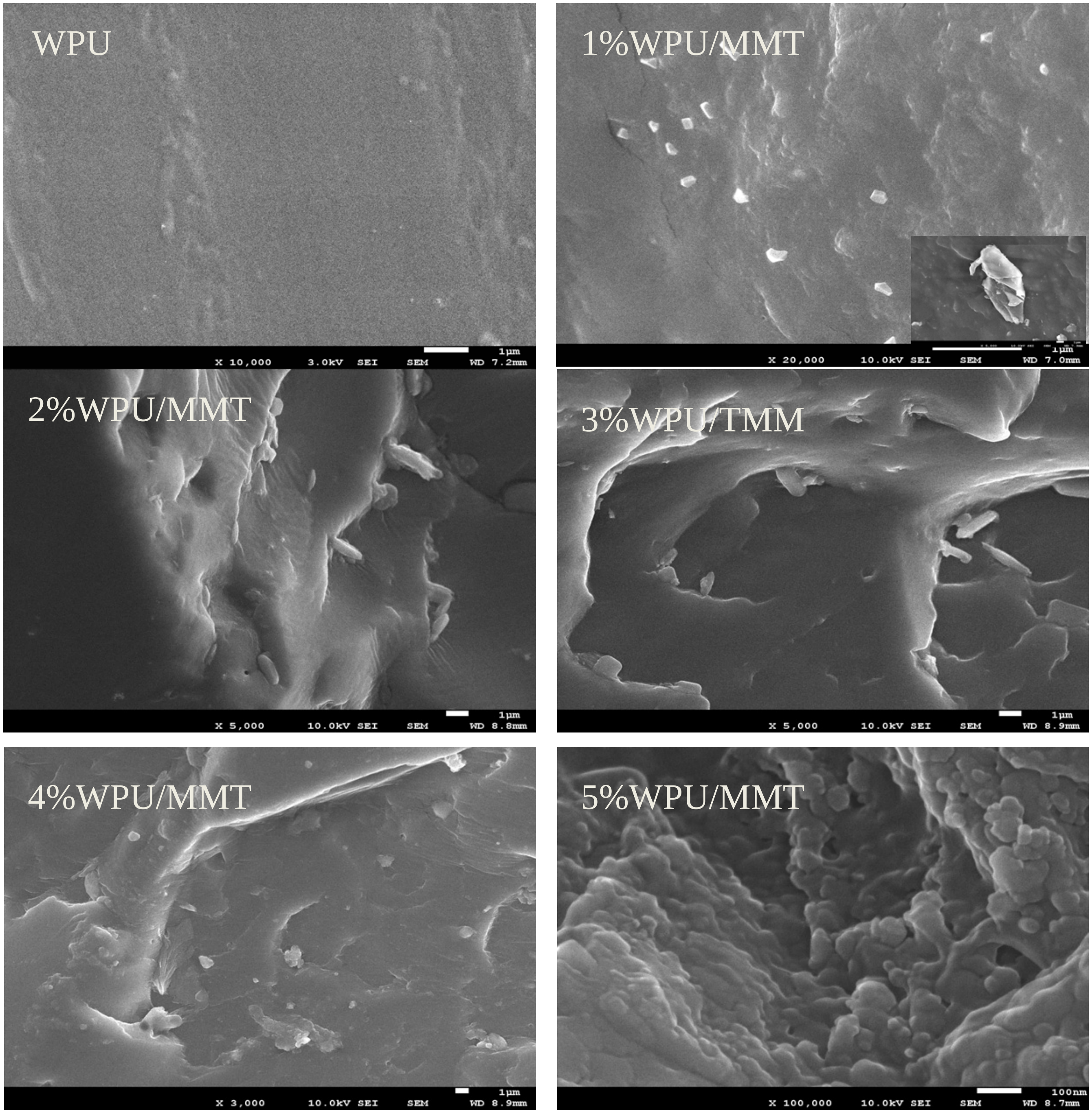

Fig. (6). SEM pictures of WPU and WPU/MMT composites.

also show that MMT can be evenly dispersed in WPU instead of simple mixing. Moreover, the WPU/MMT composites bearing MMT less than 4% show the best dispersion ability. When the MMT content was more than 5%, nanoparticles will be aggregated easily [30].

3.5. TGA of WPU and WPU/MMT Composites

TGA curves of the WPU and WPU/MMT composites are shown in Fig. (**7**). These curves indicate that the WPU/MMT composites are more stable than pristine WPU. Compared to pristine WPU, WPU/MMT composites exhibited enhanced thermal stability owing to the crosslinking of WPU and MMT by click reaction [9, 31]. The progress of thermal degradation can be described by two stages [32]. At the first stage, the decomposition of oligomer and small organic molecules in polyurethane occurs. In this stage, the thermal stability of the composites is enhanced by more contents of MMT [33], so the composite with 5% MMT behave the highest one. The decomposition process of cross-linked macromolecules in polyurethane belongs to the second stage (more that 400^{o}C). The composites contained 2 to 4% MMT show high thermal stability. When temperature reaches higher than 500^{o}C, the least weight loss and the best thermal stability of the composite is obtained in the case that the MMT content in WPU/MMT composite is 2%. This is probably attributed to a compact carbon layer formed on the composite's surface under high temperature, which acts as a diffusion barrier to delay the decomposition process [34, 35].

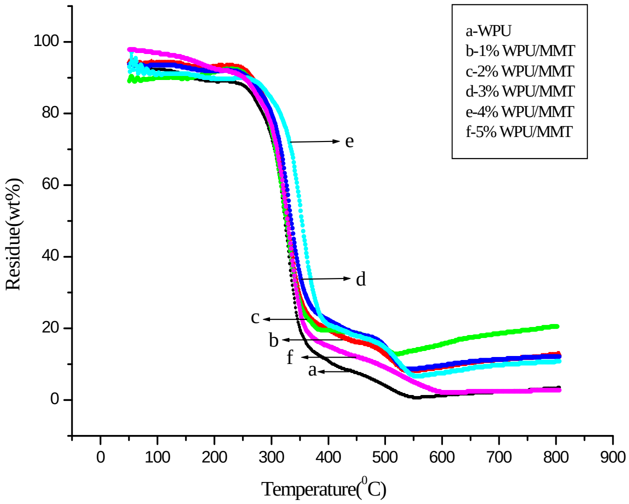

Fig. (7). TGA thermographs of WPU and WPU/MMT films.

3.6. Water Absorption and Mechanical Property of WPU/MMT Composites

Water absorption ability and mechanical property of the nano composite were listed in Fig. (**8**). The water absorption ability remarkably decreased with the increase of MMT content, and 4% content of MMT exhibited the best water resistance ability. The result indicates that the water resistance of the WPU/MMT composites synthesized by "click" chemistry method was effectively improved, and the improvement may be due to the anchoring of organoclay onto WPU by click reaction. The formation of dense intercalated structure effectively blocks the passage of water molecules and decreases the water absorption of the films accordingly.

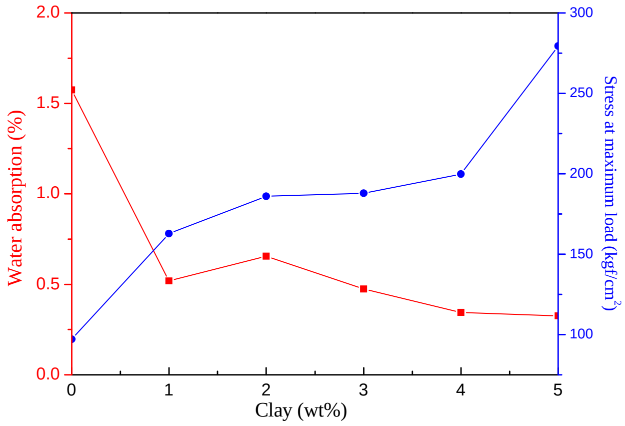

Fig. (8). Influence of MMT content on water absorption and tensile strength of films.

The tensile strength of WPU/MMT composites is distinctly higher than that of pure WPU, and more than 270% increase was achieved by the addition of only 5 wt% of the MMT. The MMT functions like fibre combining in the composites to enhance the tensile strength of the materials, and the effect may be due to the hydrogen bonds and intercalation formed between MMT and the polyurethane molecule [36]. It is also due to chemical bonds formed between the silanol group of silane coupling agent and the groups of residual IPDI.

3.7. Cone Calorimetry of WPU and WPU/MMT Composites

Cone calorimeter was designed in accordance with the principle of oxygen consumption, and the release of heat energy could be calculated according to the oxygen consumption during materials combustion. When one kilogram oxygen is used up, 13.1 MJ heat will be released, and the energy error for most polymer materials is not more than 5%. So cone calorimeter could test the parameters such HRR and MLR, etc.

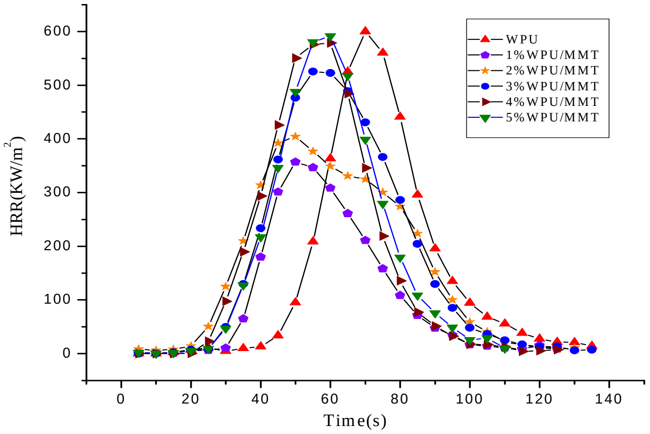

Fig. (9). HRR curves of WPU and MMT/WPU composites.

The HRR plots for pure WPU and WPU/MMT composites at 25 kwm^{-2} are shown in Fig. (**9**). The content of MMT changed the HRR of the composites. When the addition of MMT were 1% and 2%, the HRR peak of WPU/MMT composites decreased 42% and 33% respectively compared with that of the pristine WPU. However, the value of HRR changed less as the addition of MMT more than 2%. This strongly indicated that the appropriate amount of MMT could enhance the stability of composite system and hinder the phase separation, and thereby accelerate the formation of the carbon layer and reduce the heat release. The MLR curves (see Fig. **10**) of pure WPU and WPU/MMT composites were similar to that of the HRR. We can know from Fig. (**10**) that the addition of MMT changed the MLR of the system. When the content of MMT was 1% and 2%, the MLR curves changed more smoothly. This behavior maybe also correlates to the formation of the compact carbon layer of flame retardant shield [37].

CONCLUSION

Based on the synthesis of azide-Modified montmorillonite and alkyne-containing WPU, we successfully prepared WPU/MMT composites by "click" chemistry method. The chemical interactions between MMT

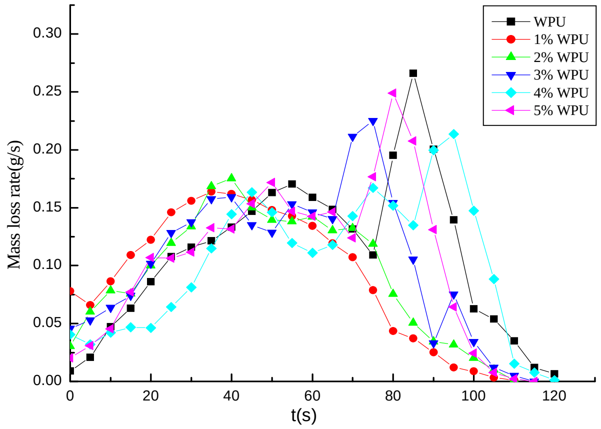

Fig. (10). MLR plots of pristine WPU and WPU/MMT composites.

and WPU were confirmed by FT-IR spectra, elemental analysis and XRD. The structure of the composites was investigated by SEM. Elementary analysis results show that azide-Modified MMT has been grafted onto WPU successfully, and the grafting density of azide group on WPU surface is 220.1 umolg^{-1}. Moreover, this method has resolved the agglomeration phenomenon of MMT in coating compared with conventional methods. Water resistance and mechanical property of the WPU/MMT composites were enhanced obviously as the increase of clay owing to the formation of compact intercalated structure. Although different composites show different behaviors and lack an explicit trend, the reinforcing effect of MMT on the properties of the WPU/MMT composites, such as the heat, flame and water resistance is evident under the concentration of MMT below 4%.

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CONFLICT OF INTEREST

Declared none.

REFERENCES

[1] Rahman, M.M.; Lee, W.K. Properties of isocyanate-reactive waterborne polyurethane adhesives: Effect of cure reaction with various polyol and chain extender content. *J. Appl. Polym.*, **2009**, *114*, 3767-3773.

[2] Florian, P.; Jena, K.K.; Shaik, A.; Narayn, R.; Raju, K.V.S.N. Preparation and characterization of waterborne hyperbranched polyurethane-urea and their hybrid coatings. *Ind. Eng. Chem. Res.*, **2010**, *49*, 4517-4527.

[3] Ochiai, B.; Sato, S.I.; Endo, T. Synthesis and properties of polyurethanes bearing urethane moieties in the side chain. *J. Polym. Sci. Part A: Polym. Chem.*, **2007**, *45*, 3408-3414.

[4] Xie, Z.G.; Lu, C.H.; Chen, X.S. *et al.* A facile approach to biodegradable poly(epsilon-caprolactone)poly(ethylene glycol)-based polyurethanes containing pendant amino groups. *Eur. Polym. J.*, **2007**, *43*, 2080-2087.

[5] Jeon, H.T.; Jang, M.K.; Kim, B.K.; Kim, K.H. Synthesis and characterizations of waterborne polyurethane–silica hybrids using sol-gel process. *Colloids Surf. A: Physicochem. Eng. Aspects.*, **2007**, *302*, 559-567.

[6] Nanda, A.K.; Wicks, D.A. The influence of the ionic concentration, concentration of the polymer, degree of neutralization and chain extension on aqueous polyurethane dispersions prepared by the acetone process. *Polymer*, **2006**, *47*, 1805-1811.

[7] Lee, S.K.; Yoon, S.H.; Chung, I.I.; Hartwig, A.; Kim, B.K. Waterborne polyurethane nano- composites having shape memory effects. *J. Polym. Sci. A: Polym. Chem.*, **2011**, *49*, 634-641.

[8] Fournier, D.; Filip, D.P. "Click" Chemistry as a promising tool for side-chain functionali- zation of polyurethanes. *Macromolecules*, **2008**, *41*, 4622-4630.

[9] Cristina, F.; De Paz, M.V.; Galbis, J.A. L-arabinitol-based functional polyurethanes. *J. Polym. Sci. A: Polym. Chem.*, **2011**, *49*, 1147-1154.

[10] Cao, X.; Lee, L.J. Polyurethane/clay composites foams: processing, structure and properties. *Polymer*, **2005**, *46*, 775-783.

[11] Gorrasi, G.; Tortor, M. Synthesis and physical properties of layered silicates/ polyurethane composites. *Polym. Sci.: Part B: Polym. Phys.*, **2005**, *43*, 2454-2467.

[12] Akat, H.; Tasdelen, M.A. Synthesis and characterization of polymer/clay composites by intercalated chain transfer agent. *Euro. Polym. J.*, **2008**, *44*, 1949-1954.

[13] Wu, Q.; Zhu, W.; Zhang, C.; Liang, Z.Y.; Wang, B. Study of fire retardant behavior of carbon nanotube membranes and carbon nanofiber paper in carbon fiber reinforced epoxy composites. *Carbon*, **2010**, *48*, 1799-1806.

[14] Lee, H.T.; Lin, L.H. Waterborne polyurethane/clay composites: Novel effects of the clay and its interlayer ions on the morphology and physical and electrical properties. *Macromolecules*, **2006**, *39*, 6133-6141.

[15] Kolb, H.C.; Finn, M.G.; Sharpless, K.B. Click chemistry: Diverse chemical function from a few good reactions. *Angew. Chem. Int. Ed.*, **2001**, *40*, 2004 -2021.

[16] Golas, P.L.; Matyjaszewski, K. Click chemistry and ATRP: A beneficial union for the preparation of functional materials. *QSAR Comb. Sci*., **2007**, *26*, 1116-1134.

[17] Reilly, R.K.O.; Joralemon, M.J.; Wooley, K.L.; Hawker, C.J. Functionalization of micelles and shell cross-linked nanoparticles using click chemistry. *Chem. Mater*., **2005**, *17*, 5976-5988.

[18] Kato, T.; Miyagawa, A.; Kasuya, M.C.Z.; Hatanaka, K. Development of membrane filter with oligosaccharide immobilized by click chemistry for influenza virus adsorption. *Open Chem. Biomed. Methods J*., **2009**, 2, 13-17.

[19] Kocalka, P.; El-Sagheer, A.H.; Brown, T. Rapid and efficient DNA strand cross-linking by click chemistry. *Chem. Bio. Chem*., **2008**, *9*, 1280-1285.

[20] Tornoe, C.W.; Christensen, C.; Meldal, M. Peptidotriazoles on solid phase: [1,2, 3]-triazoles by regiospecific copper(I)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides. *J. Org. Chem*., **2002**, *67*, 3057-3064.

[21] Malkoch, M.; Thibault, R.J.; Drockenmuller, E., Messerschmidt, M.; Voit, B.; Russell, T. P.; Hawker, C. J. Orthogonal approaches to the simultaneous and cascade functionalization of macromolecules using click chemistry. *J. Am. Chem. Soc*., **2005**, *127*, 1942-1949.

[22] Mamat, C.; Ramenda, T.; Wuest, F. R. Recent applications of click chemistry for the synthesis of radiotracers for molecular imaging. *Mini-Rev. Org. Chem*., **2009**, *6*, 21-34.

[23] Xie, J.; Seto, C.T. A two stage click-based library of protein tyrosine phosphatase inhibitors. *Bioorg. Med. Chem*., **2007**, *15*, 458-473.

[24] Evansa, R.A. The rise of Azide–Alkyne 1,3-dipolar 'Click' cycloaddition and its application to polymer science and surface modification. *Aust. J. Chem*., **2007**, *60*, 384-395.

[25] Majumdar, K.C.; Mondal, S. A Short route to [1,2,3]-triazolyl coumarin and quinolone derivatives by Cu(I) catalyzed 1,3-dipolar cycloaddition and fluorescence studies. *Lett. Org. Chem*., **2009**, *6*, 82-87.

[26] Salisburya, C.M.; Cravatt, B.F. Click chemistry-led advances in high content functional proteomics. *QSAR Comb. Sci*., **2007**, *26*(11-12), 1229-1238.

[27] Peng, J.Y.; Yu, P.R.; Zeng, S.J. Application of click chemistry in the fabrication of cactus-like hierarchical particulates for sticky super hydrophobic surfaces. *J. Phys. Chem. C*, **2010**, *114*, 5926-5931.

[28] Li, Q.X.; Fang, Y. Simultaneous “Click Chemistry” and atom transfer radical emulsion polymerization and prepared well-defined cross-linked nanoparticles. *Macromolecules*, **2009**, *42*, 6385-6392.

[29] Lei, M.; Song, W.Z.; Zhan, Z.J.; Cui, S.L.; Zhong, F.R. Multicomponent reactions stereo- and regioselective three-component reaction in water: Synthesis of triazole substituted -lactams *via* click chemistry. *Let. Org. Chem.*, **2011**, *8*, 163-171.

[30] Sun, D.X.; Miao, X.; Zhang, K.J.; Kim, H.; Yuan, Y.A. Triazole-forming waterborne polyurethane composites fabricated with silane coupling agent functionalized nano-silica. *J. Colloid Interf. Sci.*, **2011**, *361*, 483-489.

[31] Rahman, M.M.; Yoo, H.J.; Jung, C. Synthesis and characterization of waterborne polyurethane/clay composite-effect on adhesive strength. *Int. Sci.*, **2007**, 249-258.

[32] Zhu, J.; Fawn, M.U.; Morgan, A.B.; Wilkie, C.A. Studies on the mechanism by which the formation of composites enhances thermal stability. *Chem. Mater*., **2001**, *13*, 4649-4654.

[33] Rahman, M.M.; Kim, H.D.; Lee, W.K. Preparation and characterization of waterborne polyurethane/clay composite: Effect on water vapor permeability. *Polym. Sci*., **2008**, *110*, 3697-3705.

[34] Song, L.; Hu, Y.; Tang, Y., Zhang, R.; Chen, Z.; Fan, W. Study on the properties of flame retardant polyurethane/ organoclay composite. *Polym. Degr. Stab*., **2005**, *87*, 111-116.

[35] Gorrasi, G.; Tortora, M.; Vittoria, V. Synthesis and physical properties of layered silicates/polyurethane composites. *Polym. Sci*., **2005**, *43*, 2454-2467.

[36] Pack, S.C.; Kashiwagi, T.; Cao, C.H., Chad, S. K.; Menachem, L.; Miriam, H.R. Role of surface interactions in the synergizing polymer/clay flame retardant properties. *Macromolecules*, **2010**, *43*, 5338-5351.

[37] Wu, Q.A.; Zhu, W.; Zhang, C.; Liang, Z.Y.; Wang, B. Study of fire retardant behavior of carbon nanotube membranes and carbon nanofiber paper in carbon fiber reinforced epoxy composites. *Carbon*, **2010**, *48*, 1799-1806.

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