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**Synthesis and Properties of Monomer Casting Nylon-6-b-Polyether Amine
Copolymers with Different structures**

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Abstract: The TDI-polyether amine macro-initiator with different structures was synthesized to initiate the caprolactam monomer successfully, and the monomer casting (MC) nylon-6-b-polyether amine copolymer with multi-branched molecular structure was prepared via an in-situ polymerization. It was found that the apparent activation energy (E) and the pre-exponential factor (A) of the reaction increased for the copolymers, and the TDI-polyether amine macro-initiator presented low reactivity due to the steric effect of multi-armed long-chain structure. The hydrogen bond and inter-molecular forces of the copolymers were weakened by introduction of multi-branched molecular chains, which was in favor of the formation of γ -crystal. The crystallization ability decreased for the copolymers, among which the MC nylon-6-b-PP3A with extra branched-chain showed highest melting and crystallization temperature and crystallinity with relatively large crystal grain size. A pseudo-plastic fluid characteristic of flow behavior was observed for MC nylon-6. The viscoelastic moduli (G) and entanglement density (ν_e) of all copolymers were higher than that of neat MC nylon-6 due to the severe entanglement through the formation of physical networks by large quantity of multi-branched molecular chains of the copolymers, while MC nylon-6-b-PP3A presented the highest. In the meantime, the values of loss factor of the copolymers increased, the storage modulus and glass transition temperature (T_g) decreased. The stress-strain curves of all copolymers showed an untypical yield point and presented an obvious strain hardening behavior, while hairy fibrous structure was observed on the fracture surface of the copolymers, indicating of the notable toughening effect of polyether amine on the nylon-6 matrix. The toughening mechanism of the

copolymers was deduced to multi-layer crack extension mechanism.

Key word: Reaction kinetics; Crystallization behavior; Molecular entanglement; Mechanical properties; Toughening mechanism.

1. Introduction

Monomer casting nylon-6 is a new type of engineering plastics, which is synthesized by anionic polymerization with caprolactam as the major raw material. Compared with ordinary nylon-6, it takes advantages of high molecular weight, high mechanical strength and excellent self-lubricating performance [1-2], and widely used to replace metallic materials for the production of gears, bearings etc. [3].

However, MC nylon-6 presents a disadvantage in its low-notched impact strength. It is not resistant to crack propagation, which often results in brittle failure. The inherent notch sensitivity of MC nylon-6 precludes its applications such as automotive fender, body panels etc., which require high impact resistance. Many attempts have been made to improve the toughening properties of MC nylon-6 by blending soft component or adding plasticizing agents, such as ultra-high molecular weight polyethylene (UHMWPE) powders [4], hexamethylphosphoric triamide (HPT) [5] etc.. Some researches attempted to toughen MC nylon-6 by preparing novel catalyst or activator with multi-functional group [6] or copolymerized with other components [7]. However, as reported, most of the copolymers with phase or micro-phase separation showed a low tensile strength even though the impact toughness was improved.

Polyether amine with low molecular weight has been widely applied in many fields. It was used as an important raw material of polyurea elastomer and acted as a hardener of epoxy resin. The flexible structure of C-O-C bond in polyether amine molecular chain endowed the material with excellent toughness, and it's a good candidate as an organic toughening material. In this work polyether amine with different

molecular structures was the first time to be used as the copolymerization component in MC nylon-6 matrix. Its active amino group may react with the isocyanate group of polyisocyanate, and thus the macro-initiator can be prepared for anionic polymerization of caprolactam. The effect of molecular structure of polyether amine on reaction kinetics of caprolactam polymerization was studied, the molecular interaction, rheology and crystallization behavior of the copolymers were characterized, and the toughening mechanism was explored.

2. Experimental

2.1 Materials

The caprolactam monomer was supplied by China Petroleum and Chemical Co. Ltd., with a commercial grade product. NaOH (sodium hydroxide) with analytical purity was purchased from Kermel Chemical Reagent Co. Ltd (Tianjin, China), and TDI (toluene-2, 4-diisocyanate) was purchased from Kelong Chemical Reagent Factory (Chengdu, China). Polyether amine with an average molecular weight of 2000g/mol (PE2A, PPAD) and 3000g/mol (PP3A) were purchased from Huntsman Polyurethanes Ltd Guangzhou Branch (Guangzhou, China). Polyether amine

2.2 Synthesis and preparation

Synthesis of TDI- Polyether amine macro-initiator

The TDI-polyether amine macro-initiators were prepared at room temperature with a constant temperature bath. A flask was equipped with magnetic stirrer and charged with 6.96 g TDI. Then 20 g polyether amine was slowly dropped into it. The reaction lasted for 2 h to make sure the reaction was completed. Then the TDI-polyether amine macro-initiator was obtained.

Synthesis of MC nylon-6-b-Polyether amine copolymers

The 4 mol caprolactam (CL) was put into a flask and heated to about 130 °C. After

completely melting, the melt was refluxed under vacuum for about 30 min to remove water in it. Then 0.01 mol NaOH was added under dramatically stirring. The melt was refluxed under vacuum for another 30 min, and 0.01 mol TDI-polyether amine macro-initiator was added. After quickly well mixed up, the melt was casted into a preheated mould at 160 °C. The reaction lasted for 40 min. The product of MC nylon-6-b-polyether amine copolymer was then obtained.

2.2 Measurements

2.2.1 Reaction kinetics analysis

Caprolactam polymerization reaction was conducted in a thermal isolated oven. The reaction temperature during polymerization was measured with a TM-902C thermometer from Shanglong Electric Co. Ltd. (Shanghai, China), and the reaction kinetics was analyzed with the recorded reaction temperature.

2.2.2 Viscosity average molecular weight

The specific viscosity η_{sp} of neat MC nylon-6 and copolymers was measured with an Ubbelohde viscometer. The formic acid was used as solvent of nylon-6 materials.

The intrinsic viscosity is described as the limit of the ratio between the specific viscosity (η_{sp}) and the polymer concentration (c), as the polymer concentration approaches zero.

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c \quad (\text{Eq.1})$$

By measuring the intrinsic viscosity of polymer solutions, the polymer average molecular weight can be predicted through the Mark-Houwink empirical equation, as described by:

$$[\eta] = KM_{\eta}^a \quad (\text{Eq.2})$$

where $[\eta]$ is the intrinsic viscosity, K and a are the parameters that depend on the solvent/polymer pair and the value of 22.6×10^{-3} and 0.82 were chosen respectively [8].

M_{η} is the viscosity average molecular weight of the polymer.

2.2.3 FTIR analysis

The structure of neat MC nylon-6 and copolymers was analyzed with a Nicolet-560 Fourier-transform infrared spectrometer (FTIR) (USA). The scanning rate was 20 min^{-1} , and the differentiate rate was 4 cm^{-1} .

2.2.4 Non-isothermal crystallization analysis

The non-isothermal crystallization of neat MC nylon-6 and copolymers was performed with a Netzsch 204 Phoenix differential scanning calorimetry (DSC) (Germany). The range of the test temperature was $20 \text{ }^{\circ}\text{C}$ to $250 \text{ }^{\circ}\text{C}$ which was calibrated with indium. The heating rate and cooling rate were $10 \text{ }^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. The crystallinity ($X_{c, DSC}$) can be calculated with the following equation:

$$X_{c, DSC} = [\Delta H_m / (w \cdot \Delta H_0)] * 100\% \quad (\text{Eq. 3})$$

where w is the mass fraction of each component; ΔH_m is the melting enthalpy of the samples and ΔH_0 is the balance melting enthalpy, i.e., the melting enthalpy of 100% crystallizing polymer, which is 230 J/g for MC nylon-6 [9].

2.2.5 X-Ray diffraction analysis (XRD)

The XRD analysis of neat MC nylon-6 and copolymers was performed with Rigaku D/max IIIB X-ray diffractometer (Japan) at room temperature. XRD data were collected from 5 to 40° .

2.2.6 Scanning electron microscopy analysis (SEM)

The morphology of the impact fractured surface of neat MC nylon-6 and copolymers was observed with a JEOL JSM-5900LV SEM (Japan). The operating voltage was 5 kV and the samples were ion beam sputter-coated with gold.

2.2.7 Dynamic rheological analysis

Rheological characterization of neat MC nylon-6 and copolymers was carried out

at 250 °C on a rheometer (TA-AR2000ex, USA) with a 25 mm-parallel plate in a frequency range of 0.01~100 Hz and 1% strain value. The testing sample disks with a thickness of 1.5 mm and a diameter of 25 mm.

2.2.8 Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis of neat MC nylon-6 and copolymers was carried out with TA Instrument Q800 (USA). All the samples were measured with a bending mode at a heating rate of 3 °C/min and a frequency of 1 Hz. The sample size was 40*10*4 mm³.

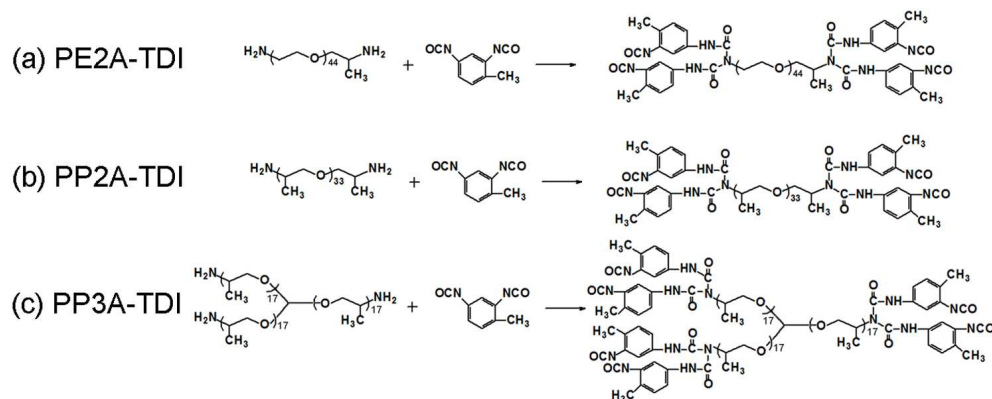
2.2.9 Mechanical properties

The tensile performance of neat MC nylon-6 and copolymers was measured with a 4302 material testing machine from Instron Co. (USA.) and the notched charpy impact strength was measured with ZBC-4B impact testing machine from Xinsansi Co. (Shenzhen,China).

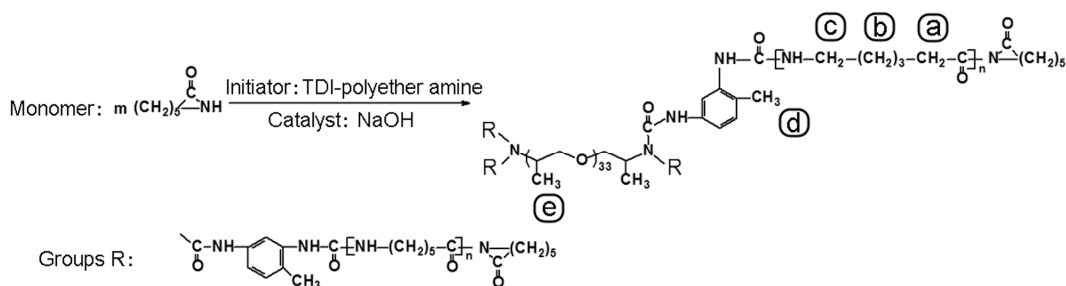
3. Results and discussion

3.1 Synthesis and structure of MC nylon-6-b-polyether amine copolymers

Polyether amine with different structures was applied to react with TDI based on the addition reaction between the amino group of polyether amine and the isocyanate group of TDI, including PE2A with ethylene oxide main chain and two end amine groups, PP2A with propylene oxide main chain and two end amine groups, PP3A with propylene oxide main chain and three end amine groups. Compared with PE2A, the unit structure of PP2A contained an extra methyl side group while the PP3A had an extra branched-chain compared with PP2A. The reaction process of multi-armed TDI-polyether amine macro-initiators was as follows:



MC nylon-6-b-polyether amine copolymers were fabricated by means of cast moulding technique via the mechanism of anionic ring-opening polymerization, using NaOH as catalyst and the above TDI-polyether amine as macro-initiator [10,11]. The reaction formula and ^1H NMR analysis of the copolymer was as follows: δH_a : 1.58 ppm; δH_b : 1.82 ppm, 1.90 ppm, 2.79 ppm; δH_c : 3.63 ppm; δH_d : 2.23 ppm; δH_e : 1.49 ppm.



Reaction kinetics

The temperature-time relationship curves of neat MC nylon-6 and copolymers during the reaction process are shown in Fig.1 (a). The polymerization process started when the caprolactam melt was cast into a preheated mould. Therefore, at first, the temperature of the reaction system decreased from mold temperature (160 °C) to caprolactam melt temperature (130 °C) and then increased gradually with time. In about 400-1200s, the temperature of the reaction system tended to be stable, indicating of the end of the polymerization process. The reaction temperature of the neat MC nylon-6 which was initiated by TDI increased rapidly and the reaction process terminated in

short time, while that of the copolymer systems increased slowly, indicating of relatively low initiation activity of TDI-polyether amine macro-initiator. Fig.1 (b) showed that the heating-rate of the copolymers increased first and then decreased with time. By introduction of polyether amine, the maximum heating-rate (R_{max}) decreased and the time corresponding to the maximum heating-rate (t_{max}) significantly prolonged.

As to an exothermic chemical reaction, the universal equation for studying the non-isothermal reaction kinetics can be described as following [12]:

$$da/dt=(1-a)^n \cdot A \cdot e^{(-E/RT)} \quad (Eq.4)$$

where α is the reaction conversion rate; t is the reaction time; n is the reaction order; A is the pre-exponential factor; T is the reaction temperature; E is the apparent activation energy of the reaction and R is the gas constant with value of 8.314 J/(K·mol).

Polymerization reaction was conducted in a thermal isolated oven. Therefore, the reaction can be considered to be conducted in a homogeneous environment. Its reaction conversion rate α can be represented by the increase of reaction temperature as follows:

$$da/dt=1/(T_f-T_0) \cdot dT/dt \quad (Eq.5)$$

where T_0 , T_f and T are the initial reaction temperature, final reaction temperature and reaction temperature at reaction time t , respectively. Finally, the Eq.6 was obtained after combining Eq.4 and Eq.5 as follows:

$$\ln[1/(T_f-T_0) \cdot dT/dt]=\ln A+n \cdot \ln[1-(T-T_0)/(T_f-T_0)]-E/RT \quad (Eq.6)$$

Calculating Eq.4 at different temperatures, and the reaction kinetics parameters can be obtained, as shown in Tab.1. The E and A of all copolymers increased, indicating that the polymerization reaction became difficult. Macro-initiator presented low reactivity due to the steric effect of multi-armed long-chain structure. The reaction order n of neat nylon-6 was approximated to 1, indicating that the copolymerization reaction process was deviated from one-step reaction. The MC nylon-6-b-PE2A

showed a highest E among the copolymers while that of MC nylon-6-b-PP2A and MC nylon-6-b-PP3A was low and similar. The initiation activity of macro-initiators was affected by the length of molecular chain when the initiators had the same structure of active center. The length of molecular chain of PP3A was the same as PP2A, which resulted in the similar initiation activity of the macro-initiators. The PE2A presented a longer molecular chain and resulted in a lower initiation activity of the macro-initiator.

Molecular weight

The molecular weight of neat MC nylon-6 and copolymers obtained by viscosity method is shown in Tab.2. It can be seen that the molecular weight of the copolymers decreased obviously compared with that of neat MC nylon-6, resulting from the decreasing reactivity and reaction rate of the polymerization process by introduction of polyether amine. The MC nylon-6-b-PP3A copolymer presented a highest molecular weight among the copolymers because of its more branched-chain while the MC nylon-6-b-PP2A and MC nylon-6-b-PE2A copolymers showed a similar molecular weight even though their reactivity had a little difference.

Molecular interaction

The FTIR spectra analysis for neat MC nylon-6 and copolymers are shown in Fig.2. Compared with neat nylon-6, the FTIR peak at 3298.4 cm^{-1} for the copolymers corresponding to the hydrogen-bonded -NH had no significant change. However, all the copolymers with different molecular structure of polyether amine showed a new peak at 3499.5 cm^{-1} which was attributed to the non-hydrogen-bonded -NH . Additionally, the absorption peak of amide II's octave at 3060.4 cm^{-1} of the copolymers showed varying degree of blue shift, indicating of the increasing number of free amide group. The result revealed that the amide group in neat nylon-6 almost presented as hydrogen-bonded -NH , while the hydrogen bond and inter-molecular forces of the copolymers were

weakened by introduction of multi-branched molecular chains.

Compared with neat MC nylon-6, the blue shift in amide II's octave of MC nylon-6-b-PP2A was more obvious than that of MC nylon-6-b-PE2A. The major methyl side group in the main chain of PP2A increased the steric hindrance of molecular chain and further weakened the hydrogen bond. Although the major methyl side group and more branched-chain in PP3A will increase the steric hindrance of molecular chain, the extra branched-chain can also form hydrogen bonds and partially offset the effect of steric hindrance on weakening hydrogen bond.

3.2 Crystallization properties of MC nylon-6-b-polyether amine copolymers

Crystallization behavior

The non-isothermal DSC curves of neat MC nylon-6 and copolymers are shown in Fig.3, the melting process presented only one melting peak in the whole temperature range which corresponded to the melting peak of nylon-6 matrix for all samples, and the similar behavior can be observed for the crystallization process, indicating that all the polyether amine component with different molecular structures, incorporated into the nylon-6 main chains, were in the amorphous state. Moreover, it can be seen that introduction of polyether amine led to an obvious decrease of the melting and crystallization temperature, and crystallinity of the copolymers compared with that of neat MC nylon-6. The increase of half peak width indicated the decrease of crystalline growth rate. Among the copolymers, the MC nylon-6-b-PP3A showed highest melting and crystallization temperature and crystallinity. Even though the more branched-chain of nylon-6-b-PP3A will increase the steric hindrance, the extra branched-chain can also crystallize and result in better crystalline properties. The methyl side group in PP2A molecular chain may lead to a relatively low degree of molecular regularity of the copolymer, which will be unfavorable for the crystallization of the copolymer.

Crystal structure

The crystal structure of neat MC nylon-6 and copolymers were evaluated by X-ray diffraction (XRD) analysis. As shown in Fig.4, for all samples, the observed diffractions at $2\theta=20^\circ$ and 23° corresponded to α crystalline form of nylon-6 matrix [13,14]. Besides, the MC nylon-6-b-polyether amine copolymers presented a new and small diffraction peak at $2\theta=9.45^\circ$ compared with neat MC nylon-6, which was attributed to the γ crystalline form. The disordered arrangement of multi-branched nylon-6 molecular chains was in favor of the formation of γ -form with long and weak hydrogen bonds. The XRD spectrogram suggested that the crystallization of copolymers mainly conducted in α -form and a small amount of γ -form also formed simultaneously. The crystallinity ($X_{c, XRD}$) and crystal grain sizes were given with the following expressions, respectively:

$$X_{c, XRD} = [I_c / (I_c + I_a)] \times 100\%, \quad L_{hkl} = k\lambda / (\beta \cos\theta) \quad (Eq. 7)$$

where I_c and I_a are the areas under the crystalline curve and amorphous curve, respectively; L_{hkl} is the size of crystallites from normal direction of hkl plane; k is Scherrer constant; λ is wave length of radiation, equal to 0.154 nm in the present case and β is the full width of half maximum of the diffraction peak (hkl); θ is Bragg angle.

As shown in Tab.3, the crystallinity of nylon-6 matrix decreased by introduction of polyether amine component which was coincident with DSC analysis. The crystal grain size of MC nylon-6-PP2A was relatively small, while MC nylon-6-PP3A with an extra branched-chain presented relatively large crystal grain size.

3.3 Rheological behavior of MC nylon-6-b-polyether amine copolymers

The molecular chain entanglement behavior of neat MC nylon-6 and copolymers was investigated by dynamical rheological measurement. As shown in Fig.5 (a), the complex viscosity as a function of frequency, a pseudo-plastic fluid characteristic of flow behavior was observed for MC nylon-6. By introduction of polyether amine, the

copolymers presented a more evident characteristic of shear-thinning compared with neat MC nylon-6. The difference in complex viscosity between neat MC nylon-6 and the copolymers may be closely related to the difference of molecular chain structure.

The linear viscoelastic moduli (G) of the neat MC nylon-6 and the copolymers are shown in Fig.5 (b,c) as a function of frequency. For all samples, both the elastic modulus and viscous modulus increased with the increase of frequency. Besides, to compare the samples at the same frequency, it can be seen that the viscoelastic moduli of all copolymers were higher than that of neat MC nylon-6. This result was due to the severe entanglement through the formation of physical networks with large quantity of multi-branched molecular chains of the copolymers. Moreover, among the copolymers, the viscoelastic moduli of MC nylon-6-b-PP3A were highest, which was probably due to its most branched molecular chain and severe entanglement. The degree of molecular regularity and crystallinity of MC nylon-6-b-PE2A was slightly higher than that of MC nylon-6-b-PP2A, which led the molecular chain to move in a high shear force.

The entanglement molecular weight (M_e) is introduced from the kinetic theory of rubber elasticity. It can be calculated from the plateau modulus (G_N^0) and interprets as the apparent average molecular weight between coupling junction as follows [15,16].

$$M_e = (4/5)\rho RT / G_N^0, \quad G_N^0 = (2/\pi) \int_{-\infty}^{+\infty} G''(\omega) d \ln \omega \quad (\text{Eq.8})$$

And the entanglement density ν_e can be calculated with the equation as follows.

$$\nu_e = \rho / M_e \quad (\text{Eq.9})$$

where ρ is the polymer density; R is gas constant; T is the absolute temperature.

The M_e and ν_e of samples were listed in Tab.4. It can be seen that by introduction of polyether amine the ν_e increased significantly and the M_e decreased significantly. Besides, the ν_e of MC nylon-6-b-PP3A was highest among the copolymers.

3.4 Mechanical properties of MC nylon-6-b-polyether amine copolymers

Static mechanical properties

Fig.6 (a) shows the tensile stress-strain curves of neat MC nylon-6 and MC nylon-6-b-polyether amine copolymers. It can be seen that the stress-strain curves of the neat MC nylon-6 presented a characteristics of brittle fracture with a typical yield point and low elongation at break. However, by introduction of polyether amine, the area under stress-strain curves of the copolymers increased dramatically, indicating of significantly increasing toughness of the copolymers. The stress-strain curves of all copolymers showed an untypical yield point and presented an obvious strain hardening behavior after a long elastic deformation stress plateau.

Fig.6 (b, c) shows the mechanical properties of all samples. It can be seen that the elongation at break and notched impact strength of the copolymers were increased by 800% compared with neat MC nylon-6, indicating of the notable toughening effect of polyether amine on the nylon-6 matrix, while the tensile strength of the copolymers still maintained on a high level. Among the copolymers, the tensile strength of MC nylon-6-b-PP3A was highest and the elongation at break and notched impact strength were lowest due to its high crystallinity and significant physical entanglement of much more branched molecular chains. The relatively low degree of molecular regularity of MC nylon-6-b-PP2A resulted in a low tensile strength and high notched impact strength.

Dynamical mechanical analysis

The numerical DMA data of neat MC nylon-6 and MC nylon-6-b-polyether amine copolymers are listed in Tab.5. It can be seen that, compared with neat MC nylon-6, the values of loss factor of the copolymers were improved significantly and the storage modulus decreased dramatically, indicated that the movement of the copolymer's molecular chains was easy and the internal friction increased by introduction of multi-branched molecular chain. The $\tan\delta$ curve of neat MC nylon-6 showed two

relaxation peaks at $-62\text{ }^{\circ}\text{C}$ and $50\text{ }^{\circ}\text{C}$ corresponding to the β relaxation and α relaxation, respectively. The α relaxation aroused by chain segmental motion of molecules in the amorphous region and corresponded to glass transition temperature (T_g). The high glass transition temperature of neat MC nylon-6 indicated the rigid molecular chains. In the case of MC nylon-6-b-polyether amine copolymers, the α relaxation peak shifted to low temperature dramatically while the change of β relaxation was not obvious. Moreover, the MC nylon-6-PP3A presented the highest storage module and glass transition temperature, and lowest loss factor among the copolymers, which may benefit from its high crystallinity and high physical entanglement of molecular chains.

3.5 Toughening mechanism of MC nylon-6-b-polyether amine copolymers

Fig.7 (a) shows a cryogenically fracture surface of MC nylon-6-b-polyether amine copolymers. It can be seen that it was difficult to distinguish the interface between the two phases, which suggested that MC nylon-6 phase and polyether amine phase were compatible. Polyether amine was covalently connected with nylon-6 molecules. Unlike the simply blending with high molecular weight soft component, the phase separation in excess of a micrometer scale between the two components was difficult to occur due to the copolymerization method and low molecular weight of polyether amine.

The fracture surface morphology of the samples was also studied by SEM technology. As seen in Fig.7 (b-e) at low magnification ($\times 500$), the fracture surface of neat MC nylon-6 was relatively smooth and showed a typical brittle fracture, while that of the copolymers was rough and accompanied by a large number of major deformation by absorbing impact energy, displaying character of tough fracture. Besides, an obvious hairy structure was observed on the fracture surface of all copolymers. To further observe the fracture surface at high magnification ($\times 5000$), as seen in Fig.7 (b'-e'), the hairy structure on fracture surface was acicular fiber of the nylon-6 matrix actually

which was formed by the way similar to wire-drawing of the matrix under shear stress. Besides, the hairy structure of MC nylon-6-b-PP2A was thickest and longest among the copolymers, which was coincident with the impact strength result.

After being suffered with shear stress, many acicular fibers formed on the impact fracture surface of the samples and the fibers were connected to the matrix resin. The front part of the acicular fibers showed whitening phenomenon while the bottom part adjacent to the matrix resin was relatively dark. The toughening mechanism of this copolymer system can be deduced to be the multi-layer crack extension mechanism. As shown in Fig.8, a certain stress defects in the nylon-6 matrix induced the formation of multi-layer micro-crack as the stress concentration points, which quickly developed into deep micro-crack vacuum layer field with face to face adhesive sheet film. Under shear stress, the molecular chain of the adhesive sheet film oriented intensively along the orientation of the stress and then developed to hairy structure with oriented-long fiber, which broke when the impact energy was higher than the surface energy and the molecular orientation energy. The whitening phenomenon in the front part of the fibers confirmed the intensive orientation of fibers under shear stress. Therefore, different from the usual craze-shear band mechanism, the super toughening break of MC nylon-6-b-polyether amine copolymers was based on the energy consumption of the extension of quantity of adhesive sheet films and the orientation of molecular chain in the matrix fibers, not only the result of energy consumption of craze-shear band.

4. Conclusions

MC nylon-6-b-polyether amine copolymers with different molecular structures were prepared via in-situ polymerization. The effect of molecular structure of polyether amine on the synthesis and properties of the copolymers was studied. The result showed that introduction of polyether amine dramatically delayed the polymerization process of

caprolactam due to the steric effect of multi-armed long-chain structure, and the value of E and A of the reaction increased for the copolymers. The hydrogen bond and inter-molecular force of the copolymers were weakened by introduction of multi-branched molecular chains. The crystallization of copolymers conducted in α -form mainly and gradually formed a small amount of γ -form simultaneously. The crystallization ability decreased for the copolymers, among which the MC nylon-6-b-PP3A showed the highest melting and crystallization temperature and crystallinity with relatively large crystal grain size due to the crystallizability of the extra branched-chain. A pseudo-plastic fluid characteristic of flow behavior was observed for MC nylon-6. The G and v_e of all copolymers were higher than that of neat MC nylon-6 due to the severe entanglement through the formation of physical networks, while MC nylon-6-b-PP3A presented the highest. The loss factor of the copolymers increased, the storage modulus and T_g decreased. The area under stress-strain curves of the copolymers increased dramatically, indicating of significantly increasing toughness of the copolymers. Hairy fibrous structure was observed on the fracture surface of the copolymers, displaying character of tough fracture. The toughening mechanism of the copolymers was deduced to multi-layer crack extension mechanism.

References

- [1] S.Y. Zeng, X. Lin, C. Liu. Production of MC nylon rod using horizontal centrifugal casting technique. *Engineering Plastics Application* **2011**, 39(10), 52-54.
- [2] F.J. Zhou, L.Q. Zhang, Y.M. Wang. Synthesis of MC Nylon. *Synthetic Technology and Application* **2012**, 27(2), 1-6.
- [3] X. Lin, P.N. Zhang, Z.L. Yin, Q.Y. Chen. Study on preparation and properties of La_2O_3 /MC nylon nanocomposites. *Journal of Rare Earths* **2005**, 23(6), 680-684.
- [4] Y.M. Zhang, X.Y. Wu, W. Hong, W. Zhang. Toughening properties of MC nylon

with UHMWPE particle. *Plastics* **2009**, 38(1), 68-69.

[5] X.H. Wang, Q. Zhang, X.B. Zhang. A study of the property characterization of MC copolymerized nylon elastomer. *China Plastics Industry* **1996**, 24(6)1996, 55-58.

[6] K.K. Jin, K.Y. Young, Y.B. Sook, Y.K. Jong. *Journal of Applied Polymer Science* **1995**, 57, 1347-1357.

[7] B.B. Wang, G.S. Hu. Preparation and characterization of nylon 6 11 copolymer. *Materials Letters* **2006**, 60(21), 2715–2717.

[8] C.S. Liu, Q. Wang. New method on preparing of nylon 6 micro-powder and PA 6/PP/wollastonite composite. *Journal of Wuhan Institute of Chemical Technology* **2001**, 23(3), 35-39.

[9] S. Xu, X.W. Zhao, L. Ye. Preparation and Properties of Monomer Casting Nylon-6/PEO Blend Prepared via In-situ Polymerization. *Polymer Engineering & Sciences* **2013**, 53(9), 1809-1822.

[10] B.L. Pan, S.P. Zhang, W.Z. Li, J.Z. Zhao, J.L. Liu, Y.Q. Zhang, Y.Z. Zhang. Tribological and mechanical investigation of MC nylon reinforced by modified graphene oxide. *Wear* **2012**, 294(30), 395–401.

[11] G. Rusu, K. Ueda, E. Rusu, M. Rusu. Polyamides from lactams by centrifugal molding via anionic ring-opening polymerization. *Polymer* **2001**, 42(13), 5669-5678.

[12] C.H. Lu, P.Y. Yeh, W.T. Hsu. Non-isothermal reaction kinetics of lithium cobalt oxide. *Journal of Alloys and Compounds* **2009**, 476(1), 749-754.

[13] J.M. Schultz, B.S. Hsiao, J.M. Samon. Structural development during the early stages of polymer melt spinning by in-situ synchrotron X-ray techniques. *Polymer* **2000**, 41 (25), 8887–8895.

[14] J.C. Ho, K.H. Wei. Induced $\gamma \rightarrow \alpha$ Crystal Transformation in Blends of Polyamide 6 and Liquid Crystalline Copolyester. *Macromolecules* **2000**, 33(14), 5181-5186.

[15] J.D. Ferry. Viscoelastic Properties of Polymers. Wiley: New york, **1980**.

[16] M. Doi, S.F. Edwards. Dynamics of concentrated polymer systems. Part 3.-The constitutive equation. *Journal of the Chemical Society, Faraday Transactions* **1978**, 74, 1818-1832.

Table captions

Tab.1 Reaction kinetics parameters of MC nylon-6-b-polyether amine copolymers

Tab.2 Viscosity average molecular weight of MC nylon-6-b-polyether amine copolymers

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Fig.7 SEM image of cryogenically fracture surface (a: magnification $\times 10000$) and impact fracture surface of MC nylon-6-b-polyether amine copolymers (b-e: magnification $\times 500$; b'-e': magnification $\times 5000$)

Fig.8 Toughening mechanism of the MC nylon-6-b-polyether amine copolymers

Tab.1 Reaction kinetics parameters of MC nylon-6-b-polyether amine copolymers

Sample	E (kJ·mol ⁻¹)	A (s ⁻¹)	n	R_{max} (°C/s)	t_{max} (s)
neat MC nylon-6	82.37	4.26*10 ⁷	0.95	0.166	295
MC nylon-6-b-PE2A	131.44	1.45*10 ¹³	1.69	0.083	598
MC nylon-6-b-PP2A	127.63	1.42*10 ¹³	1.62	0.087	544
MC nylon-6-b-PP3A	128.34	1.39*10 ¹³	1.64	0.085	551

Tab.2 Viscosity average molecular weight of MC nylon-6-b-polyether amine copolymers

Sample	neat MC nylon-6	MC nylon-6-b-PE2A	MC nylon-6-b-PP2A	MC nylon-6-b-PP3A
Molecular weight (g/mol)	94508.7	50648.9	48483.8	58138.4

Tab.3 XRD parameters of MC nylon-6-b-polyether amine block copolymers

Sample	Angle (2 θ)			$X_{c, XRD}$ (%)	Grain size (Å)
	α_1 (°)	α_2 (°)	γ (°)		
neat Nylon-6	20.19	23.77		35.68	88
MC nylon-6-b-PE2A	20.29	24.02	9.48	30.04	71
MC nylon-6-b-PP2A	20.39	24.11	9.42	29.35	69
MC nylon-6-b-PP3A	20.18	23.91	9.45	32.11	75

Tab.4 G_N^0 , v_e and M_e of MC nylon-6-b-polyether amine copolymers

Sample	G_N^0 (Pa)	v_e (mol/m ³)	M_e (g/mol)
neat MC nylon-6	3173.16	0.91	1228153
MC nylon-6-b-PE2A	13642.15	3.92	285668
MC nylon-6-b-PP2A	7851.16	2.25	496376
MC nylon-6-b-PP3A	17442.70	5.01	223424

Tab.5 Numerical DMA data of MC nylon-6-b-polyether amine copolymer

Sample	Storage modulus (MPa)	α peak (°C)	β peak (°C)	Loss factor tan δ
neat MC nylon-6	5090	50.2	-62.6	0.137
MC nylon-6-b-PE2A	3446	7.3	-64.6	0.155
MC nylon-6-b-PP2A	3104	7.4	-63.1	0.156
MC nylon-6-b-PP3A	3930	22.5	-61.3	0.150

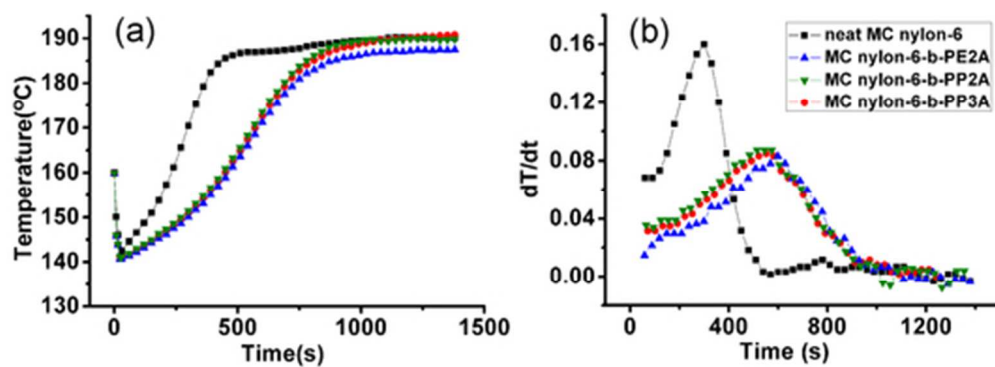


Fig.1 Temperature-time relationship curves of the synthesis of MC nylon-6-b-polyether amine copolymers
45x16mm (300 x 300 DPI)

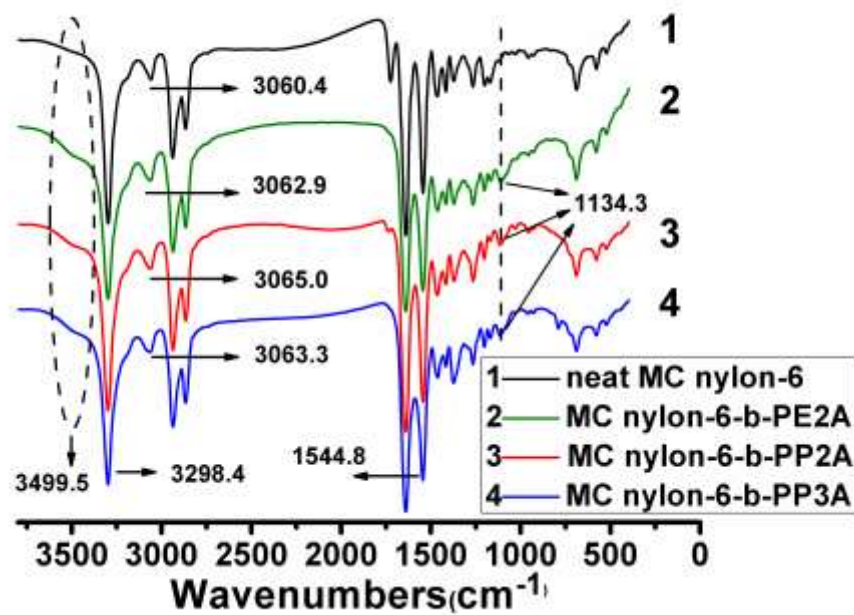


Fig.2 FTIR spectra of MC nylon-6-b-polyether amine copolymers
297x208mm (300 x 300 DPI)

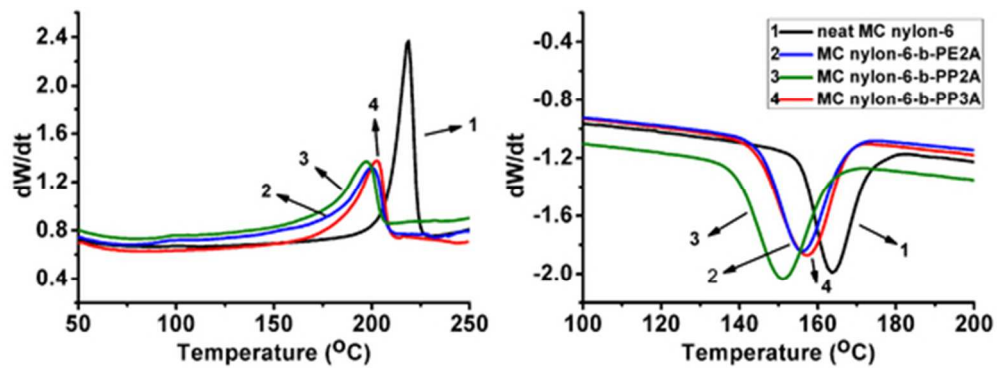


Fig.3 Non-isothermal process of MC nylon-6-b-polyether amine copolymers
46x17mm (300 x 300 DPI)

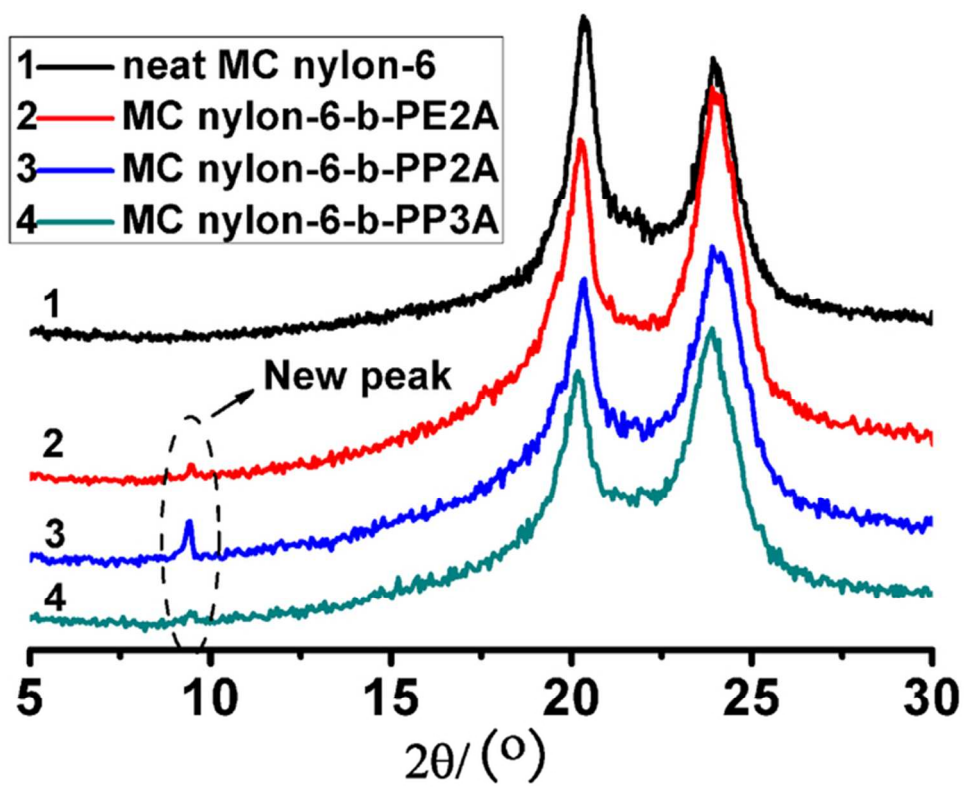


Fig.4 XRD spectra of MC nylon-6-b-polyether amine copolymers
60x48mm (300 x 300 DPI)

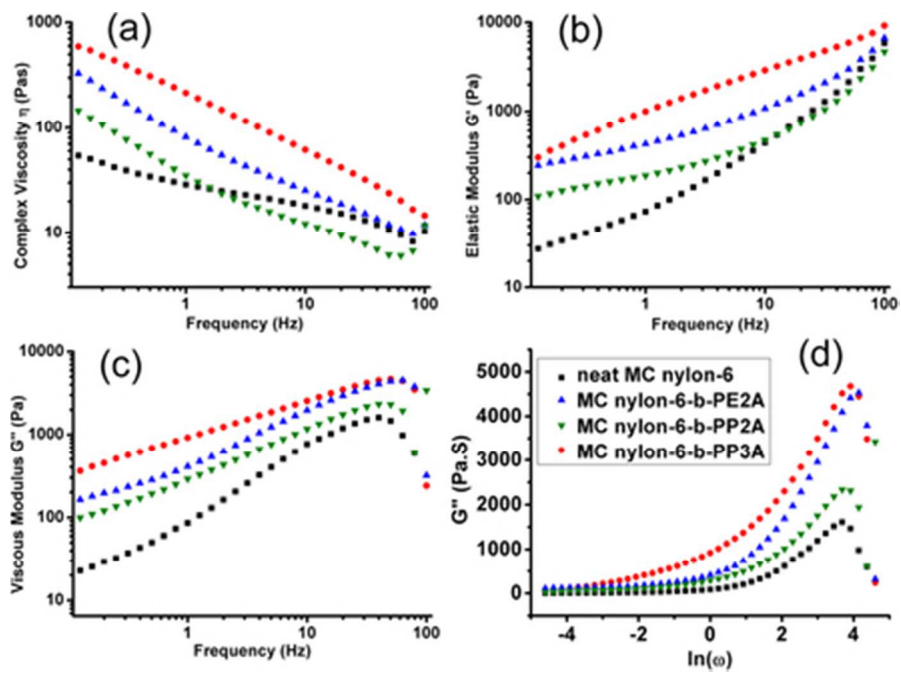


Fig.5 Rheological behavior of MC nylon-6-b-polyether amine copolymers
37x27mm (300 x 300 DPI)

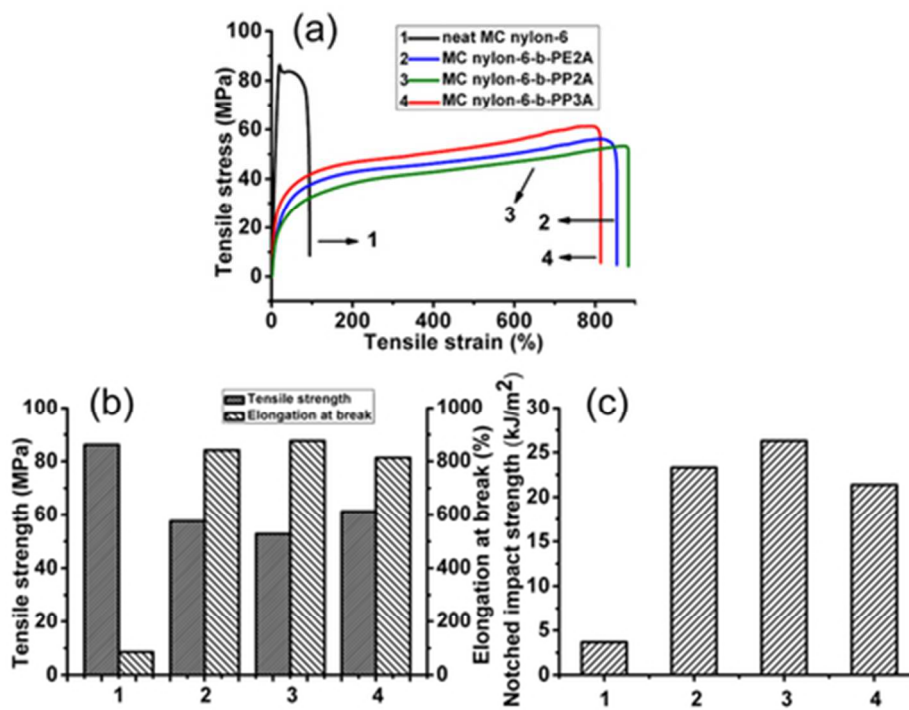


Fig.6 Mechanical properties of MC nylon-6-b-polyether amine copolymers 39x30mm (300 x 300 DPI)

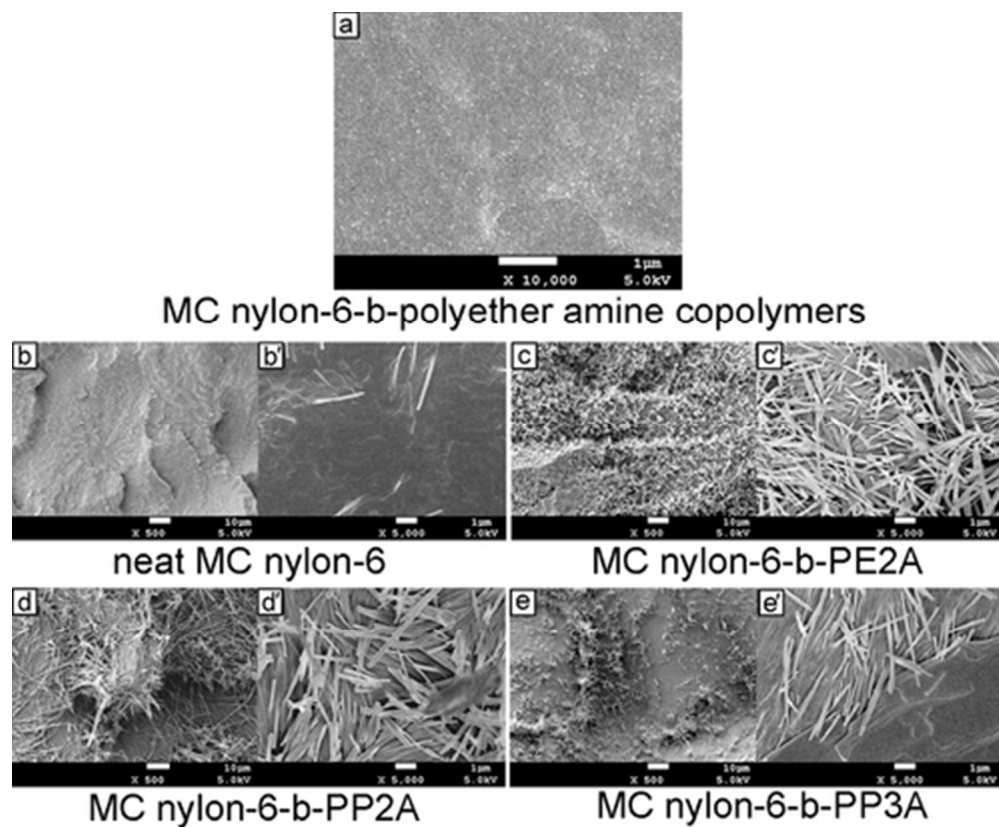


Fig.7 SEM image of cryogenically fracture surface (a: magnification $\times 10000$) and impact fracture surface of MC nylon-6-b-polyether amine copolymers (b-e: magnification $\times 500$; b'-e': magnification $\times 5000$) 41x34mm (300 x 300 DPI)

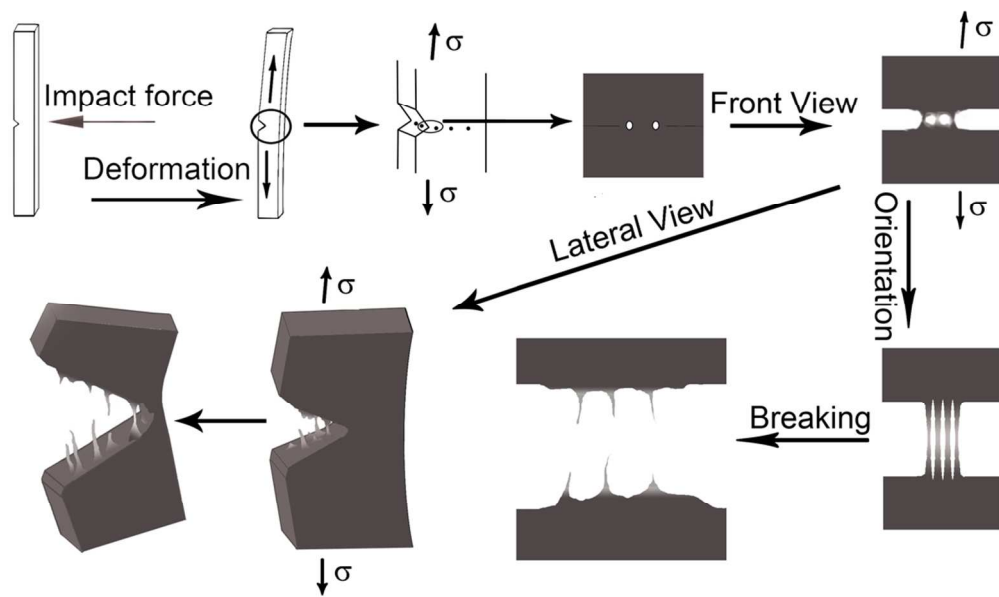


Fig.8 Toughening mechanism of the MC nylon-6-b-polyether amine copolymers