Glass Transition and Stress-Strain Curve of Polyaspartic Ester Polyurea at Different Tension Condition

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Abstract. The tensile properties of polyurethane are related to the microstructure due to the change of hydrogen bond and hard segment domains at different temperature and velocity. In this paper, the structure and glass transition before and after tensile breakage of polyaspartate (PAE) based polyurea (PU) coatings were analyzed by Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC) and tensile strain energy of stress-strain curve. The PAE-PU has not changed its allophanoyl (C=O in urea) and amino (N-H) hydrogen bond content apparently by the comparison of their IR absorption peak height. The PAE-PU has two glass transition temperatures related to soft and hard segments, which move to greater distance after tension. Moreover, the Enthalpy relaxation accompanied by hard segment glass transition almost disappears after tensile break. The dependency of tensile curve of PAE-PU on tensile rate at the same temperature is different from ordinary polymer materials; i.e.it has greatest yielding, strength and strain energy at medial rate of 100mm/min rather than higher ones.

1. Introduction
Polyaspartic ester polyurea (PAE-PU) is reacted from the condensation polymerization of polyaspartate and aliphatic isocyanate that has special steric hindrance effect of secondary amine in PAE to show good permeation and wetting ability, moderate reacting rate and high adhesive strength [1-6]. The so-called PAE is a kind of aliphatic secondary amine with two reactive hydrogen atom but hindered by the impendent crown-like structure and the carbonyl inductive effect, which both decreases the polymerization velocity with isocyanate (figure 1). Thus, the PAE could be used to not only spray polyurea (SPUA) but also brush by hand to be absorbed by the base material in long curing time [7-13].

However, the ambient condition of PAE-PU sprayed in concrete surface is so complicated with high loading, wide temperature variation and crack tension [14-16] that the dependency of coating protection in different tension state should be paid more attention. Nowadays the effect of reactive component, temperature and mechanical load are mainly reported while only a few amount of work [17-21] is aimed at the relationship between PAE-PU microstructure and deformation. In this paper, the Fourier transform infrared spectrum (FTIR) and differential scanning calorimeter (DSC) was used...
to analyse the change of PAE-PU, and the dependency of tensile rate on the stress - strain curve was discussed to understand the tension mechanism.

\[ \text{(a) Molecular structure of PAE-PU; (b) Schematic reaction of polyurethane and polyurea.} \]

2. Experimental Section

2.1. Materials and Sample Preparation
The component A and R of PAE-PU were weighted by 1:1 ratio and mixed to spray on surface of stainless steel plate. After 7-day curing reaction, the sheet was cut by normalized knife to get dumbbell shape (II) of which the whole length is 75 mm, the width of two end 12.5 mm, and the work length 25 mm, the width 4mm. Each sample was measured the thickness to be used in the tensile test.

2.2. Measurements
Fourier transformed infrared (FTIR) spectrum analyser (Bruker VERTEX 70, Germany) was used to test the spectrum of PAE-PU before and after tensile break by the attenuated total reflection mode. Thermal properties were also measured by differential scanning calorimetry (Netzsch DSC 204F1, Germany) after precisely weighted. Stress - strain curves were obtained from the tensile test by high temperature servo-controlled tensile machine (Gotech AI-7000S, China) at different temperature (27, 40, 60, 80 and 100 ℃) and different tensile rate (500, 200, 100, 50 and 20 mm/min).

3. Results and Discussion

3.1. FTIR Analysis of PAE-PU before and after Tensile Break
Hydrogen bond plays important role in mechanical property of PAE-PU that could be characterized by the absorption peak in FTIR. The spectrum of PAE-PU before and after tensile break were shown in figure 2 in which the peak height of C-O-C at 1094 cm\(^{-1}\) was used as internal standard.

\[ \text{Figure 2. Infrared spectra of PAE-PU before and after tension break.} \]
Strong absorption at 1094 cm\(^{-1}\) comes from large amount of C-O-C group in PAE, and peak at 1371 cm\(^{-1}\) belongs to -N=C=O. The hydrogen bonding allaphanyl C=O and free C=O contribute to the peak at 1636 cm\(^{-1}\) and 1728 cm\(^{-1}\) by which the hydrogen bond content can be calculated as 34.59\% before and 36.00\% after break. Peak height at 2263 cm\(^{-1}\) from -N=C=O rises as similar as peak at 3358 (hydrogen bonding N-H) and 3462 cm\(^{-1}\) (free N-H), which implies there are new surfaces after break. According to the ratio of peak height at 3358/3462 cm\(^{-1}\), the hydrogen bonding N-H content are 54.79\% before and 54.42\% after break. This means there is no apparent change of hydrogen bond after break which might be caused by quickly rebuilding of the intermolecular force.

Hydrogen bond from C=O and N-H was usually thought as the cause of polyurea, but the above FTIR does not show change of those peaks and no proof to new chemical structure after tensile break.

### 3.2. DSC Analysis

Allophanate physical crosslinks can form hard segment domains in PAE-PU tested by DSC curve (firstly cooled to -80 °C then heated to 150 °C at rate of 20 °C/min) in figure 3.

![Figure 3. DSC spectra of PAE-PU before and after tensioning.](image_url)

The PAE-PU has two glass transition temperature 17.9 °C and -46.9 °C related respectively to the \(T_{gh}\) of allophanate hard segments and \(T_{gs}\) of PAE soft segments, which means two micro phases to show different mechanical state at the similar temperature zones. Besides, an irreversible enthalpy relaxation as glass transition of hard segments at \(T_{gh}\) indicates that non-equilibrium state of hard segment phase will release the extra energy through relaxation of allophanate movement hindered by crosslinks with activation of more energy. After tension break, the enthalpy relaxation almost disappears because of activation of tensile stress forcing allophanate segments to move at lower temperature before DSC test.

In contrast with \(T_{gs}\) of PAE-PU before break, the sample after break has lower \(T_{gs}\) and higher \(T_{gh}\) because of further micro phase separation, i.e., tensile deformation destroys hard segment domains to free the soft segment mobility, and yielding makes hard segment flow to orient into harder state with higher \(T_{gh}\). It is consequently inferred that sprayed PAE-PU was cured before complete relaxation of rigid allophanate segments in hard domains to remain inner stress which would be released at \(T_{gh}\) or freed by stress to form thermally stabilized and oriented structure (figure 4).

![Figure 4. Microstructure rearrangement of PAE-PU before and after tension.](image_url)
3.3. Effect of Tensile Rate on Tensile Properties of PAE-PU

The movement of PAE-PU segments influences its thermal property; it is easily understood that mechanical property might be effected by the strain rate. The so-called time-temperature equivalence (TTE) principle in case of most polymer during single movement of only one kind of microstructure.

As shown in figure 5, PAE-PU stress-strain curve gets much higher when tensile rate raises from 20 mm/min to 100 mm/min, however it shifts down from 100mm/min to 500mm/min. Thus the strain energy (area below stress-strain curve), yield strength and strength at break also show maximum value at 100 mm/min, however the Young’s modulus at small strain monotonically decreases. Maximum strain energy is thought to be caused by the most difficult moving of chain segment when hard segment has close velocity to external stress speed. In this case the hard domains responses to external force with the strongest extent and brings the biggest internal stress to resist the strain. Hard segment cannot move at higher tensile rate to be destroyed and not capable to bear stress, while it would keep unbroken at low tensile rate and show higher modulus.

![Figure 5. Effect of tensile rate on stress-strain curve of PAE-PU at 27 °C.](image)

The influence of tensile rate on stress-strain curve at higher temperature in figure 6 is similar as the biggest strain energy at room temperature in figure 5, although the yielding point disappears to result in lower Young’s modulus and strength at break. This kind of dependency on temperature and strain rate is different from the common time-temperature equivalence principle for understanding the motion of only one stable system. TTE principle can be applied in the case of low tensile rate (<100 mm/min) when hard segment crosslinks are not broken. Oppositely, the higher rate of tension may destroy the crosslinks to show negative relationship between lower strain energy and higher rate.

Further comparison of tensile properties in figure 7 indicates the similar highest strength (yield and break) and strain energy (area below the curve) at 100mm/min but different influence of rate on yield strain between 27 °C - 100 °C. The lower yield strain keeping increasing at 27 °C means breakage of hard segment crosslinks, while the higher ones at 80 °C and 100 °C decrease at higher tensile rate is caused by motion of the soft one after disappearing of physical crosslinks at temperature above $T_{gh}$.

In conclusion, the characteristic dependency of tension curve on strain rate are related to the restraint of hard segment crosslinks to movement of soft segment and the whole system. It is understood that the physical crosslinks were broken by tension and at the same time new crosslink comes into being because of strong intermolecular forces. At lower tensile rate the soft segment moves more rapidly and forces hard domains to deform slowly which needs low strain energy. However, at higher rate the physical crosslinks of hard segments are destroyed because of slower motion than the system so as not to need more energy to deform. Only at the appropriate tensile rate close to those of crosslink breaking and soft segment moving are the motion restricted to the greatest extent by inner surroundings. In other word, the highest yielding point, forced elasticity and strain energy appears at moderate tensile speed of 100 mm/min, i.e., about strain rate of 0.83 s$^{-1}$ or relaxation time of 1.20 s.
4. Conclusion

(1) The hydrogen bonding content in PAE-PU doesn’t change after tensile break according to FTIR.

(2) Two glass transition in DSC curve are related to hard segment and soft segment domains of PAE-PU. Thermal entropy relaxation happens at the glass transition of hard segments. After tensile break the hard segment’s glass transition temperature shift to higher temperature while the soft one shift to lower temperature. Thermal entropy relaxation almost disappears after break.

(3) Stress-strain curve of PAE-PU shows apparent different change from ordinary polymer as tensile rate increased at the same temperature, which is caused by breakage of hard segment crosslinks. The highest strain energy, yield strength and strength at break at moderate tensile rate
implies that at this speed the destruction of physical crosslink and motion of soft segment go on simultaneously to restrain the chain motion to the greatest extent.

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