Effect of Temperature on Tensile Curve of Polyaspartic Ester Polyurea and Its Activation Energy Analysis

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Abstract. The influence of ambient temperature on the tensile stress-strain curve of polyaspartic ester polyurea (PAE-PU) was investigated to discuss the yield and breakage mechanism of tensile deformation. Temperature has a significant effect on the tensile stress-strain curve of PAE-PU. At low temperature (27, 40 °C), it shows obvious yield and forced high elasticity. After the temperature exceeds 80 °C, the yield phenomenon disappears and shows high elasticity of rubber: the strain energy and breakage energy are significantly reduced. The yield activation energy of PAE-PU was calculated by yield strain time at different temperatures. It was found that the yield activation energy decreased with the increase of tensile rate. When the tensile rate is 500mm/min, among the activation energies calculated by breakage strength, yield strength and Young’s modulus at different temperatures, the ordinary elastic deformation activation energy is higher, while the yield and breakage activation energy are close and lower. The latter two are close to the hydrogen bond energy and one order of magnitude lower than the chemical bond energy of molecular chain.

Keywords. Polyaspartic ester polyurea, tensile stress-strain curve, activation energy.

1. Introduction

Polyaspartic ester (PAE) is an aliphatic secondary amine. The active hydrogen atom on the secondary amine can react with isocyanate to generate urea group to form a hard segment structure, which plays the role of physical cross-linking point so that aspartic polyurea shows excellent mechanical properties [1-3]. Because the two secondary-amine hydrogen atoms of PAE are affected by the steric hindrance of adjacent coronal structures (figure 1), the reaction activity and reaction rate are so low that brush coating and other method can be used for processing. Furthermore, the urea group unique molecular structure gives PAE-PU molecular chain special mobility and temperature dependence.

Figure 1. Molecular structure of PAE.
It is generally believed that the urea based structure in PAE-PU molecular chain can form rigid hard-segment micro region and play the role of physical crosslinking and reinforcement \[4, 5\]. Moreover, this structure is easy to soften and flow at high temperature, which affects the mechanical properties of the material. In this paper the temperature dependence of the stress-strain relationship in the tensile process of PAE-PU is studied and calculated to obtain its yield and breakage activation energy. Furtherly, it is compared with the thermal decomposition activation energy from TGA, so as to analyze the structural change in the tensile process and its correlation with the stress-strain curve.

2. Experimental Section

2.1. Materials and Sample Preparation

The component A and R of PAE-PU were prepared before the mixing and curing. Wherein, A is a semi prepolymer with isocyanate as the end group prepared by the reaction of PAE and isocyanate, and B is a mixture of PAE and chain extender. Then mixture of A and R evenly in the ratio of 1:1 was sprayed on surface of stainless steel plate, and cured for 7 days, then put in normalized laboratory condition to cut by dumbbell-shape (II) knife. Its whole length is 75 mm, the width of two end 12.5 mm, and the work length 25 mm, the width 4 mm. The thickness of each sample was measured to be used in the tensile test.

2.2. Measurements

Stress-strain curves of PAE-PU were obtained by high-temperature servo-controlled tensile machine (Gotech AI-7000S, China) at different temperature (27, 40, 60, 80 and 100 ℃) and tensile rate 500 mm/min.

TG curves of PAE-PU were measured by TG analyzer (Netzsch TG209F1, Germany) under nitrogen protection. The heating rate is 5, 10 and 20 ℃/min.

3. Results and Discussion

3.1. Effect of Temperature on Tensile Curves of PAE-PU

Figure 2 shows the stress-strain curves obtained by stretching PAE-PU at different temperatures, and the stretching rate is 500 mm/min.

![Figure 2. Tensile stress-strain curves of PAE-PU (500mm/min).](image-url)
It can be seen from figure 2 that the tensile stress-strain curve of PAE-PU material at low temperature (27 °C) can be divided into five regions: general elastic deformation, yield and strain softening, forced high elastic deformation, strain hardening and breakage [6-9]. The general elastic deformation region at the initial stage (< 10%) conforms to Hooke's law, and its slope, that is, the elastic modulus (Young's modulus), decreases with the increase of temperature. Beyond the elastic deformation zone, the stress of the sample does not change or even decreases when the strain increases, which means that yield and strain softening occur. Then as the strain increases, the stress changes little, that is, forced elastic deformation occurs. When the temperature is below 40 °C, there is an obvious yield point on the stress-strain curve. Within 40-60 °C range, the yield point become invisible and the forced high elastic deformation increase. At 80 °C and above, the yield point disappears. When the strain reaches about 50%, strain hardening begins to appear, and the stress increases with the increase of strain until breakage.

Table 1. Tensile properties of PAE-PU at different temperature.

| Temperature (°C) | 27   | 40   | 60   | 80   | 100  |
|------------------|------|------|------|------|------|
| Strength at break (MPa) | 14.34 | 12.65 | 7.85 | 5.36 | 2.35 |
| Yield strength (MPa)   | 7.96  | 4.01  | 2.73 | 1.66 | 1.01 |
| Yield strain (%)       | 20.17 | 40.35 | 51.25 | 0   | 0   |
| Total breakage energy (KJ/m³) | 2.94 | 2.97 | 2.17 | 1.13 | 0.34 |
| Yield energy (KJ/m³)   | 1.78  | 1.88  | 1.54 | 0.85 | 0.21 |

In addition, the area under the stress-strain curve, that is, strain energy firstly increases slightly and then decreases with the increase of temperature (table 1), in which the strain energy and breakage energy of the material are the highest at low temperature 27-60 °C. According to the glass transition analysis [10], the strain energy is consequently thought to be closely related to the yield and forced high elastic deformation of materials: in the glass transition range, the more obvious the yield and forced high elastic deformation are, the greater the strain energy is. The irreversible deformation corresponding to yield comes from the segment motion in PAE-PU, so it is related to the physical crosslinking network and segment motion of its hard segment.

Generally speaking, at higher temperature (> 60 °C), the stress-strain curve shows a behavior similar to that of rubber; while at the lower temperature (27 °C), the material is leather like, with high initial modulus and obvious yield and strain softening. It is thought that at relatively low temperature, the motion of the chain segment is frozen, and the soft and hard segments are embedded, thus there is a certain degree of physical cross-linking network to show high breakage strength. Between room temperature and 40 °C, the hydrogen bond of PAE-PU begins to break or the hard segment structural unit begins to move due to the increase of thermal movement. Consequently it is in the stage of glass transition, showing high strain energy. When the temperature exceeds 40 °C to 60 °C, more physical crosslinking points are destroyed and gradually change from network to separation state [11-13]. Therefore, the apparent yield point disappears, and the strain energy and breakage energy decrease. When the temperature exceeds 80 °C, the PAE-PU has softened obviously, and the stress-strain curve has changed from soft and tough type to soft and weak type. In this temperature range, the hydrogen bond and hard segment cross-linking point almost completely disappear, and only van der Waals force exists. Therefore, the strain energy and breakage energy have decreased sharply, the breaking strength and elongation at break have decreased. The structural changes during the above stretching process can be described by figure 3.
As mentioned above, PAE-PU has obvious yield point below 40 °C; the yield is not obvious between 40 °C and 60 °C; at 80–100 °C, the yield point disappears, and the young's modulus in the low strain zone is very low, which is completely different from that at low temperature. In order to further confirm the yield irreversible deformation mechanism of PAE-PU, the length recovery of first-stretched and unbroken sample was observed and shown in table 2. It was found that when there were not yielding (5%, 10%, 27.5% in room temperature), the length could quickly recover to their original length at low temperature(< 15 °C), but the yielded ones could not recover to their original length and maintain a certain permanent deformation. Contrarily in a 70 °C incubator, the yielded sample can return to its original length. Combined with previous studies in which the glass transition temperature of polyurea 17.9 °C [10] and its wide enthalpy relaxation temperature range, it is considered that the permanent deformation caused by tensile yield of polyurea is related to segment movement: the sample before yield can recover completely at low temperature (< 15 °C); those after yield cannot recover quickly because the temperature is lower than the glass transition temperature. When it is higher than the glass enthalpy relaxation temperature range (~70 °C), the permanent deformation can recover rapidly and completely.

Table 2. Length change of tensile samples with different first-deformation in 70 °C incubator.

| Fisrt-stretch deformation (%) | 5    | 10   | 27.5 | 100  | 200  |
|-------------------------------|------|------|------|------|------|
| 0 min length (mm)             | 20.0 | 20.0 | 20.0 | 21.2 | 22.5 |
| 10 min length (mm)            | 20.0 | 20.0 | 20.0 | 20.0 | 20.2 |
| 20 min length (mm)            | 20.0 | 20.0 | 20.0 | 20.0 | 20.0 |
| 30 min length (mm)            | 20.0 | 20.0 | 20.0 | 20.0 | 20.0 |

To sum up, PAE-PU begins to soften at about 40 °C. Below this temperature, the chain segment motion in PAE-PU molecular chain is frozen by the physical cross-linking network from hydrogen bond or hard segment structure [10], and the initial modulus of the material is high. Due to the activation of higher stress or strain, the physical crosslinking network is destroyed, and the chain segments are forced to move to result in the yield.

### 3.2. Effect of Temperature on Tensile Properties and Its Analysis of Activation Energy

The yield activation energy was calculated from yield strength-temperature dependence, while the breakage activation energy was calculated by the breakage strength-temperature dependence of PAE-PU. Thus the relationship can inferred between yield, breakage and molecular chain structure to help understand the deformation mechanism. Figure 4 shows the tensile properties at different temperatures. It can be seen that with the increase of temperature, the variation laws of Young's modulus, breakage strength and yield strength are similar, which all show a nonlinear downward trend in accordance with Arrhenius equation.
Figure 4. Effect of temperature on Young's modulus, yield strength and strength at break and three activity energy of PAE-PU.

Through the temperature dependence curves of Young's modulus, yield strength and breaking strength (figure 4), the activation energy of PAE-PU in different tensile states can be calculated. The temperature dependence of Young's modulus is higher than the yield strength and breakage strength, and the latter two are almost the same. This means the activation energy of PAE-PU is higher in the general elastic deformation region, but lower in the case of yield and breakage. In other words, the general elastic deformation of PAE-PU requires higher energy - corresponding to the movement of units below the chain segment in the hard segment micro region. In the contrast, the yield occurs due to the movement of the chain segment, so it requires a lower activation energy - 24.88 KJ/mol, which is close to the bond energy of hydrogen bond (~20 KJ/mol). The breakage activation energy is close to the yield activation energy, which is 1 order of magnitude lower than the thermal decomposition activation energy measured by TGA method (382.50 KJ/mol at 98% weight loss, table 3) according to

\[
\lg \beta = -\frac{0.457E}{RT} + \left(\lg \frac{AE}{g(\alpha)R} - 2.315\right),
\]

wherein \(\beta\) - heating rate, \(E\) - reaction activation energy, \(R\) - gas constant, \(T\) - temperature, \(A\) - pre-exponential factor, \(g(\alpha)\)-integral function of conversion \(\alpha\). It infers that the breakage process of polyurea is mainly the local slippage of molecular chain caused by chain segment movement, rather than molecular chain breakage.

| Mass loss (%) | 10     | 30     | 50     | 70     | 90     | 98     |
|---------------|--------|--------|--------|--------|--------|--------|
| Activation energy (KJ/mol) | 200.29 | 228.74 | 210.69 | 238.81 | 287.87 | 382.50 |
| ±9.75         | ±36.59 | ±20.59 | ±39.74 | ±84.92 | ±18.52 |
| Log(A/s⁻¹)    | 16.68  | 16.29  | 14.47  | 16.47  | 19.32  | 25.36  |

4. Conclusion
(1) Temperature has a significant effect on the tensile stress-strain curve of PAE-PU. It shows obvious yield and forced high elasticity at low temperature (27, 40 °C), no obvious yield point after 60 °C, and high elasticity of rubber after exceeding 80 °C. When the temperature increases, the strain energy decreases obviously, and the properties such as yield strength and breakage strength decrease.

(2) PAE-PU after tensile yield cannot return to its original length at low temperature, and can recover rapidly after exceeding the enthalpy relaxation temperature range associated with glass transition temperature.

(3) Through the temperature dependence calculation of Young's modulus, yield strength and breakage strength, it is found that the activation energy of ordinary elastic deformation is higher than
the yield activation energy and breakage activation energy. The activation energy of the latter two is similar and equivalent to the hydrogen bond energy, but far lower than the thermal decomposition activation energy of molecular chain.

Acknowledgment
We are grateful for financial support from the National Science Foundation of China (No. 51773104 and 51373085). We thank Open Project (No. JZA2018Kj02) of the National Enterprise Technology Center of China Jingye Engineering Technology Co., Ltd and Doctoral Scientific Fund Project of Qingdao University of Science and Technology.

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