Study on thermodynamic properties of polyurethane fibers under small strain

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Abstract. In this work, dynamic thermodynamic analyzer (DMA) was used to determine the stress-temperature relationship of polyurethane fibers to research the thermodynamic properties under small strains. The results show that the stress of polyurethane fibers increases with the increase of temperature. The study of the energy conversion during the heating process of polyurethane fibers demonstrates that the entropy change decreases with the increase of the strain while the enthalpy change has the contrary tendency. The entropy change is the key reason for the stress of polyurethane fibers.

1. Introduction
Polyurethane is a block copolymer with alternating hard and soft segments, which is wildly used in foams [1, 2], adhesive [3], actuator [4], polymeric binder [5], thermoplastic elastomers [6], medical appliance [7] etc. To the best of our knowledge, most relevant scholars [8-11] have analyzed many aspects of polyurethane in the microstructure, mechanical properties, swelling properties and so on, but little literature focused on its thermodynamic properties. Though some literatures have focused on investigating the thermal elasticity of natural rubber and synthetic rubber [12-14], there is only few study about the thermoelasticity of polyurethane. Nierzwicki et al. [15] revealed that thermoelastic properties of polyurethane were dependent on compositional variations and interpreted in terms of the extent and stability of microphase separation, whereas Dzier et al. [16] considered the properties strongly dependent on structure and experimental conditions. Godovsky et al. [17-19] studied the thermodynamic properties and thermal effect of polyurethane by deformational calorimetry, and it was found that the initial small strain deformation was owing to the volume elasticity of the hard phase, and a decrease in the fraction of energy changes was largely attributed to hard block structurization in the course of re-building the network of hydrogen bonds. Pieczyska et al. [20] researched the thermomechanical properties of polyurethane and the influence of the strain rate on the strain localization behavior basing on the mechanical data and the relevant temperature changes, and identified the material parameters for the one-dimensional rheological model of the polyurethaneshape memory polymer. Jian et al. [21] confirmed that the thermal processing clearly imparted significant changes to the H-bonded environment by small-angle X-ray scattering (SAXS). Barikani et al. [22] proposed that the thermal properties and thermal stability of polyurethane were strongly affected by the molecular structure of the dianiline chain extender. Qu et al. [23] presented that the introduction of silver nano-particles would promote to increase the thermal stability and tensile properties of the polyurethane fibers.
The thermodynamically incompatible thermoplastics polyurethane leads to the separation of soft segments and hard segments, while soft segments are responded for its high deformability [24, 25]. Therefore, the purpose of the present work surveys how the thermal history of polyurethane fibers affects the thermodynamics of deformation. In previous studies on thermodynamics experiments of polyurethane, a simple experimental device was used to obtain the relationship of stress-temperature which is composed of forces at different temperatures. In this work, the dynamic thermodynamics analyzer (DMA) was utilized to obtain a continuous stress-temperature curve, which can greatly reduce the experimental error.

2. Experimental

2.1. Materials
Polytetramethylene ether glycol (PTMG) was provided by Sichuan Tianhua Fubon Chemical Industry Co., Ltd. Diphenylmethane-4,4'-diisocyanate (MDI) was obtained from Wanhua Chemical Group Co., Ltd. Ethylenediamine (EDA) was purchased from Japan Tosoh Corporation. N,N-dimethylacetamide (DMAc) was bought from Zhejiang Jiangshan Chemical Co., Ltd. Nitrogen was homemade. All these chemicals reagents were of industrial grade and used without any purification.

2.2. Fabrication of Polyurethane Fibers
The two-step polymerization method was commonly used: the preparation of segmented structural polyurethaneurea and spinning polyurethane fibers. In the first step, MDI and PTMG were mixed together at molar ratio of 1.0 to 1.6 and reacted at 80°C to form urethane linkage by alternatively connected with hard and soft segments of pre-polymer. Then the pre-polymer was solved with DMAc to form 35% solution. The molecular main chain of the prepolymer in solution was extended with ethylene diamine to form segmented polyurethaneurea copolymers with the molecular weight ranged from $5 \times 10^5$ to $8 \times 10^5$.

The copolymer solution was pumped and sprayed through spinneret plates into spinning heating channels at 244°C, where the trickle of the solution was dried to form polyurethane fibers.

2.3. Testing Methods
A TA Q800 instrument was used to test the dynamic mechanical property of the samples. Set test mode as iso-strain temperature ramp. Set strain as 2%, 5%, 10% and 15%, respectively, with temperature programming from 35 °C to 80 °C at 5 °C /min.

3. Results and Discussion

3.1. The Relationship between Temperature and Stress of Polyurethane Fibers
Figure 1 shows the linear fitting relationship between stress and temperature at different elongations, with correlation coefficient above 0.97. All the curves present the information that the samples achieve the same varied. When the strain range from 0 to 15%, the stress of polyurethane fibers increases with the temperature rises, and at the same temperature, the variation of stress of polyurethane fibers is in agreement with the strain. The reason is that the motion of the polymer chain is more intense with the higher temperature and strain.
3.2. Effect of Strain on Entropy and Enthalpy

In the isothermal isobaric conditions, according to the First Law and the Second Law of thermodynamics, the variation of internal energy (U) is expressed as:

\[ dU = TdS - dW \]  

(1)

Where \( dW \) is the work done when the system satisfies the reversible condition and accompanies the heat of the \( TdS \), which means product of temperature and entropy.

For polyurethane fibers filaments with elongated \( dL \), a stress \( f \) is generated. Where \( dV \) is the volume expansion of polyurethane fibers filament elongation, and \( P \) is atmospheric pressure. Therefore, \( dW \) refers to the mechanical work, \(-fdL\), and expansion work, \( PdV \). So the variation of internal energy is also expressed as:

\[ dU = TdS - dW \]  

(2)

Since the experiment is operated at constant pressure, the enthalpy is expressed as:

\[ dH = dU + PdV \]  

(3)

Base on Equation (2) and (3), Equation (4) is deduced and presented:

\[ dH = TdS + f dL \]  

(4)

Therefore, under the constant temperature and constant pressure conditions, the stress generated by the polyurethane fibers is deduced and presented:

\[ f = \left( \frac{\partial H}{\partial L} \right)_{T,P} - T \left( \frac{\partial S}{\partial U} \right)_{T,P} \]  

(5)

It is shown that the stress of polyurethane fibers due to deformation is caused by the variations of entropy and enthalpy. We make \( \left( \frac{\partial S}{\partial U} \right)_{T,P} \) equal to the entropy change \( \Delta S \), \( \left( \frac{\partial H}{\partial L} \right)_{T,P} \) equal to the enthalpy change \( \Delta H \). For the stress-temperature curve, the slope is \(-\Delta S\) and the intercept is \( \Delta H \). The variations in entropy and enthalpy of polyurethane fibers under small strain are presented in Figure 2, where the data are derived from the slope and the intercept of lines in Figure 1. It can be seen from Figure 2(a) that the entropy variation decreases with the increase of strain, which means the system entropy decreases. The reason is that the molecular chain changes from the curled state to the straightened state when the polyurethane fiber is stretched, and the reduction in conformation number leads the conformational entropy to decrease. Meanwhile, Figure 2 (b) displays that the enthalpy variation increases with increasing strain, which means the system enthalpy increases, simultaneously. The enthalpy variation consists of two parts, one is the change of the internal energy due to the change of length; the other is the volume. And the internal energy of the polyurethane fibers increases with the increase of the length, which is the main component of the enthalpy change.
3.3. The Distribution of Stress to Entropy and Internal Energy

For the ideal rubber elastomer, its volume keep in a constant value during the stretching process, so for the isothermal reversible process the stress is expressed as:

\[
f = \left(\frac{\partial u}{\partial T}\right)_{TV} - T \left(\frac{\partial S}{\partial T}\right)_{TV} = f_u + f_s
\]  \hspace{1cm} (6)

Where \( f_u \) is the stress generated by internal energy, \( f_s \) is the stress generated by entropy.

Take the derivative with respect to \( T \) in Equation (6), it is deduced and presented:

\[
\left(\frac{\partial f}{\partial T}\right)_{LV} = -\left(\frac{\partial S}{\partial L}\right)_{TV}
\]  \hspace{1cm} (7)

Using Equations (6) and (7), Equation (8) is deduced and presented:

\[
\frac{f_u}{f} = 1 - \frac{T}{f} \left(\frac{\partial f}{\partial T}\right)_{LV} = 1 - \frac{\partial n f}{\partial n T}
\]  \hspace{1cm} (8)

Through the Gaussian chain Equation, it achieves Equation (9):

\[
f = G_0 A_0 \left(\lambda - \frac{1}{\lambda}\right)
\]  \hspace{1cm} (9)

Where \( G_0 \) is a characteristic constant of the material, \( A_0 \) is the cross-sectional area of polyurethane fibers, \( \lambda \) is the strain of polyurethane fibers. \( G_0 \) is a function of temperature and does not vary with the experimental conditions under constant volume or constant pressure, while \( A_0 \) and \( \lambda \) do not change with temperature. Take the derivative with respect to \( T \) in Equation (9) after taking the logarithm in the case of constant volume and constant length, Equation (10) is obtained:

\[
\left(\frac{\partial n f}{\partial n T}\right)_{LV} = \frac{\partial n G_0}{\partial n T}
\]  \hspace{1cm} (10)

Substituting Equation (10) in Equation (8), Equation (11) is deduced and presented:

\[
\frac{f_u}{f} = 1 - \frac{\partial n G_0}{\partial n T}
\]  \hspace{1cm} (11)

Equation (12), (13), (14) are utilized to achieve the value of \( G_0 \),

\[
\sigma = \frac{f}{A_0}
\]  \hspace{1cm} (12)
\[
A_0 = \frac{\pi}{4} d^2
\]  \hspace{1cm} (13)
\[
d = \left(\frac{4 \times 10^3}{9 \pi \gamma} N_{d0}\right)^{1/2}
\]  \hspace{1cm} (14)
Where \( \sigma \) is the stress (i.e. stress per unit area) of polyurethane fibers, \( d \) is the diameter of polyurethane fibers, \( N_D \) is the denier of polyurethane fibers, \( \gamma \) is the density of polyurethane fibers which takes 1.21 g/cm³.

Through the above formula, the contribution of internal energy to stress of polyurethane fibers can be obtained. Figure 3 displays the relationship between \( \sigma \) and \( \left( \lambda - \frac{1}{\lambda^2} \right) \) at the temperature of 308.15K (35°C), and the slope is the \( G_0 \) value. Figure 4 shows the correlation between \( \ln G_0 \) and \( \ln T \). \( G_0 \) is calculated by the above method at the temperature ranges from 308.15 K to 343.15 K, with a 5K step. It presents that the curve of Figure 4 is fitted with a quadratic function to obtain \( \frac{\partial G}{\partial \gamma} \), contribution of internal energy to stress of polyurethane fibers. The results are listed in Table 1. It can be seen that the contribution of internal energy to stress decreases with the increase of temperature, and its maximum is only 26.7%. Therefore, entropy variation is the key reason for the stress of polyurethane fibers when it is stretched at different temperatures.

**Figure 3.** The \( \sigma \) to \( \left( \lambda - \frac{1}{\lambda^2} \right) \) diagram of polyurethane fibers at 308.15 K

**Figure 4.** The \( \ln G_0 \) to \( \ln T \) diagram of polyurethane fibers
Table 1. The contribution of internal energy to stress at different temperatures

| Temperature (K) | lnT | ∂lnG₀ | ∂lnT/₀ | 𝜕𝜕𝜕𝜕𝑇𝑇 | 𝜕𝜕𝜕𝜕𝐺𝐺₀ | 𝜕𝜕𝜕𝜕𝜕𝜕𝑇𝑇 | 𝜕𝜕𝜕𝜕𝜕𝜕𝐺𝐺₀ | 𝑓𝑓 | 𝑓𝑓₀ |
|----------------|-----|-------|--------|--------|-------|--------|--------|-----|-------|
| 308.15         | 5.731 | 0.733 | 0.267  | 5.731  | 0.733 | 0.267  | 0.245  | 0.223 | 0.202 |
| 313.15         | 5.747 | 0.755 | 0.245  | 5.747  | 0.755 | 0.245  | 0.223  | 0.202 | 0.180 |
| 318.15         | 5.763 | 0.777 | 0.223  | 5.763  | 0.777 | 0.223  | 0.202  | 0.180 | 0.159 |
| 323.15         | 5.778 | 0.798 | 0.202  | 5.778  | 0.798 | 0.202  | 0.180  | 0.159 | 0.139 |
| 328.15         | 5.793 | 0.820 | 0.180  | 5.793  | 0.820 | 0.180  | 0.159  | 0.139 | 0.118 |
| 333.15         | 5.809 | 0.841 | 0.159  | 5.809  | 0.841 | 0.159  | 0.139  | 0.118 |       |
| 338.15         | 5.823 | 0.861 | 0.139  | 5.823  | 0.861 | 0.139  | 0.118  |       |       |
| 343.15         | 5.838 | 0.882 | 0.118  | 5.838  | 0.882 | 0.118  |       |       |       |

4. Conclusion

In this study, the dynamic thermodynamics analyzer (DMA) was utilized to obtain a continuous stress-temperature curve, which is more accurate than previous methods. It was concluded that the thermodynamic properties of polyurethane fibers under small strain (≤15%) as follows:

(i) The stress of polyurethane fibers increases with the temperature rises, and at the same temperature, the variation of stress of polyurethane fibers is in agreement with the strain.

(ii) The entropy variation decreases with the increase of strain, while the enthalpy variation increases.

(iii) The contribution of internal energy to stress decreases with the increase of temperature, and its maximum is only 26.7%. Entropy variation is the key reason for the stress of polyurethane fibers when it is stretched at different temperature.

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