

# Mechanical responses of filled thermoplastic elastomers

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**Abstract.** In this paper, several mechanical responses of thermoplastic polyurethane (TPU) filled with nano-scale attapulgite (AT) particles, including cyclic loading-unloading behavior, dynamic mechanical behavior and stress relaxation have been investigated. With the addition of AT, it is noticed that the strength, modulus and stress relaxation time of TPU increased significantly compared to that of unfilled materials. It is also observed that, whether filled or unfilled TPU, pronounced inelastic mechanical features such as Mullins effect, residual strain and hysteresis, occurred mainly during the first load loop, but became more notable with AT increase.

## 1. Introduction

TPU is one of the most thermoplastic block polymers composed of soft and hard segments. Because of its good elasticity and easy of melt-processing, TPU can be fabricated by diverse method and displays many excellent properties, such as high elasticity, wear resistance, good resistance to oils, and good weather stability [1-3]. However, relative to chemical crosslinked thermoset polymer materials, TPU does not show high mechanical properties and desired heat resistance. Therefore, in recent years, many efforts have been devoted to improve the polyurethane matrix and reduce costs by introducing various fillers, including inorganic clay, metallic oxide and carbon nanoparticles [4-6]. Attapulgite (AT), a natural fibrillar clay with many hydroxyl groups on the surfaces, it is known to be very effective for material enhancement [7,8]. In this paper, we firstly prepared the TPU/AT composites by solution blending method, and then discussed the effect of AT on mechanical properties. In particular, the inelastic mechanical behaviors of materials were mainly studied and analyzed because of its importance in practical application [9].

## 2. Materials and methods

### 2.1. Materials

AT and TPU were purchased from Jiangshu XuYi MinChem Co., Ltd. and BASF chemical company, respectively. TPU/AT composites were prepared by solution blending and the detailed process has been reported in our earlier paper [10]. The elastic composites with AT contents of 0, 1, 2, and 5% were marked as TPU/AT0, TPU/AT1, TPU/AT2 and TPU/AT5.

### 2.2. Experimental methods

SEM tests were conducted on a JEOL JSM-5600LV instrument. The surface of samples was all coated



with a gold layer for the observation of cross-section images.

FTIR were conducted on a Nicolet 8700 spectrometer. The spectra for all samples were obtained at a resolution of  $4\text{ cm}^{-1}$ , and the resulting spectra were the average of 32 scans to meet an adequate signal-to-noise.

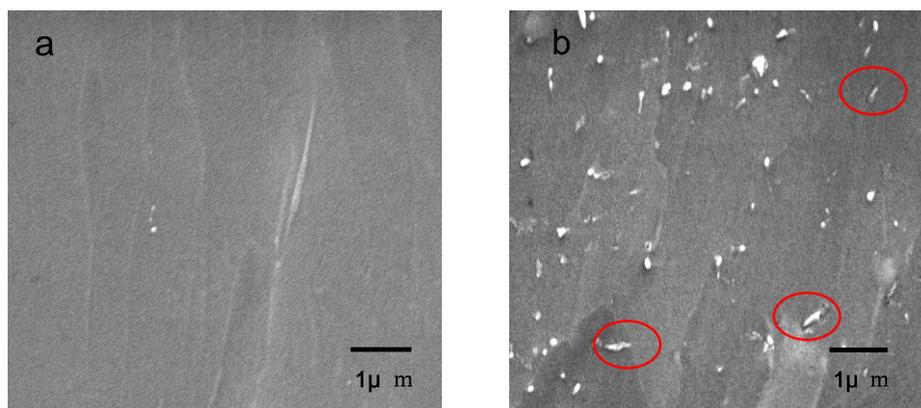
Cyclic mechanical tests were made on thin-sheet samples approximately  $50 \times 2 \times 0.2\text{ mm}^3$  on an elastic testing machine with a 500 mm/min rate. The initial tensile modulus ( $E$ ) was determined by first loading slope  $d\sigma/d\varepsilon$  at  $\varepsilon = 0.1$ , and residual strain ( $\varepsilon_r$ ) was irreversible strain after experiencing first cyclic deformation.

DMA measurements were performed from 30-90°C at frequency of 10 Hz and at heating rate of  $2^\circ\text{C}/\text{min}$  using a TA Q800 instruments.

Stress relaxation behaviors were tested when the elastomers were stretched to 300% strain with a 1000 mm/min rate.

### 3. Results and discussion

SEM photographs of the TPU/AT0 and TPU/AT1 composite are showed in figure 1. It is found that the fractured section of TPU/AT1 sample shows many AT nano-fibrils with irregular distribution, while that of pure TPU is smooth. Furthermore, there is not a clear interface between AT and the TPU matrix and only a few AT marked in red circle are pulled out from matrix, which implies that AT is uniformly dispersed and randomly oriented in TPU.

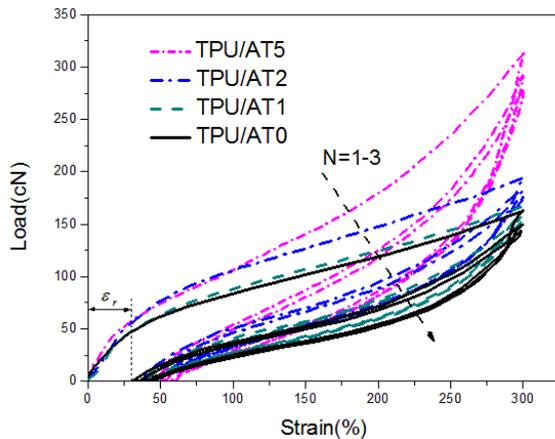


**Figure 1.** SEM photographs of elastomers. (a) TPU/AT0; (b) TPU/AT1.

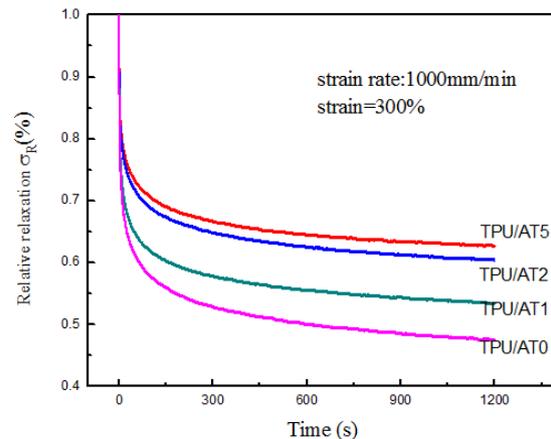
Figure 2 presents the load-strain curve of TPU composites at 500 mm/min cyclic tensile rate. It is clear that filled TPUs have discernibly higher strength and initial tensile modulus than those of pure TPU in first loading process. When subjected to cyclic loading (cycle number,  $N=1-3$ ), all materials also exhibit a significant stress softening behavior (e.g. Mullins effect) [11]. There is a distinct stress reduction after the first load loop, while the stress achieves a stable state in the subsequent cycles. At the same time, there is also pronounced hysteresis in the first cycle, which exhibits a large hysteresis loop with a distinct residual strain. In the following cycles, the loading and unloading paths are both less independent of cycle numbers and the corresponding hysteresis loops become quite small than that of the first loading-unloading cycle.

The stress relaxation of TPU/AT composites can also reflect the inelastic mechanical behaviors caused by large viscous dissipation. Figure 3 shows the curves of tensile stress relaxation, where the relative relaxation value,  $\sigma_R$  is plotted against time,  $t$ .  $\sigma_R$  is expressed by

$$\sigma_R = \sigma_t / \sigma_0 \times 100\%$$

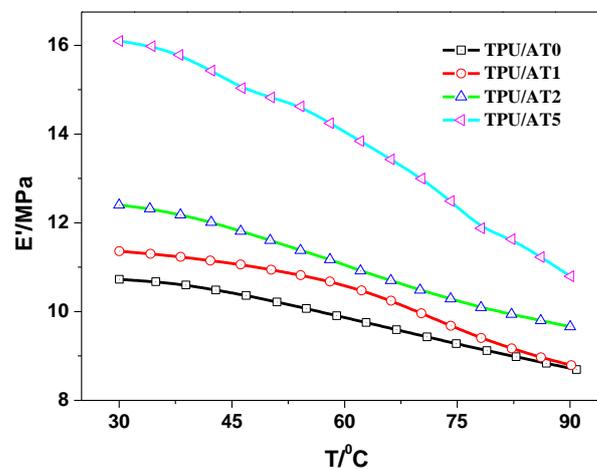


**Figure 2.** The load-strain curve of TPU/AT composites during thrice cyclic deformation.



**Figure 3.** Impact of AT concentration on stress relaxation of TPU/AT composites.

where  $\sigma_0$  is instantaneous stress of the initial holding period,  $\sigma_t$  is stress with time during the holding period. It can be seen that there are two phenomenon happening with increasing AT content, (1) the overall relative strain is higher (strain=300%) at any time during loading, and (2) the stress decreases gradually during the strain hold period and shows a wide relaxation time spectrum. However, the relaxation behavior is strongly dependent on AT content, decreasing with the increase of AT content, which means that there may be a larger viscous friction between AT and TPU matrix.

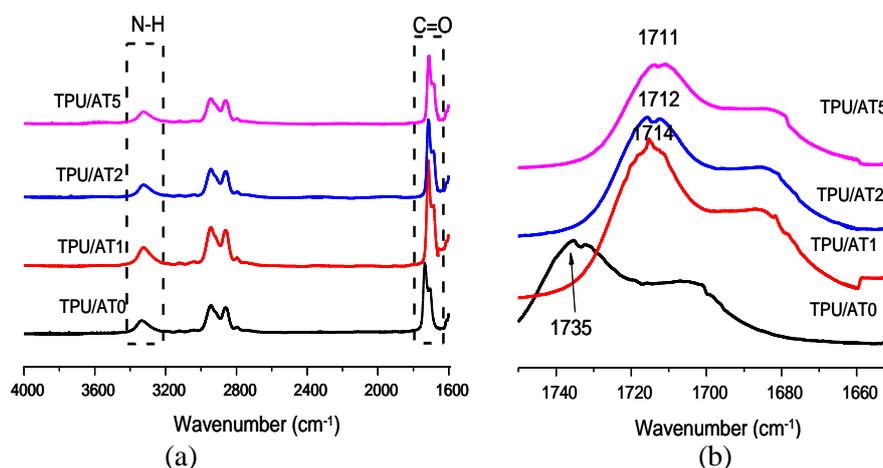


**Figure 4.** Impact of AT concentration on the storage modulus of TPU/AT composites.

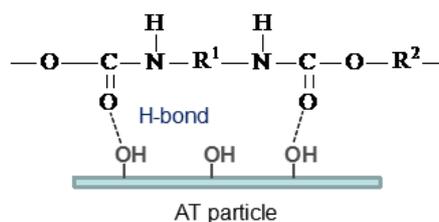
Figure 4 shows that the dynamic storage modulus ( $E'$ ) of TPU/AT composites has a significant temperature dependence. In the range of measuring temperature (30-90°C), the magnitude of  $E'$  increases consistently with the content of AT in the composites, which can reflect the physical interaction formed between AT and TPU matrix. However, the dynamic storage modulus is getting smaller and smaller as the temperature increases and becomes more sensitive to temperature with the increase of AT content. It is clear that the physical bond between AT and TPU can be destroyed at high temperature.

The FTIR spectra of the TPU/AT composites are displayed in figure 5(a). Distinct bands related to the amine ( $-NH$ ) and carboxyl ( $C=O$ ) groups were observed at  $3300\text{ cm}^{-1}$  and  $1725\text{ cm}^{-1}$ , respectively. Figure 5(b) exhibits the carboxyl spectra of the TPU/AT composites that are expanded from figure 5(a).

In this group curves, it is noticed that the carboxyl peaks move distinctly to lower wave number than that of the unfilled polymer, and it is a clear and convincing evidence of the H-bond forming between the –OH of AT particle and C=O of TPU matrix [12], and the corresponding schematic diagram of H-bond is shown in figure 6.



**Figure 5.** (a) Infrared spectrum of the TPU/AT composites; (b) C=O stretching region of the composites.



**Figure 6.** Hydrogen bond between TPU matrix and AT.

#### 4. Conclusions

The strength, modulus, and relaxation time of thermoplastic polyurethane elastomers filled with AT nano-fibrils are higher than those of unfilled elastomer. In addition, for both filled and unfilled elastic materials, pronounced inelastic mechanical behaviors are also observed during the loading-unloading cycles. These results strongly suggest that AT enhances the viscous friction of the inter-molecular force, because of physical cross-link forming between AT and the TPU matrix by the hydrogen bond.

#### Acknowledgments

This work was supported by the National Natural Foundation of China (51403099) and National Key R & D Program of China (SQ2017ZY060105, 2017YFD0200705).

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