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Stress-Strain Behavior of the Electrospun Thermoplastic Polyurethane Elastomer Fiber Mats

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Abstract: Thermoplastic polyurethane elastomer (TPUe) fiber mats were successfully fabricated by electrospinning method. The TPUe fiber mats were subjected to a series of cycling tensile tests to determine the mechanical behavior. The electrospun TPUe fiber mats showed non-linear elastic and inelastic characteristics which may be due to slippage of crossed fiber (non-bonded or physical bonded structure) and breakage of the electrospun fibers at junctions (point-bonded or chemical bonding structure). The scanning electron microscopy (SEM) images demonstrated that the point-bonded structures of fiber mats played an important role in the load-bearing component as determined in loading-unloading component tests, which can be considered to have a force of restitution.

Keywords : thermoplastic polyurethane elastomer (TPUe), electrospinning, mechanical behavior, morphology.

Introduction

Recently, thermoplastic polyurethane elastomers (TPUe) have gained a considerable significance, because they offer a combination of characteristics of rubber and plastic such as abrasion resistance, chemical resistance, clarity, and tensile strength, which are very essential for a good engineering thermoplastic material.[1]

Electospinning technique patented by Formhas in 1934,[2] has become more popular during the last decade because it can produce fibers with diameter in the range of nano-meter to sub-micron scale.[3-7] The electrospinning process involves the application of an electrical field between a capillary tip and a metallic collector by a high voltage power supply. This technique has the advantages of being simple, convenient and inexpensive in comparison with conventional methods such as wet, dry and melt spinning. Unfortunately, the practical applications have been limited because they have poor mechanical properties, low molecular orientation, and broad distribution of fiber diameter. Hence, an enhancement in both mechanical and physical properties of the electrospun fiber mats is very important from an industrial point of view. Earlier studies on the electrospinning process have been more focused on the basic principles[8-12] and processing parameters like the voltage applied, tip-to-collector distance, and viscosity of solution.[13,14] Recently, several authors investigated the mechanical properties of electrospun fiber mats.[15,16]

In general, the non-linear behavior of elastomeric materials is very complicated due to very high deformability, quasi-incompressibility, stress-softening effect (Mullins effect), and time-dependent viscoelastic effects.[17-19] There are many structural factors that affect the mechanical behavior of elastomeric materials. It has been known that a cyclic loading of elastomers produces a unrecoverable hysteresis energy loss depending on the molecular nature of the elastomer.

In this paper, the cyclic tensile test was carried out for the electrospun TPUe mats, which were composed of randomly-oriented sub-micron fibers where each fiber was restricted by physical netting and entanglements. The fiber morphology

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was monitored during the cycling test with a scanning electron microscope (SEM).

Experimental

Materials. Thermoplastic polyurethane elastomer (TPUe) (Pellethane 2363-80AE, Dow Chemicals Co., USA.) was used as received without further purification. TPUe was dissolved in a mixture of tetrahydrofuran (THF) and dimethylformamide (DMF) (60/40, v/v) at room temperature to a concentration of 8 wt%. After electrospinning, fiber mats produced were dried in a vacuum oven at room temperature for 3 days to remove any residual solvent.

Morphology. The morphology of electrospun TPUe fiber mats was observed by atomic force microscopy (AFM, XE-100, PSIA. Co., Korea) and scanning electron microscopy (SEM, GSM-5900, Jeol. Co., Japan).

Tensile Property. Tensile behavior of electrospun TPUe fiber mats were determined with a universal testing machine (UTM, AG-5000G, Shimadzu Corp., Japan) at a crosshead speed of 10 mm/min at room temperature. All samples were prepared in the form of standard dumbbell-shaped according to ASTM D-638 by die cutting the electrospun TPUe fiber mats. All the tests were conducted for five samples, and the averaged-valued were reported.

Electrospinning. A high voltage power supply (CPS-60 K02v1, ChungpaEMT Co., Republic of Korea), capable of generating voltages up to 60 kV, is used as a source of electric field. TPUe solution was supplied through a plastic syringe attached to a capillary tip of about 0.6 mm inner diameter using a micro-syringe pump. The copper wire connected to a positive electrode (anode) was inserted into the polymer solution and a negative electrode (cathode) was attached to a grounded rotating metallic collector. The distance between the capillary tip and the collector was fixed to be 12 cm, and the plastic syringe was placed at an angle of 10 ^{o} from the horizontal direction. When the applied voltage becomes larger than the surface tension of polymer solution, a charged jet is formed and ejected towards the metallic collector. The jet is triggered by the electrically driven bending instability, alternatively referred to as whipping instability and divided into multiple filaments by radial-charge repulsion, known as splaying. The solvent evaporates in the air and dried fibers are collected in the form of fiber mats. A schematic diagram of electrospinning setup is shown in Figure 1.

Results and Discussion

In general, electrospun fibers are deposited as a randomly-orientated fiber mats, forming a highly porous structure, which is held together by connecting sites such as crossing and bonding between the fibers. From the AFM image, it is clear that there exist many connecting sites between the fibers (Figure 2).

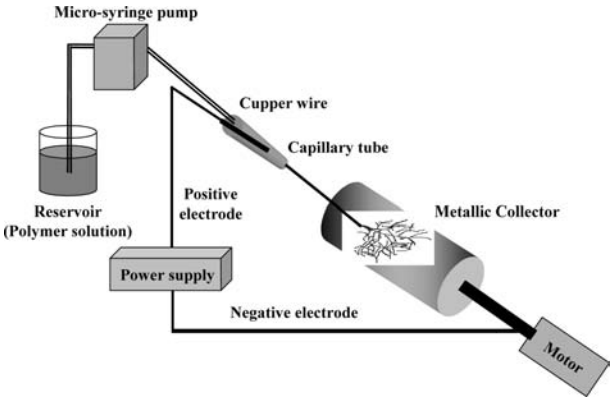

Figure 1. Scheme of the electrospinning process.

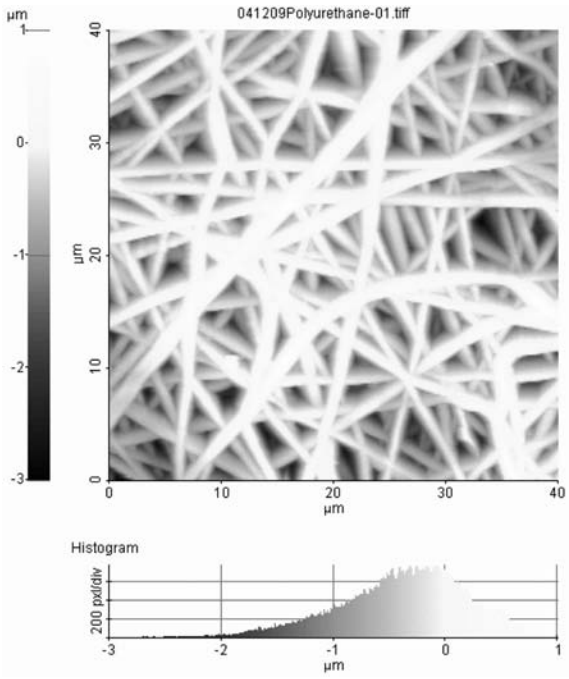

Figure 2. AMF image of electrospun TPUe fiber mats.

The mechanical behavior of electrospun fiber mats depends primarily on point-bonded structure (size and distribution) and geometrical arrangement of the fibers formed during the electrospinning process.[15] As can it seen in Figure 2, the fiber mats are made up of randomly-oriented TPUe fibers. Thus the point-bonded structure will more significantly affect the mechanical behavior.

The stress-strain curve of an electrospun TPUe fiber mat under static loading condition is shown in Figure 3. Almost linear elastic behavior was seen until the fiber mats undergo breaking.

For TPUe, both the point-bonding and non-bonding, but physically crossed structure occurred during electrospinning process as shown in Figure 4(a). When a small external load

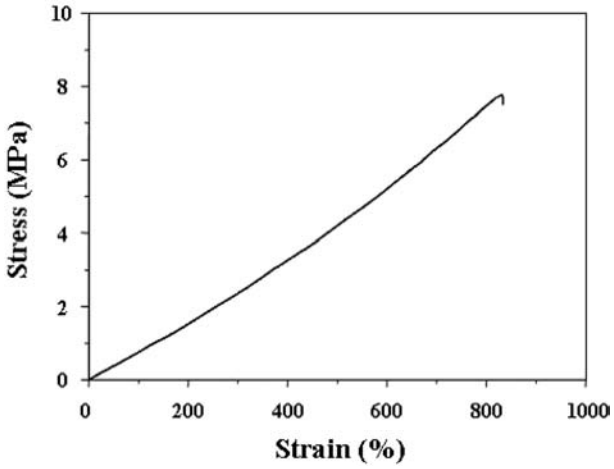

Figure 3. Stress-strain behavior of electrospun TPUe fiber mats.

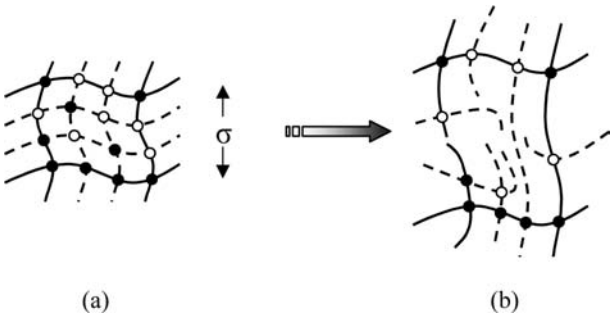

Figure 4. Schematic fiber structure of electrospun TPUe fiber mats; (a) before and (b) after external loading is applied. (σ: applied stress, ●: point-bonding structure, ○: non-bonding structure between fibers).

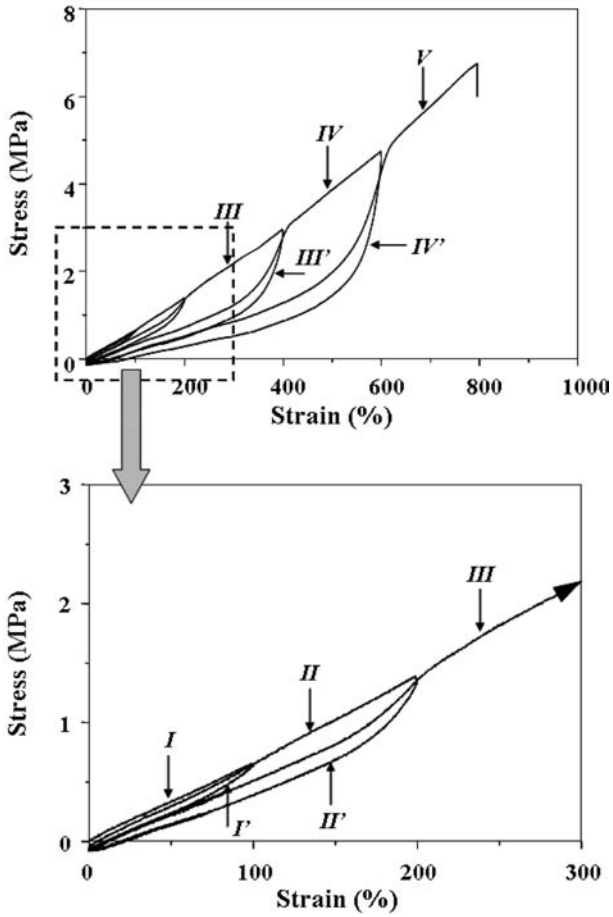

Figure 5. Stress-strain behavior of the electrospun TPUe fiber mats, which is similar to the Mullins effect in filled rubber vulcanizates; *I*: first loading, *I'*: first unloading, *II*: second loading, *II'*: second unloading, *III*: third loading, *III'*: third unoading, *IV*: fourth loading, *IV'*: fourth unloading, and *V*: fifth loading.

is applied, the relatively weak non-bonded structures tend to break or slip-apart, resulting in the elastomeric hysteresis and stress-softening behavior in cyclic loading experiments. Therefore, the non-bonding structures do not contribute effectively for carrying the load in comparison with the point-bonded structures (Figure 4(b)).

A cyclic loading-unloading elastomer results in a non-linear elastic and inelastic behavior. Electrospun TPUe fiber mats are expected to show such a behavior. The non-linear mechanical behavior of the electrospun TPUe fiber mats was analyzed during a series of cyclic tensile loading-unloading deformation, as shown in Figure 5.

As shown in Figure 5, a typical hysteresis loop was observed, where the loading stress was always higher than that of unloading one due to the energy dissipation. This phenomenon known as the Mullins effect observed for typical carbon black filled rubber vulcanizates.[20] At a given strain, electrospun TPUe fiber mats showed a permanent change due to increase in the hysteresis. At low strain, the non-bonding structures crossed among fibers easily slip-apart, leaving frictional energy dissipation, while the point-bonding structures withstand the applied load.

The slippage of the electrospun fibers seems to be a major cause of energy loss and stress-softening at relatively low strains. At higher strains, the breaking of electropsun fiber at point-bonding junctions, as well as the slippage crossed fibers occurred as a further source of the dissipation energy, as shown in Figure 6.

Toughness defined as the energy absorbed by the electrospun TPUe fiber mats until breaking, of the uniaxial loading test has higher value (40×10^{-3} Joule) than that of uniaxial loading cycles test until breaking (26×10^{-3} Joule). Hence, the electrospun TPUe fiber mats can be considered as a quasi-elastic material, because of its similar behavior of elastic materials.

As shown in Figure 7, the SEM images demonstrate that the point-bonding structure in the electrospun TPUe fiber mats plays an important role in load-bearing component. Initially random-oriented fiber morphology was observed

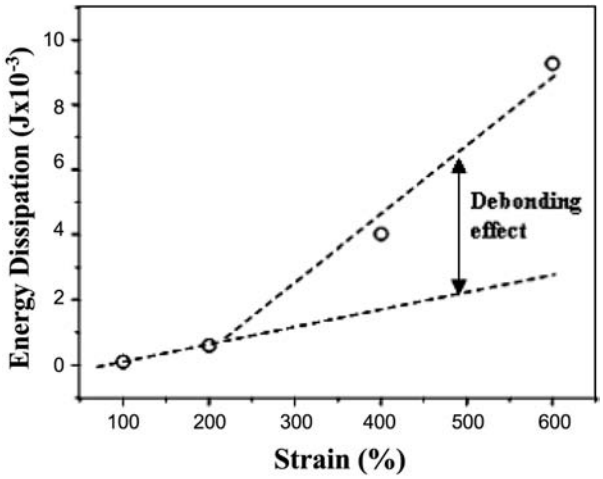

Figure 6. Energy dissipation of electrospun TPUe fiber mats under different strains.

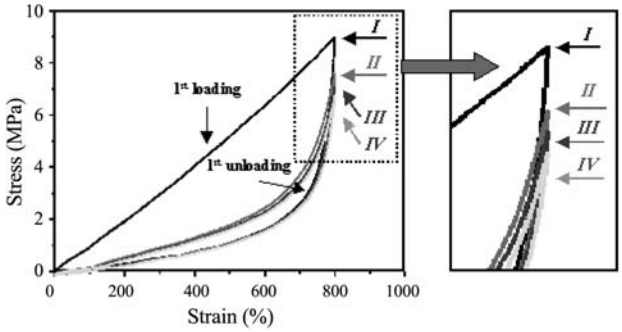

Figure 8. Stress-strain curves of electrospun TPUe fiber mats for various cycles under fixed strain of 800%.

(Figure 7(a)). Upon deforming the mats by 300%, most of the fibers were oriented to the direction of applied strain (Figure 7(b)), and then recovered almost to their original morphology (Figure 7(c)).

In the higher strain ranges, uniaxial strain experiments are carried out in various predetermined strain levels (100, 200, 400, 600, 800%), where four cyclic loading deformations were made for each strain level. Figure 8 shows a typical stress-strain behavior for 800% strain level. The linear elastic and inelastic behavior was found during the first loading-unloading cycle, giving a huge hysteresis loss. The curves of the successive cycles during both loading and unloading show nonlinear inelastic behaviors similar to that of the first unloading, giving a much less hysteresis loss. This is very similar phenomenon to that of the Mullins effect (the stress-softening) due to hysteresis or viscous effects.

Conclusions

In this paper, a systematic study on the mechanical behaviors of electrospun TPUe fiber mats was presented. The

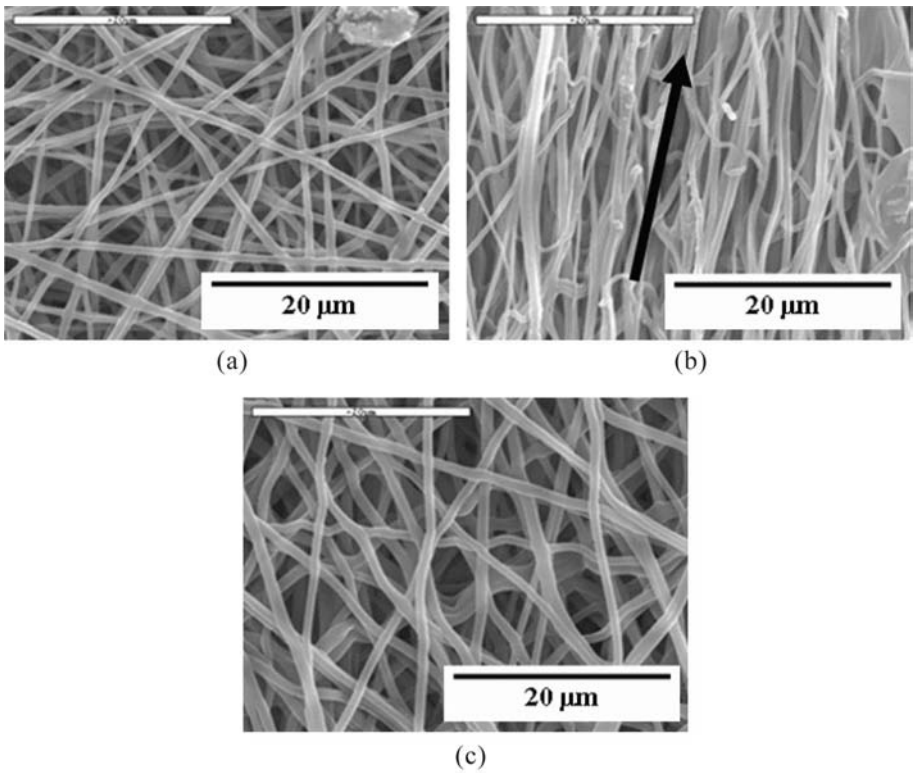

Figure 7. SEM images of electrospun TPUe fiber mats; (a) no strain, (b) 200% strain, and (c) un-loaded state.

uniaxial cyclic loading-unloading experiments of the fiber mats showed a non-linear elastic and inelastic response due to viscoelastic behavior with hysteresis. Energy dissipation value of the fiber mats calculated on the basis of stress-strain curves for each cycles showed the permanent deformation due to external load. The deformation is caused by the slippage of the crossed fiber and the breakage of electropsun fiber occurred at junctions. SEM images demonstrated that point-bonding structures could be considered to have a strong effect as the load-bearing components.

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