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# DYNAMIC MECHANICAL BEHAVIORS OF LASER SINTERED POLYURETHANE INCORPORATED WITH MWCNTS

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**ABSTRACT:** The multi-walled carbon nanotubes (MWCNTs) reinforced thermoplastic polyurethane (TPU) powders were firstly introduced into selective laser sintering system; and the systematic sintering parameters were investigated for the newly developed nanocomposite powders. The soft elastomeric behaviors of TPU composites are temperature and frequency dependent. Dynamic thermomechanical analysis was conducted to study the dynamic modulus and damping factors of laser sintered TPU nanocomposites. Laser sintered specimens exhibited the improved damping factor but the inferior storage modulus and loss modulus compared with the hot-compressed ones. The newly sintered MWCNTs/TPU composites maintain the intrinsic flexible and bendable properties of the neat TPU, and possess the improved damping resistance, which are significant factors to consider in the aerospace and automotive industries.

**KEYWORDS:** Selective laser sintering, thermoplastic polyurethane, 3D printing, additive manufacturing.

## INTRODUCTION

Energy dissipation (damping) in structures and materials is essential as it reduces resonant amplitudes and noise levels for the aerospace, automobile and civil engineering (Zhang & To (2014)). Whereas, additive manufacturing techniques are widely known as their advantages on the design and manufacturing freedom, enabling produce graded and structural damping parts such as cellular and honeycomb structures (Chua & Leong (2014)). While the design of high-performance vibration absorbing structural components requires materials having high viscosity and moderate to high stiffness. As usual, foam structural and rubble-like materials are favorable for damping purpose. The three-dimensional (3D) printed structural components have high potential in the field of energy dissipation, therefore, the investigation of printable rubbery materials with proper viscosity and stiffness are critical now (Zhang et al. (2015)).

Carbon nanotubes (CNTs) reinforced polymeric composites exhibit the improved static and dynamic mechanical properties due to the mechanical damping or internal friction in nanoscale or microscale (Bokobza (2007)). The complex modulus  $E^* = E' + iE''$ , with the real part  $E'$  (storage modulus) and imaginary part  $E''$  (loss modulus) being proportional to the storage energy and dissipated energy in the materials. Additionally, the ratio  $\tan \delta = E''/E'$  is known as the viscosity or damping factor,

indicating the energy dissipation capability of materials (Feng & Guo (2016)). CNTs reinforced rubbery polymers offer the opportunity to provide damping materials with high viscosity and enhance stiffness simultaneously.

Selective laser sintering (SLS) is an additive manufacturing process, which is used to produce polymer parts through a layer-by-layer method (Bai et al. (2015)). It provides the great design freedom and is well-suitable to obtain the three-dimensional (3D) complex geometry (Yeong et al. (2004)). In theory, hypothetically most polymeric materials is possibly proceeded by SLS, but semi-crystal thermoplastic is favorable to form condensed bulk products by sintering. In addition, the specific requirements of polymeric powders, such as shape, size, flowability and melt viscosity, are a complicated combination to qualify the SLS system (Bai et al. (2015)). Thus, few of thermoplastic elastomers is open to the SLS system now. Meanwhile, the carbon nanotube reinforced polymeric composite powders are also newly introduced to SLS system in recent years (Bai et al. (2014)). To validate the feasibility and to develop the systematic set of sintering parameters of TPU and its composite powders still remain difficulties to overcome.

In this study, thermoplastic polyurethane (TPU) and its carbon nanotube reinforced (TPUC) powders were successfully sintered by the commercialized SLS system. The temperature and frequency dependent dynamic mechanical properties (such as storage modulus, loss modulus and  $\tan \delta$ ) were investigated to evaluate the damping performance of TPU and TPUC specimens, which were produced by laser sintering and hot-compression. Hot-compressed TPUC parts exhibited improved stiffness and loss modulus, while laser-sintered parts were with high damping factor compared with hot-compressed ones.

## **EXPERIMENTATION**

### **Composite powder preparations**

The suspension of MWCNTs (3 wt%, with the purity greater than 95% from Nanostructured & Amorphous Materials Incorporation) was diluted, and MWCNTs were dispersed into an aqueous solution with the probe sonication (BRANSON Model 102C) at 70 W. Thermoplastic polyurethane (TPU) powders (DESMOSINT X92) used for laser sintering were purchased from BASF Germany. Density of this TPU is 1.2 g/cm<sup>3</sup>, and the density of powders is 0.58 g/cm<sup>3</sup>. Melt volume-flow rate at 190 °C is 18 cm<sup>3</sup>/10 min, and the fully melting temperature is around 160 °C. The carbon nanotubes reinforced TPU (TPUC) powders are produced through a novel solution-based process, which could coat CNTs onto the surface of polymeric powders with the loading of 1 wt%. (Cai et al. (2009))

### **Selective laser sintering**

SLS technique as a free-form fabrication process was introduced to construct the designed three-dimensional structures. In order to investigate the feasibility of TPU and its composite in laser sintering and study the dynamic mechanical properties of sintered parts, the testing specimens were produced by SLS on EOS P395 system (EOS GmbH Munch, Germany). The process parameters used for part production are as shown in Table 1.

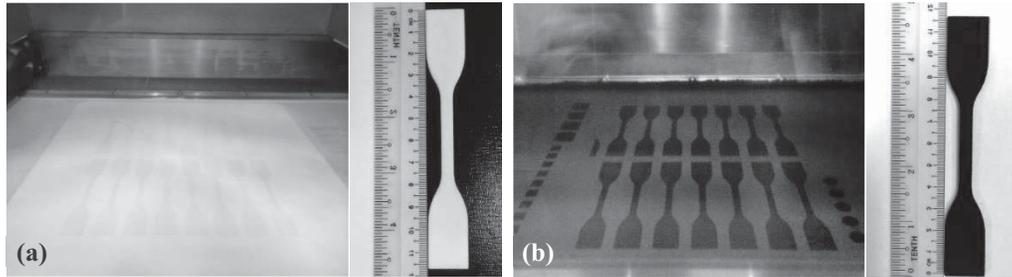


Figure 1. (a) TPU powder bed and (b) TPUC powder bed of laser sintering platform and specimens.

Table 1. Optimized laser sintering parameters

Process parameter	TPU	TPUC	Unit
Laser power ( $p$ )	10	10	W
Scanning speed ( $v$ )	3000	3000	mm/s
Hatching spacing ( $s$ )	0.1	0.1	mm
Bed temperature ( $T_b$ )	96	108	°C
Chamber temperature ( $T_c$ )	60	88	°C
Layer thickness ( $h$ )	120	120	$\mu\text{m}$

### Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) (TA Instruments Q800 dynamic analyzer) was used to study the frequency and temperature dependent mechanical properties involving storage modulus, loss modulus and  $\tan \delta$ . The isothermal temp/freq sweep and temp ramp/freq sweep modes of DMA were selected to test the dog bone specimens. The rectangular cross sections of dog bones are used for these specimens in order to be in compliance with the ASTM standards for dynamic testing of plastics (i.e. ASTM D4065 and ASTM D5026). Through the isothermal temp/freq sweep, dog bone (ASTM D63 Type IV, scaled down by a factor of 4) was stretched at the room temperature with amplitude of  $15 \mu\text{m}$ , vibrating frequency ranging from 0.1 to 100 Hz. Through the temp ramp/freq sweep, dog bone was cyclically stretched with the amplitude of  $15 \mu\text{m}$ , fixed frequency of 1 Hz and heated from  $25 \text{ }^\circ\text{C}$  to  $100 \text{ }^\circ\text{C}$  with the ramp rate of  $5 \text{ }^\circ\text{C}/\text{min}$ . All specimens were manufactured with their thickness direction normal to each printing layer (X-Y plan) and longitudinal axis along the Y direction.

### RESULTS AND DISCUSSION

The dynamic mechanical properties ( $E'$ ,  $E''$  and  $\tan \delta$ ) of TPU and TPUC specimens manufactured by laser sintering and hot-compression were investigated by using a dynamic mechanical analyser. The storage modulus ( $E'$ ) is an elastic part and related to the material stiffness and the stored energy; the loss modulus ( $E''$ ) is the viscous part, and associated with the sample ability to dissipate

mechanical energy by the cycle of motion. The dynamic (complex) modulus ( $E^*$ = stress/strain) is given as:

$$E^* = E' + iE''$$

Where  $E' = \sigma_0 \cos(\delta) / \epsilon_0$  and  $E'' = \sigma_0 \sin(\delta) / \epsilon_0$ , with  $\sigma_0$  and  $\epsilon_0$  being the stress and strain amplitudes respectively and  $\delta$  being the angular shift between the stress and the corresponding strain. The  $\tan \delta$  (the damping factor) which is defined as the ratio of storage modulus to loss modulus per cycle of the applied force, and given as

$$\tan \delta = E'' / E' \quad (2)$$

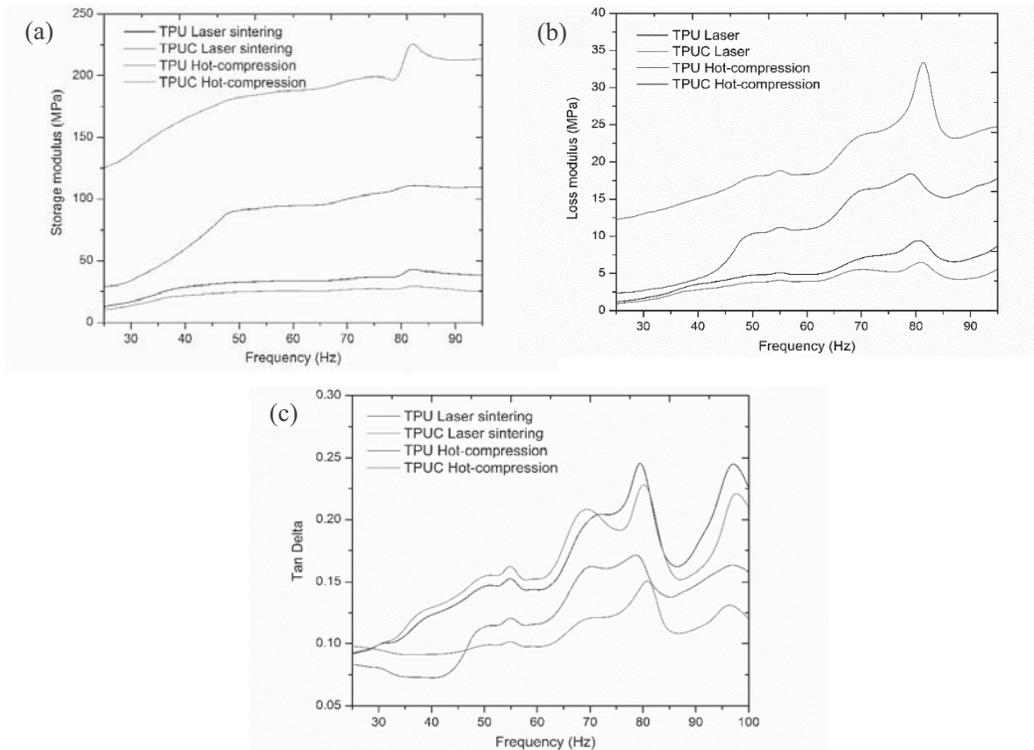


Figure 2. (a) The frequency dependent storage modulus, (b) loss modulus and (c)  $\tan \delta$  damping factor) of the TPU and TPUC specimens produced by laser sintering and hot-compression at the room temperature.

Figure 2 (a) shows that the curves of storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of TPU and its nanocomposites increased as the frequency increased from 0.1 to 100 Hz. Whereas, the hot-compressed specimens exhibit relative high storage modulus, compared with the laser-sintered ones. Additionally, the sharp peaks indicate that TPUC composites by hot-compression have higher stiffness and enable to store and dissipate more energy than the original TPU elastomer. The intrinsic frequencies of TPU elastomer are around 78 Hz and that of TPUC slightly shifts to 81~83 Hz due to loading of CNTs. The diagram of the viscoelastic damping factor ( $\tan \delta$ ) (Figure 2c) illustrated that the laser-sintered specimens possess the higher energy dissipation capability than the hot-

compressed specimens due to the presence of enhanced damping factor in laser-sintered specimens. Meanwhile, the damping peak height is related to the internal energy dissipation of the fiber/matrix interfaces. The decrease in the value of  $\tan \delta$  at its maximum peak represents the elastic character of the film due to the strong adhesion at filler/matrix interfaces. Therefore, the higher viscoelastic behaviours over the range of frequency are obtained in laser-sintered specimens probably owing to the strong friction at interfaces.

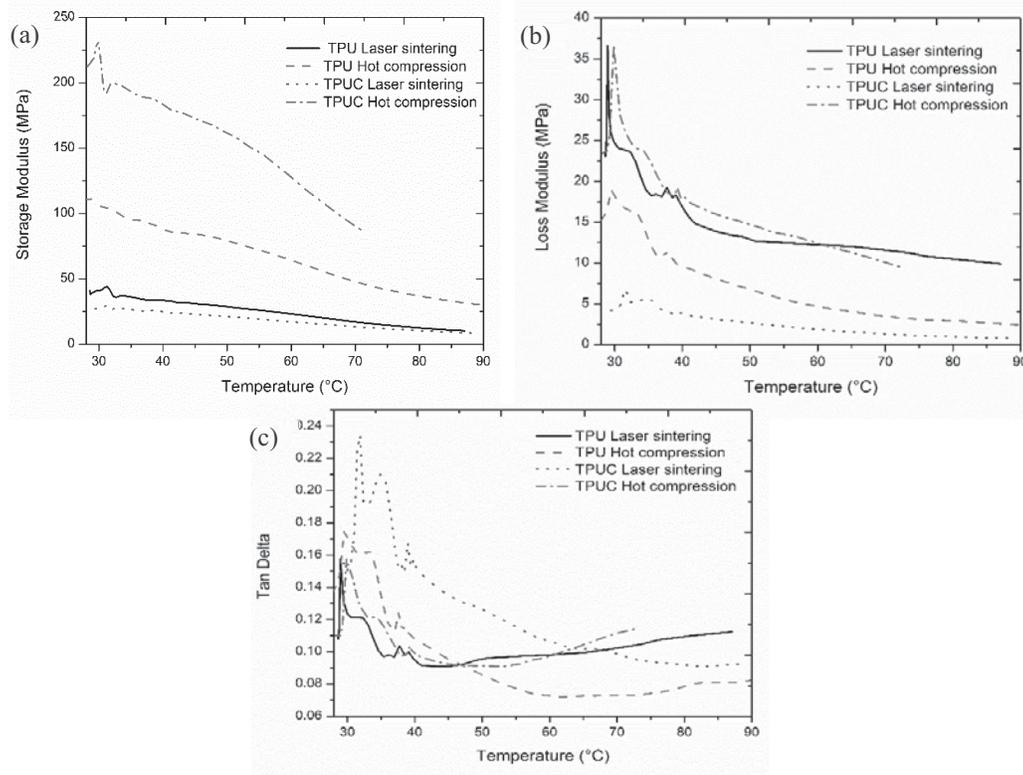


Figure 3. (a) The temperature dependent storage modulus, (b) loss modulus and (c) tan delta (damping factor) of the TPU and TPUC specimens produced by laser sintering and hot-compression. (Frequency at 1 Hz)

The temperature dependent storage modulus ( $E'$ ), loss modulus ( $E''$ ) and  $\tan \delta$  of TPU and its composites are investigated by DMA (Figure 3). The storage modulus and loss modulus dropped as the temperature increased. Sharp peaks of loss modulus (Figure 3b) and  $\tan \delta$  (Figure 3c) are present in the temperature range from 25 °C and 40 °C, these peaks indicated the phase transfer of polymer, which is in the glass transition range of TPU and TPUC. Within the temperature range, the damping peaks imply that the TPU and TPUC are with high viscosity and enhanced energy dissipation compared the rest range of temperatures. Laser-sintered TPUC exhibits the lowest storage modulus and loss modulus among these samples, but it has highest value of damping factor. This is because the nanofillers weakly interact with the matrix materials but the porous structure of laser-sintered TPUC still dissipate energy due to the structural energy adsorption. Hot-compressed TPUC possesses the highest storage modulus and loss modulus but the lowest damping factor because the

nanofillers strongly interact with the matrix materials and thus dissipate energy through momentum transfer and friction.

## CONCLUSION

Selective laser sintering process was successfully applied to fabricate TPU and its CNTs reinforced composite parts, which exhibited relatively high damping factor over the wide range of frequency and temperature compared with the hot-compressed parts. The TPU and TPUC parts in the glass transition range were with high viscosity and energy dissipation capability due to polymer phase transition. The lower storage modulus and loss modulus but higher  $\tan \delta$  of laser sintered specimens are owing to the porous foam structure in microscale. The highest stiffness and loss modulus could be observed in hot-compressed TUPC because of the strong interactions of CNTs with matrix to dissipate energy and friction at interfaces.

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