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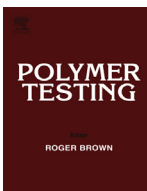
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## Material properties

## Influence of carbon nanotubes on the rheology and dynamic mechanical properties of polyamide-12 for laser sintering



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## ABSTRACT

The rheological behaviour of polymer nanocomposites is very important for polymer processing and understanding the structure-properties relationship. In this paper, the rheological properties of a polyamide 12 (PA12) - carbon nanotube (CNT) nanocomposite for laser sintering were studied. Compared to neat PA12, the presence of CNTs resulted in higher storage modulus ( $G'$ ), loss modulus ( $G''$ ) and viscosity ( $\eta$ ). With an increase in temperature, viscosity showed an unusual increase for both PA12 and the PA12-CNT nanocomposites, which is likely to result from incomplete melting of powder particles. Dynamic mechanical analysis was carried out to examine the effect the CNTs were having on the laser sintered parts. The laser sintered PA12-CNT nanocomposite had an increased elastic modulus compared to that of neat PA12. The CNT and polymer matrix interaction hindered the chain motions, which resulted in higher loss modulus and decreased the thermal expansion coefficient.

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## 1. Introduction

Additive Manufacturing (AM) is a group of technologies which are applied to produce end-use products directly from 3D model data. Due to the greater flexibility with respect to product design and manufacture compared to conventional manufacturing methods, AM has been attracting more and more attention from both academic and industrial communities in recent years. One of the most well-established additive manufacturing technologies, laser sintering (LS), is a powder-based process which uses a laser as a heat source to fuse polymer powder into three dimensional parts [1].

Several polymers, such as polyamide (PA), polypropylene (PP), polystyrene (PS), polycarbonate (PC) and poly(ether-

ether-ketone) (PEEK) have been supplied as laser sintering materials [2], with PA being the most common polymeric material used, mainly due to its ease of processing [3]. However, current laser sintering materials cannot completely meet the needs of all products [4]. To meet the requirements for different applications, polymer/filler composites have been investigated to enhance the properties of laser sintered parts. With a small quantity of nano-filler, polymer nanocomposites have shown a significant improvement over the base polymer's mechanical, thermal and electrical properties [5]. Various reinforcing nanofillers combined with base polymers have been investigated for laser sintering [6–8]. In the work carried out by Goodridge et al. [6], a 3 wt% PA12/carbon nanofibre composite was prepared by melt mixing and cryogenic milling. The dynamic mechanical properties of the nanocomposite were 22% higher than those of the base PA12 laser sintered parts. However, irregular powder morphology weakened the

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reinforcement effect from the nanofillers. In the research performed by Athreya et al. [7], PA12/carbon black (4 wt%) nanocomposite powder was prepared and laser sintered. The PA12/carbon black parts showed improved electrical conductivity but decreased flexural modulus compared to neat PA12 parts. The reduction in flexural modulus was due to agglomeration of the carbon black particles in the laser-sintered part. Another study showed that CNT agglomerates caused a reduction in elongation at break for PA12-CNT laser sintered parts [8]. It is, therefore, essential for laser sintering of polymer nanocomposites that both the morphology of the powder particles and the dispersion of the nanoparticles within the polymer matrix are optimised.

To address this, in our previous work [9], individual PA12 powder particles were coated with carbon nanotubes (CNTs) in order to produce well-dispersed PA12-CNT nanocomposite powder with spherical morphology and suitable particle size for processing by laser sintering. Results showed that the PA12-CNT laser sintered parts had enhanced flexural properties (13.0% higher) and impact properties (123.9% higher). This was achieved without sacrificing elongation at break, which was in contrast to previous studies in the literature which showed some decrease in strength or decrease in elongation at break [7,8].

One of the aims of the study reported in this paper was to study the rheological behaviour of the nanocomposites produced by our coating method; rheology is a very important factor in polymer processing which has rarely been investigated for laser sintering nanocomposites.

In the laser sintering process, polymers melt and flow. Understanding the motion of the polymer composites liquid is very important for analysis of the processing operation and optimisation, as well as investigating the structure-property relationship of the nanocomposites. From studies carried out on conventional polymer nanocomposites, rheological properties have been shown to influence the fabrication and processing (residual stress, void content, etc.) of such materials [10,11]. Jin and co-workers [12] found that the amount of nanoclay loading had a significant influence on the rheology of a polyol/nanoclay mixture when processing polyurethane (PU) nanocomposites. It was found that to achieve good dispersion of the nanoclay with critical viscosity, 3 wt% was the optimum nanoclay loading. This finding provided useful information for the preparation of PU/nanoclay composites in their study, which could also be a helpful guideline for polymer nanocomposite preparation for laser sintering. Several studies have shown that the composite phase morphology and the interfacial interactions between polymer chains and nanofiller also have a direct correlation with the rheological properties of nanocomposites [13–15]. Lim and Park [14] reported these effects on the rheological behaviour of different polymer/nanoclay composites by oscillatory frequency and shearing rheological tests. The results indicated the existence of strong interactions between polymer matrix and nanoclay, and the formation of some particle network structure and randomly oriented silicate layers. These rheological studies with conventional polymer nanocomposites could also be carried out on polymer nanocomposites for laser sintering to offer a

fundamental understanding of the processability of these materials, as well as the structure-properties relationship in the nanocomposites.

In this work, a comprehensive rheological investigation of a polymer nanocomposite for laser sintering was carried out to examine the influence of the nanofiller on the rheology properties of the polymer matrix. Due to their excellent mechanical, thermal and electrical properties, carbon nanotubes are considered to be ideal reinforcing nanofillers for polymers [16] and were, therefore, chosen as the nanofiller. PA12 was chosen as the polymer matrix in this study due to its established use for laser sintering. In addition to rheological experiments, to examine the changes in mechanical properties of laser sintered parts within a temperature range, dynamic mechanical analysis was applied. The effect of the CNTs on the modulus and damping of the laser sintered PA12 samples was analysed.

## 2. Experimental

### 2.1. Materials

The polyamide 12 (PA12) powder used in this study was obtained from EOS GmbH (trade name 'PA2200'), and is a commonly used laser sintering polyamide material. Multi-walled carbon nanotubes, supplied by NanoAmor Materials Inc., had an average diameter of 10 nm and length of 1.5  $\mu\text{m}$  (according to the manufacturer's datasheet). PA12-CNT nanocomposites were prepared by coating the CNTs on the surface of the PA12 particles using a patented method [17]. With this method, the final PA12-CNT nanocomposites powders have been shown to exhibit near-spherical morphology [9]. The nanocomposites were produced with two different CNT contents, 0.1 wt% (referred to herewith as PA12-CNT0.1) and 0.2 wt% (referred to herewith as PA12-CNT0.2).

### 2.2. Melt rheology

Dynamic oscillatory shear tests were conducted on a RADII instrument (Rheometrics®, Inc) to measure the melt rheology. Tests were performed using parallel plate geometry with plate diameter of 25 mm. Neat PA12 (referred to herewith as PA12), PA12-CNT0.1 and PA12-CNT0.2 powders, which were dried in a vacuum oven at 80 °C for 12 hours, were formed into sheets by hot pressing at 210 °C. Sample discs with a diameter of 25 mm and thickness of 1 mm were prepared.

In a dynamic oscillatory shear test, a time dependent strain is applied during the test, and the resulting shear stress is:

$$\sigma(t) = \gamma_0 [G' \sin(\omega t) + G'' \cos(\omega t)]$$

where  $\gamma_0$  is the strain amplitude,  $\omega$  is the test frequency,  $t$  is the time,  $G'$  is the in-phase, elastic or storage modulus and  $G''$  is the out-of-phase, viscous, or loss modulus, which is a measure of the energy dissipated per cycle. To maintain a linear response, a strain amplitude of 10% was used to obtain reasonable signal intensities at elevated temperature or low frequency. The testing temperature range was

220 °C–260 °C. The master curves were obtained at a reference temperature of 230 °C by using a time-temperature superposition principle.

### 2.3. Dynamic mechanical analysis

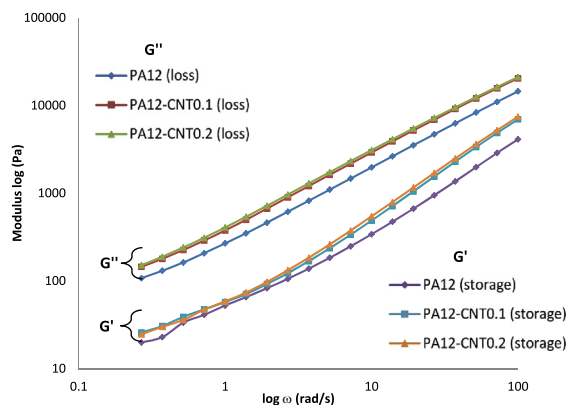
Dynamic mechanical analysis (DMA) applies a small oscillatory stress at a set frequency to the sample and examines changes in modulus and damping. In this study, the DMA tests were performed on a RDAII instrument (Rheometrics®, Inc) through a temperature range of –150 °C to 180 °C with a heating rate of 2 °C/min. The frequency (angular), strain amplitude and auto-tension sensitivity were constant at 6.2832 rad/s, 0.05% and 1.0 gm, respectively. All tests were carried out in a nitrogen atmosphere. DMA samples (35 mm × 12 mm × 1 mm) of PA12 and PA12-CNT were prepared by laser sintering on an EOS P100 laser sintering machine. The processing parameters were optimised for each material [9].

## 3. Results and discussion

### 3.1. Melt rheology properties

A parallel disc oscillatory shear test is a small amplitude deformation test, which does not change the material structure during the test. This is a major advantage for a small deformation test, especially for multiphase composites systems [18]. In this work, the parallel disc shear rheology tests were performed as a function of frequency and a function of temperature.

Fig. 1 shows the storage modulus  $G'$  and loss modulus  $G''$  of PA12 and PA12-CNT nanocomposites with various CNT loadings as a function of frequency at 230 °C. At 230 °C, the samples were in the molten state, and acted as viscous liquids, which can explain the  $G' < G''$  for both PA12 and PA12-CNT nanocomposites. Compared to the PA12 samples, PA12-CNT showed an increase in  $G'$  and  $G''$ . With the increase in CNT loading,  $G'$  and  $G''$  were also increased slightly; however this was minimal and not to the extent of the increase of the PA12-CNT0.1 to PA12. It was observed that, even although the CNT loadings were very low (0.1



**Fig. 1.** Storage modulus  $G'$ , and loss modulus  $G''$  as a function of frequency of PA12-CNT nanocomposites at reference temperature 230 °C.

**Table 1**

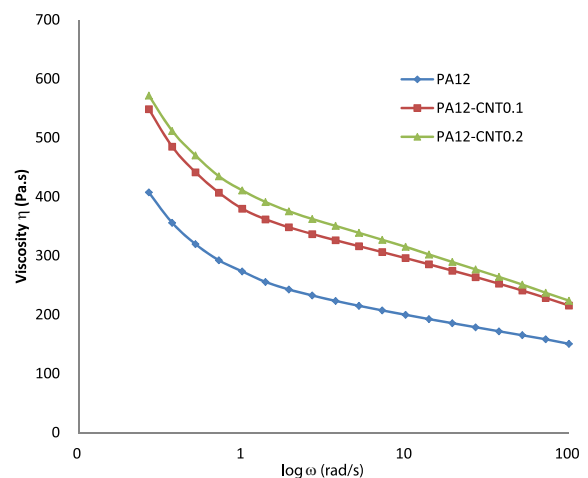
Power relations of  $G'$  and  $G''$  at low frequency region for PA12 and PA12-CNT nanocomposites.

	$G' \sim \omega$	$G'' \sim \omega$
PA12	$G' \sim \omega^{1.28}$	$G'' \sim \omega^{0.73}$
PA12-CNT0.1	$G' \sim \omega^{0.72}$	$G'' \sim \omega^{0.65}$
PA12-CNT0.2	$G' \sim \omega^{0.65}$	$G'' \sim \omega^{0.64}$

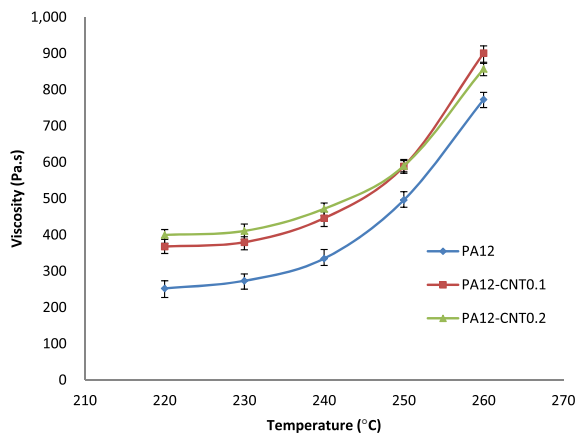
and 0.2 wt%), the effect on the matrix rheology was still noticeable. An increased  $G'$  meant a more elastic structure, which indicated the restriction of polymer chain motion due to the CNT nanofillers.

It is known that for linear mono-dispersed polymer melts, where polymer chains are fully relaxed, there is an approximate relation of  $G' \sim \omega^2$  and  $G'' \sim \omega$  [19]. When the frequency is low, there is enough time for the molecular relaxation process, which makes the measurement of  $G'$  and  $G''$  more sensitive. Table 1 shows the power relations of  $G'$  and  $G''$  in the low frequency region for PA12 and PA12-CNT nanocomposites. The slopes of  $G'$  and  $G''$  for PA12 were smaller than 2 and 1 respectively, which might be affected by the polydispersity of the polymer chain lengths [20]. Compared to PA12, the slopes of  $G'$  and  $G''$  for the PA12-CNT nanocomposite were lower, which could be explained by polymer-nanotube and nanotube-nanotube interaction in the matrix leading to a modified matrix microstructure [21,22].

The viscosity  $\eta$  for PA12 and PA12-CNT nanocomposites as a function of frequency at 230 °C is shown in Fig. 2. It can be seen that, with the increase in frequency, the viscosity for all samples decreased, which is called shear thinning. This can be explained as the greater the shear rate, the more quickly two molecules move relative to each other, which leads to reduced chain entanglement density. As a result, fewer polymer chains remain in the entanglement state for a sufficiently long time, which causes the drop in viscosity [18]. For the PA12-CNT nanocomposite, the shear thinning effect was as obvious as PA12, which indicated



**Fig. 2.** Viscosity  $\eta$  as a function of frequency of PA12-CNT nanocomposites at reference temperature 230 °C.

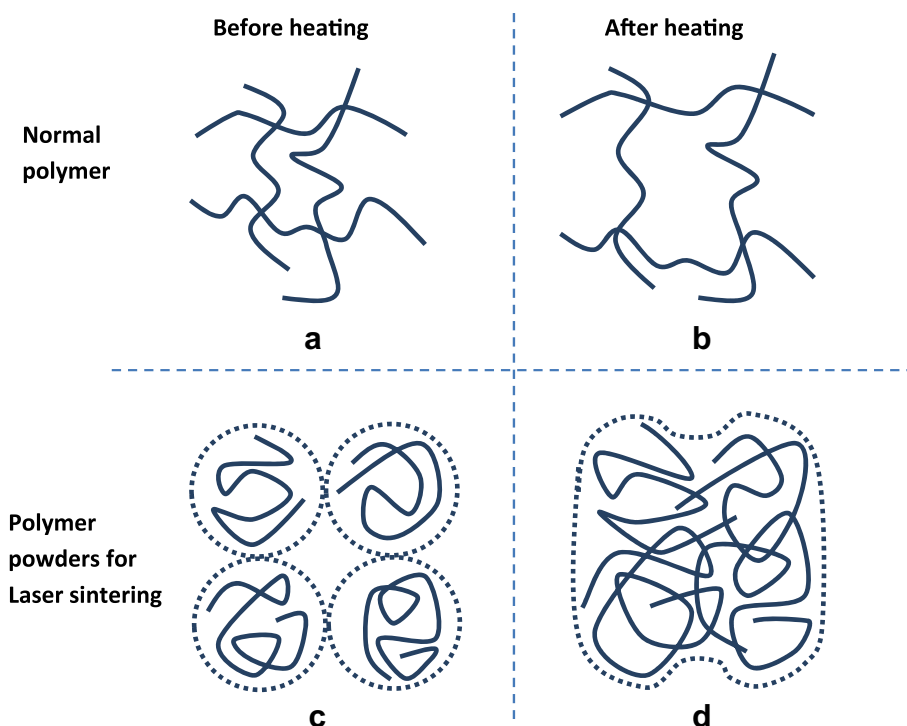


**Fig. 3.** Viscosity of PA12 and PA12-CNT nanocomposites at different temperatures with frequency  $\omega = 1$  rad/s.

good dispersion of the CNTs, as dispersed CNTs aligned with the flow direction and caused the viscosity to decrease. The shear thinning effect will become weak if CNT agglomerates exist [5]. Compared to PA12, the viscosity of PA12-CNT nanocomposites was raised significantly, and this effect was enlarged with an increase in CNT loading. Increased viscosity for PA12-CNT is a common phenomenon for filler reinforced polymers, which can be explained by the interaction between the CNTs and PA12 hindering the movement of the PA12 chains.

The variation in viscosity at different temperatures at  $\omega = 1$  rad/s for PA12 and PA12-CNT nanocomposites is plotted in Fig. 3. The viscosity of PA12-CNT remained higher than that of PA12 at all temperatures. The most notable result in Fig. 3 is the viscosity increase with the increase in temperature for both PA12 and PA12-CNT nanocomposites. This was a converse result compared to common polymers and polymer nanocomposites [5,13,18].

For conventional polymers, polymer molecular chains are dispersed and entangled homogeneously, where free volumes exist between these chains. When the temperature is raised, the free volumes expand and the space between polymer chains increase, as shown in Fig. 4(a) and (b). This thermal expansion strengthens the polymer chains flow, which results in the decrease in viscosity. For the PA12 and PA12-CNT composites specimens in this study, which were made from powders, there may be voids and unmelted PA12 particles left inside the specimens. Polymer chains did not disperse and entangle well between those unmelted particles, as shown as Fig. 4(c). When the temperature was increased, the unmelted particles were fused further, which led to the decrease in the number and size of voids and more entanglement of the polymer chains between particles. Even the free volumes inside of the particles expanded; the major influence on the viscosity might count as void decrease and entanglement increase between particles, which caused the increase in viscosity as the temperature increased. As voids and unmelted particles were reported for laser sintered parts in the literature [23], a similar viscosity phenomenon could occur.



**Fig. 4.** Schematic explanation of: (a) normal polymer structure before heating, (b) normal polymer structure after heating, (c) polymer powders for laser sintering before heating, (d) polymer powders for laser sintering after heating.

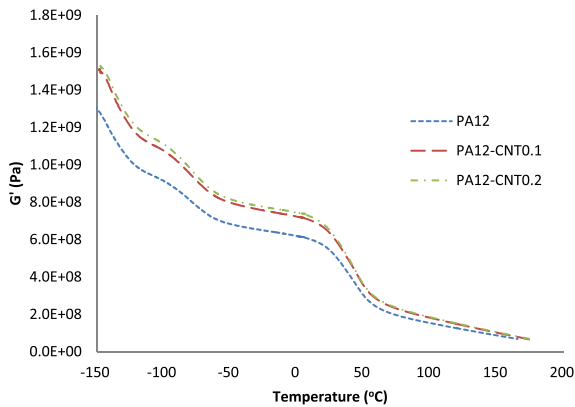


Fig. 5. Elastic modulus vs. temperature for PA12 and PA12-CNT nanocomposites laser sintered parts.

### 3.2. Dynamic mechanical analysis

Dynamic mechanical analysis was carried out to determine the elastic modulus ( $G'$ ), loss modulus ( $G''$ ) and thermal expansion coefficient ( $\alpha$ ) of the laser sintered parts as a function of temperature. Fig. 5 records the temperature dependence of  $G'$  for the PA12 and PA12-CNT laser sintered parts. Compared to PA12, both PA12-CNT0.1 and PA12-CNT0.2 showed improved elastic modulus over the experiment temperature range. The enhancement effect was significant below the glass transition temperature ( $T_g$ ), where average reinforcement of 16.9% (PA12-CNT0.1) and 20.0% (PA12-CNT0.2) was achieved. With the rise in temperature above  $T_g$ , the reinforcement effect declined and the modulus of the PA12-CNT approached that of PA12. This suggested that at elevated temperature the modulus of the PA12-CNT composites was mainly decided by the PA12 matrix, which also has been reported for other polymer composites [5,24,25].

Fig. 6 plots the loss modulus  $G''$  of the PA12 and PA12-CNT laser sintered parts as a function of temperature, in which three peaks can be clearly seen. The first peak at a temperature of about  $-140$  °C is termed ' $\gamma$  relaxation',

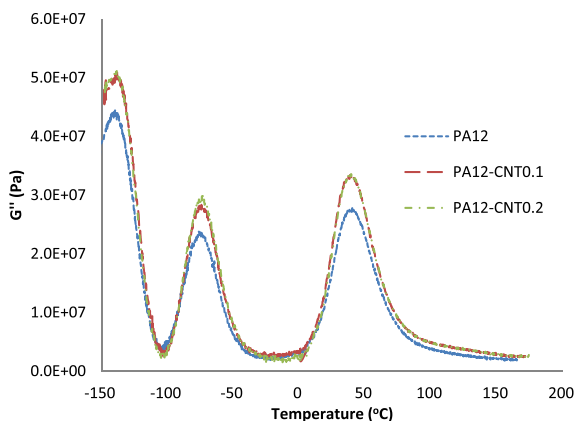


Fig. 6. Loss modulus vs. temperature for PA12 and PA12-CNT nanocomposites laser sintered parts.

which is from the movement of a few methylene groups between amide groups in the amorphous regions. The second peak temperature (around  $-80$  °C), which is defined as ' $\beta$  relaxation', is caused by the segmental motions of the weak bonded amide groups and methylene groups [26]. As the temperature increased, the polymer chains in the amorphous regions started to move, which is defined as  $T_g$ , the third peak (around  $40$  °C). PA12-CNT composite samples showed higher  $G''$  compared to PA12, especially at the peak temperatures.  $G''$  is the dissipated energy within the materials every cycle during the test. Higher  $G''$  could be due to the interaction between the CNT and polymer matrix, which hindered the motion of functional groups and chains. This phenomenon was also observed in other polymer nanocomposite studies [11,24]. From  $G'$  and  $G''$ , the  $\tan\delta$  (ratio of  $G''/G'$ ) was calculated and shown in Fig. 7.  $\tan\delta$  is used to evaluate the energy loss of materials from segment rearrangements and internal friction during the test. There was a notable increase in  $\tan\delta$  for PA12-CNT at temperature between  $90$  °C and  $160$  °C, which was due to the damping effect of the CNT fillers, as the CNTs restricted the molecular motion and increased the internal friction.

Thermal expansion coefficient ( $\alpha$ ) is used to describe how the volume of a sample changes as the function of temperature, which is calculated as:

$$\alpha = \Delta L / (\Delta T \cdot L_0)$$

where  $\Delta L$  is the length change of the sample,  $\Delta T$  is the change in temperature and  $L_0$  is the original sample length [27]. The average value of thermal expansion coefficient ( $\alpha$ ) from  $-150$  °C to  $20$  °C for PA12 and PA12-CNT samples is shown in Table 2. For PA12-CNT0.1 and PA12-CNT0.2, the  $\alpha$  values were reduced compared to PA12. This decrease could be explained by the mechanical constraint of the CNT in the polymer matrix.

### 4. Conclusions

In this study, the influence of CNTs on the melt rheology and dynamic mechanical properties of PA12 for laser

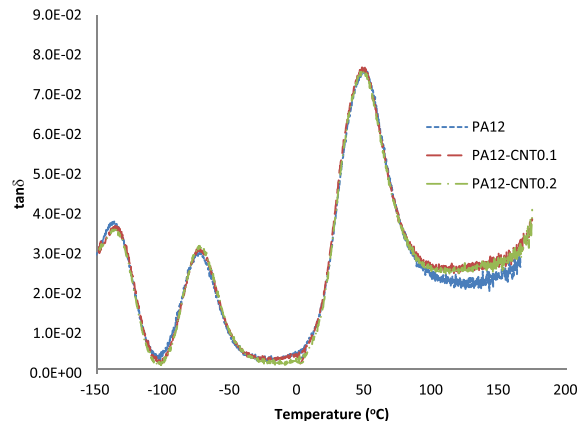


Fig. 7.  $\tan\delta$  vs. temperature for PA12 and PA12-CNT nanocomposites laser sintered parts.



**Table 2**

Thermal expansion coefficient of PA12 and PA12-CNT nanocomposite laser sintered parts.

Sample	PA12	PA12-CNT0.1	PA12-CNT0.2
$\alpha$ (°C)	$1.61 \times 10^{-4}$	$1.39 \times 10^{-4}$	$1.34 \times 10^{-4}$

sintering has been investigated. Parallel oscillatory test results demonstrated that CNTs have a substantial effect on the melt rheological properties of the PA12-CNT nanocomposites, as the storage modulus  $G'$ , loss modulus  $G''$  and viscosity  $\eta$  of the PA12-CNT nanocomposites increased compared to PA12. A strong shear thinning effect is observed for PA12-CNT nanocomposites, which may suggest good dispersion of CNT. A notable observation is the viscosity increase with the increase of temperature for both PA12 and its composites, which is a converse result compared to common polymeric materials. This result might be attributed to insufficient melting of the PA12 and PA12-CNT powder particles. Dynamic mechanical analysis shows that the incorporation of CNTs provides a considerable improvement in the elastic modulus for laser sintered parts. Higher loss modulus for PA12-CNT nanocomposite is due to the interaction between CNT and polymer matrix, which causes restricted segmental motions, and this also leads to a decrease in the thermal expansion coefficient.

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### References

- [1] N. Hopkinson, R.J.M. Hague, P.M. Dickens, *Rapid Manufacturing: An Industrial Revolution for the Digital Age*, John Wiley, England, 2006.
- [2] J.P. Kruth, G. Levy, F. Klocke, T.H.C. Childs, Consolidation phenomena in laser and powder-bed based layered manufacturing, *CIRP Ann – Manuf Techn* 56 (2007) 730–759.
- [3] R.D. Goodridge, C.J. Tuck, R.J.M. Hague, Laser sintering of polyamides and other polymers, *Prog. Mater. Sci.* 57 (2012) 229–267.
- [4] I. Gibson, D.W. Rosen, B. Stucker, *Additive Manufacturing Technologies: Rapid Prototyping to Direct Digital Manufacturing*, Springer, Atlanta, 2009.
- [5] V. Mittal, *Optimization of Polymer Nanocomposite Properties*, John Wiley & Sons, Weinheim, 2010.
- [6] R.D. Goodridge, M.L. Shofner, R.J.M. Hague, M. McClelland, M.R. Schlea, R.B. Johnson, C.J. Tuck, Processing of a polyamide-12/carbon nanofibre composite by laser sintering, *Polym. Test.* 30 (2011) 94–100.
- [7] S.R. Athreya, K. Kalaitzidou, S. Das, Processing and characterization of a carbon black-filled electrically conductive nylon-12 nanocomposite produced by selective laser sintering, *Mat. Sci. Eng. A-Struct.* 527 (2010) 2637–2642.
- [8] G.V. Salmoria, R.A. Paggi, A. Lago, V.E. Beal, Microstructural and mechanical characterization of PA12/MWCNTs nanocomposite manufactured by selective laser sintering, *Polym. Test.* 30 (2011) 611–615.
- [9] J. Bai, R.D. Goodridge, R.J.M. Hague, M. Song, Improving the mechanical properties of laser-sintered polyamide 12 through incorporation of carbon nanotubes, *Polym Eng Sci* 53 (2013) 1937–1946.
- [10] R.K. Gupta, *Polymer and Composite Rheology*, Second ed., Taylor & Francis, 2000.
- [11] S. Sinha Ray, M. Okamoto, Polymer/layered silicate nanocomposites: a review from preparation to processing, *Prog Polym Sci* 28 (2003) 1539–1641.
- [12] J. Jin, L. Chen, M. Song, K. Yao, An analysis on enhancement of fatigue durability of polyurethane by incorporating organoclay nanofillers, *Macromol Mater Eng* 291 (2006) 1414–1421.
- [13] H.S. Xia, M. Song, Preparation and characterization of polyurethane-carbon nanotube composites, *Soft Matter* 1 (2005) 386–394.
- [14] Y.T. Lim, O.O. Park, Phase morphology and rheological behavior of polymer/layered silicate nanocomposites, *Rheologica Acta* 40 (2001) 220–229.
- [15] Y.H. Hyun, S.T. Lim, H.J. Choi, M.S. Jhon, Rheology of poly(ethylene oxide)/organoclay nanocomposites, *Macromolecules* 34 (2001) 8084–8093.
- [16] M. Rahmat, P. Hubert, Carbon nanotube-polymer interactions in nanocomposites: a review, *Compos. Sci. Technol.* 72 (2011) 72–84.
- [17] D. Cai, J. Jin, M. Song, Process, (2009) WO/2009/0343612009.
- [18] C.W. Macosko, *Rheology: Principles, Measurements, and Applications*, John Wiley & Sons, 1994.
- [19] C. Mizuno, B. John, M. Okamoto, Percolated network structure formation and rheological properties in nylon 6/Clay nanocomposites, *Macromol Mater Eng* 298 (2013) 400–411.
- [20] R. Krishnamoorti, E.P. Giannelis, Rheology of end-tethered polymer layered silicate nanocomposites, *Macromolecules* 30 (1997) 4097–4102.
- [21] M. Wang, W. Wang, T. Liu, W.-D. Zhang, Melt rheological properties of nylon 6/multi-walled carbon nanotube composites, *Compos. Sci. Technol.* 68 (2008) 2498–2502.
- [22] W.D. Zhang, L. Shen, I.Y. Phang, T. Liu, Carbon nanotubes reinforced nylon-6 composite prepared by simple melt-compounding, *Macromolecules* 37 (2003) 256–259.
- [23] H. Zarrinhalam, N. Hopkinson, N.F. Kamperman, J.J. de Vlieger, Effects of processing on microstructure and properties of SLS nylon 12, *Mat. Sci. Eng. A-Struct.* 435 (2006) 172–180.
- [24] S. Karamipour, H. Ebadi-Dehaghani, D. Ashouri, S. Mousavian, Effect of nano-CaCO<sub>3</sub> on rheological and dynamic mechanical properties of polypropylene: experiments and models, *Polym. Test.* 30 (2011) 110–117.
- [25] R. Abu-Zurayk, E. Harkin-Jones, T. McNally, G. Menary, P. Martin, C. Armstrong, M. McAfee, Structure-property relationships in biaxially deformed polypropylene nanocomposites, *Compos. Sci. Technol.* 70 (2010) 1353–1359.
- [26] A.E. Woodward, J.M. Crissman, J.A. Sauer, Investigations of the dynamic mechanical properties of some polyamides, *J Polym Sci* 44 (1960) 23–34.
- [27] P.A. Tipler, G. Mosca, *Physics for Scientists and Engineers*, W. H. Freeman, 2007.