

The SLS characteristics of 1.8wt% clay nanoparticle/Nylon 6 composite

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Abstract: Selective laser sintering (SLS) characteristics of clay nanoparticle/Nylon 6 composite were studied for the applications in Rapid Prototyping and Manufacturing (RP&M). Differences of sintering behaviors between the nanocomposite and standard SLS polymers were investigated. Nanoparticles change the material's properties and this requires, modification of SLS processing parameters. An attritor ground the as-received pellets into 100 μ m-sized particles. The nanocomposite's sintering behavior showed higher porosity compare with standard polymers.

Key words: Nanocomposite, SLS

Introduction

Polymer nanocomposites (PNCs) represent a radical alternative to the conventional polymer composites, which are composed of a second organic or inorganic phase.⁽¹⁻⁵⁾ In terms of second phase, especially in RP industry, nanoparticles have great merits in SLS processing compared with using short fiber reinforcement because of the rearrangement of reinforcement can be done before SLS processing and the possible powder size can be further reduced due to nano sized reinforcement.

Nanometer sized reinforcements are classified as spherical silica nanoparticles (all three dimensions are in the order of nanometers), nanotubes or whiskers (two dimensions are in the order of nanometers) and sheet nanoparticles (one to a few nanometer thick sheets extending to 10~1000 nanometers).⁽⁶⁾ Nanocomposites were first referenced as early as 1950⁽⁷⁾ but it was not until Toyota researchers⁽⁸⁾ began a detailed examination of polymer/layered silicate clay mineral composites that nanocomposites became more widely studied in both academic and industrial laboratories. The typical advantages⁽⁹⁾ of nanocomposites are increment of tensile modulus and strength without sacrificing impact resistance as well as the heat distortion temperature up to 100°C. Dimensional stability and flame retardation characteristics are also increased.

These improvements occur because the exfoliated clay lamellae structure inhibits the polymer

chain movement. Since high degrees of stiffness and strength are realized with less of the high-density inorganic phase, they are much lighter compared to conventional polymer.⁹⁾ For these reasons, this new material has great potential for application in automotive, aerospace, and medical device industries. To apply these new class materials into RP&M field, some modification of processing parameters may be required, because the nanoparticles interact with the polymer chain. This paper is concentrated on finding out the best processing conditions such as part-bed temperature, laser power of nanoparticle/Nylon 6 composite. Finally, we compare the SLS flow behavior between this new class material and conventional Nylon 6 polymer.

Experiment

Since the as-received nanocomposite is approximately 3mm by 3mm by 3mm pellet, an attritor first makes the pellets into powders. The attritor is a stirred ball mill that operates at liquid nitrogen temperature with a rotor speed of 2500 rpm. To minimize contamination, blocks of the same polymer system were used as a grinding media. Namely nanocomposite blocks were used for grinding nanocomposite and neat nylon 6 blocks were used for generating neat nylon 6 powder. Figure 1 (a) and (b) shows an attritor and its schematic drawing respectively.

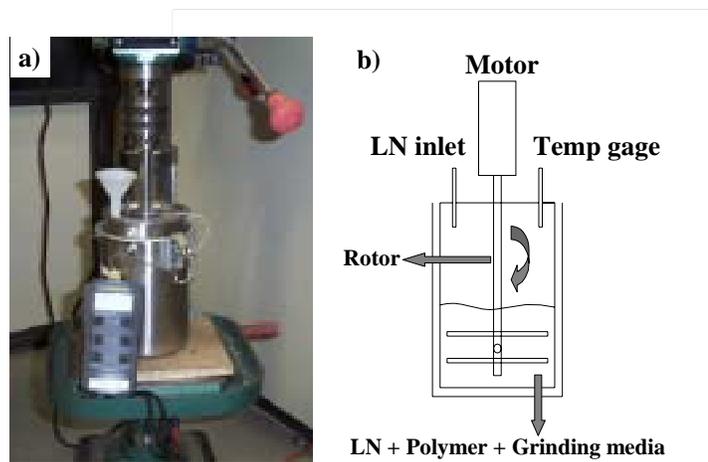


Fig. 1. a) Outer shape of attritor b) Schematic drawing of attritor

Thermal and flow properties of nanocomposite were measured by Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA), and Melt Flow Index (MFI). DSC is the equipment for measuring the melting point (T_m), crystallization temperature of the material. The DSC task was performed using both powder and as-received pellet and in case of using

pellet, small portions were cut from the edge of the pellet.

DMA is the technique, which intended to be used as a mechanical test (through torsion) for evaluating viscoelastic properties of material. Through this test, we can determine loss modulus, storage modulus and glass transition temperature (T_g) of polymer. For this test, the specimens were cut and machined from plaques, which were made by extrusion.

MFI is basically defined as the weight of the polymer (in grams) extruded in 10 minutes through a capillary of specific diameter and length by pressure applied through dead weight at fixed temperature condition. For the Nylon experiment, ASTM 1238D condition was applied i.e. 2.16kg dead load at 235 °C condition was used.

The Sinterstation 2000 by DTM cooperation sintered the clay nanoparticle/Nylon 6 composite. Due to the limited quantity of candidate powders, the sintering work was performed for only one layer (0.005in thick) without supplying fresh powders from powder feed cartridge, after sintering in the Sinterstation Scanning Electron Microscopy (SEM) analysis was performed to investigate the sintering results. The sintering job was done with 140°C part-bed temperature and 25w laser power conditions. Before all the experiments, powders were dried at 100°C-10h under vacuum condition to minimize the possible moisture absorption. Table. 1 indicates the basic properties of the as-received nanocomposite.

Table. 1. Mechanical property and composition of Nylon 6-clay reinforced nanocomposite

	Unit	Method	Value
Mass fraction of clay	wt %	Ash analysis	1.83
Fracture stress	MPa	ASTM D-882	95
Elongation	%	ASTM D-882	430
Young's modulus	MPa	ASTM D-882	1000

Results and Discussion

Figure 2 (a) and (b) show the SEM images of nanocomposite and neat nylon 6 powders respectively, which are produced by stirred ball mill technique. This size reduction method is not efficient; it produce approximately 1g yields for 1h job of grinding. This method makes each powder shape and size irregular. The size measurement is done by both Martin's⁽¹⁰⁾ method and sieve, and in both cases, most powders are located in 100~150µm range. However sintering work

is performed using below 90 μ m sized powders, because smaller sized powders have higher surface area and with this reason, exhibit good consolidation behavior.

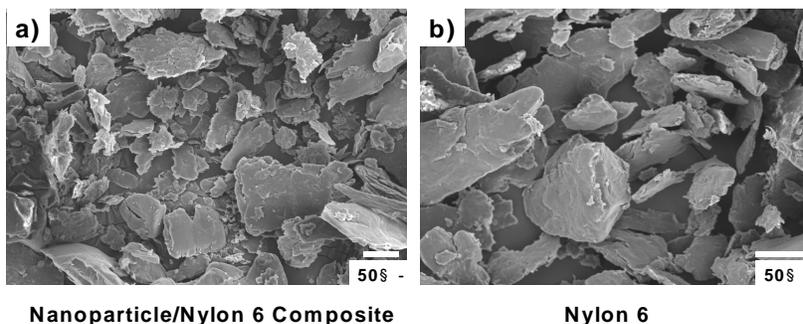


Fig. 2. Powder shape and size distribution of a) Nanocomposite b) Neat nylon 6

The DSC result exhibits interesting facts, i.e. in the nanocomposite case, the T_m value varies according to the shape of material. When using a shaving from the pellet itself, the T_m is 272 °C, but using powders, the T_m is located in the range of 228~232 °C, while the T_m of neat nylon 6 is 220 °C. These differences are probably due to two facts. First is an irregular distribution of clay in the polymer matrix and second is during the size reduction process certain weak regions, namely clay-poor regions break from the pellet first and these powders may be composed of much smaller contents of clay than the pellet. DSC shows that some clay is present in the powder because the T_m difference between nanocomposite powder and neat nylon 6 is about 10 °C. This difference is due to the clay-molecular chain interaction that makes molecular chain movement difficult. And also this small T_m difference may be originated from the insufficient clay content; in other words if we use higher clay content (5wt%) pellet, the T_m difference might be large.

Figure 3 indicates DMA result of nanocomposite and neat nylon 6. From Figure 3 (a), the nanocomposite exhibit about 0.1GPa higher storage modulus at room temperature region than neat nylon 6. This means clay prevents free molecular chain movement but again, this small difference of storage modulus show that clay does not prevent molecular motion efficiently. And this phenomenon also may come from insufficient amount of clay contents or the clay may not exfoliated well. And this insufficient content of clay causes almost same T_g values, which are shown in Figure 3 (b). From DSC and DMA results, we can suspect that low content of clay dose not affect much effect on the SLS processing.

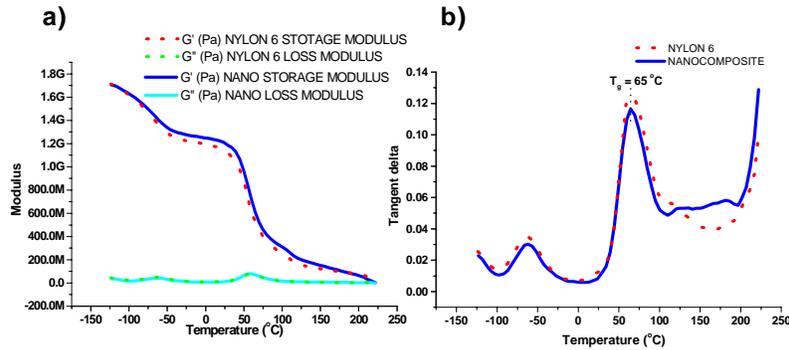


Fig. 3. DMA result of nanocomposite and neat nylon 6
 a) Storage and loss modulus b) Tangent delta value

The MFI experiment result is listed in Table. 2. From this result, neat nylon 6 show approximately 14% higher MFI value but 32~61% higher shear rate value than nanocomposite because of the density difference. This means nanocomposite has higher viscosity than conventional neat nylon 6. This is because the nano clay prevents the flow of the matrix polymer.

Table. 2. MFI result of Nanocomposite and Neat nylon 6

	Density (g/cm ³)	MFI (g/sec)	Shear rate (/sec)
Neat nylon 6	0.773	6.85± 0.71	16.22± 0.84
Nanocomposite	0.993	6.03± 0.55	11.11± 0.51

It is also suspected that clay content greater than 1.8wt% will cause an additional increase in viscosity and we may need to apply still more heat for flow by combination of increased part-bed temperature and increased laser power of the DTM machine. Figure 4 (a) is the SEM image of polycarbonate using 25w laser power and 120 °C part-bed temperature and (b) and (c) are the laser sintered surface and magnification picture of nanocomposite powder interface under the part-bed temperature of 140 °C and laser power of 25w of nanocomposite respectively. As we expected, the sintering surface is composed of many pores, this may come from both the clay effect and poor powder compaction. And at the powder interfaces (neck regions), especially for

the nanocomposite powders, which are located near the pores, several stripes are detected but at this time, further investigation is not performed on these stripes.

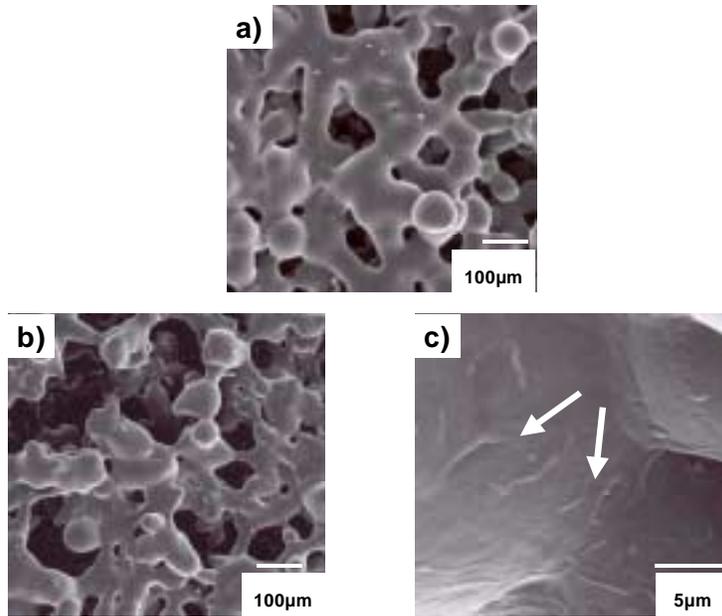


Fig. 4. Sintering result of a) polycarbonate surface morphology (x45) b) nanocomposite surface morphology (x45) and c) morphology near the pore (x2000)

Conclusion

Based on the results presented, we have these conclusions:

1. Sintering of nanoparticle/Nylon 6 composite requires higher part-bed temperature and laser power than neat Nylon 6 for the SLS processing.
2. DSC results on ground material showed no significance change although the pellet sample showed ~ 50 °C higher T_m value than neat nylon 6; entire pellets should be ground up for further experiments.
3. Further research on the clay structure and distribution aspect are also required.

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