

# Rheological Properties of Ferrite Nanocomposites based on Nylon-66

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## ABSTRACT

Effects of ferrite nanoparticles (0.1–20 wt %) on the rheological and other physical properties of nylon-66 were investigated. The presence of ferrite nanoparticles less than 1 wt % increased the crystallization temperature ( $T_c$ ) by 4.2 °C with ferrite content, but further addition decreased  $T_c$ . The onset temperature of degradation was increased by 7.3 °C at only 0.1 wt % loading of ferrite, after which the thermal stability of nylon-66 was decreased with ferrite content. The incorporation of ferrite nanoparticles more than 5 wt % increased the dynamic viscosity ( $\eta'$ ) with the loading level. Further, it produced notably shear thickening behavior in the low frequency, after which high degree of shear thinning was followed with ferrite content. In the Cole–Cole plot, the nanocomposites with ferrite lower than 5 wt % presented a single master curve, while further addition gave rise to a deviation from the curve. The relaxation time ( $\lambda$ ) was increased with ferrite content and the difference of  $\lambda$  between nylon-66 and its nanocomposite was greater at lower frequency.

**Keywords:** dynamic viscosity, ferrite, nanocomposites, nylon-66, tensile properties

## 1 INTRODUCTION

Until now, majority of current researches have focused on the nylon-6 nanocomposites among polyamide matrices because they exhibit preferably improved properties. Thus,

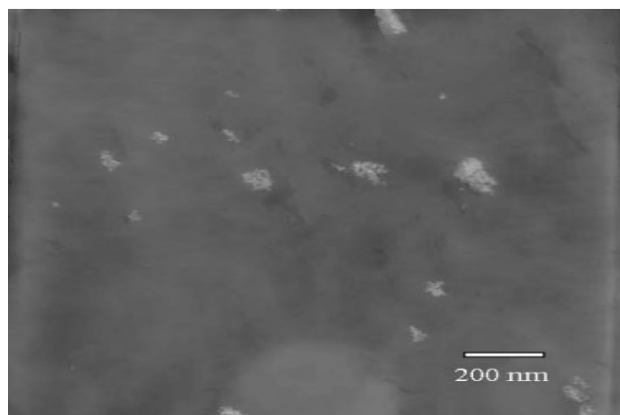


Figure 1 : TEM images of nylon-66 nanocomposites with 5 wt % ferrite.

this made it possible for commercial success by some research group.[1-3] Even though there has been very limited research on nylon-66 nanocomposites,[4-7] they are expected to have a wider field of applications than those of nylon-6 nanocomposites because of its superior properties; high heat-distortion temperature, high modulus and strength, dimensional stability at high temperature, chemical resistance to many organic solvents, and gas barrier properties. Further, the success in nylon-6 nanocomposites can pave the way to develop nylon-66 nanocomposites. Polymer nanocomposites containing the nanoparticles with magnetic properties attract great attention because of their applications, including potential high-capacity magnetic storage media, magnetic refrigeration at high temperature, color imaging, ferrofluids, bioprocessing, medical diagnosis, electromagnetic wave absorption, and so forth.[8-12] They are usually prepared by in situ polymerization, sol-gel processing, and melt compounding. Among them, the direct mixing in melt state is very promising because this allows using conventional processing equipment. Additionally, melt compounding is less restricted in selecting polymer grades and loading levels of inorganic particle. This makes it possible that the nanocomposites with various combinations are fabricated. Introducing inorganic/metal nanoparticles into polymer influences the microstructure of polymer chains, which may result in a different flow behavior from the pure polymer or micron-sized conventional filled polymeric system. The rheological properties of polymeric system are closely associated with its processing. Thus, understanding the rheological properties of nanocomposites gives significant clues to determining optimum condition of polymer processing. However, little work has been done with nanoparticle-filled suspensions. In this study, nylon-66/ferrite nanocomposites with various loading levels (0.1–20 wt %) were prepared by melt compounding, and their physical properties were investigated in terms of rheology and thermal properties.

## 2 EXPERIMENTAL

### 2.1 Materials

The nylon-66 pellet (intrinsic viscosity  $\frac{1}{4}$  1.51) was supplied by Kolon, Inc (Korea). The nylon-66 was vacuum-dried at 100 °C for 24 h prior to melt mixing with ferrite nanoparticles ( $\text{Fe}_2\text{O}_3$ ). The nanoparticles were incorporated a fine powder, whose primary particle size ranged from 50 to 200 nm. The nylon-66 and ferrite nanop-

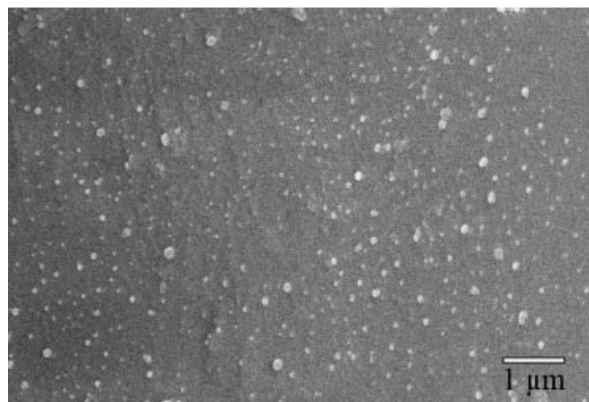


Figure 2: FESEM images of nylon-66 nanocomposites with 20 wt % ferrite

articles were dry mixed via tumbling in a bag. This preblend was melt-mixed in a Haake Mini-Lab twin screw extruder (Thermo Electron Corp., Karlsruhe, Germany) for 3 min at 60 rpm at 270 °C using a counterrotating screw configuration. The loading levels (X) of the nanocomposites were 0.1, 0.5, 1.0, 5, 10, and 20 wt %, and they were coded Ny66-X.

## 2.2 Measurement of Physical Properties

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2000FXII microscope, with an accelerating voltage of 200 kV. As shown in Figure 1, the size of the ferrite embedded in the nylon-66 matrix is

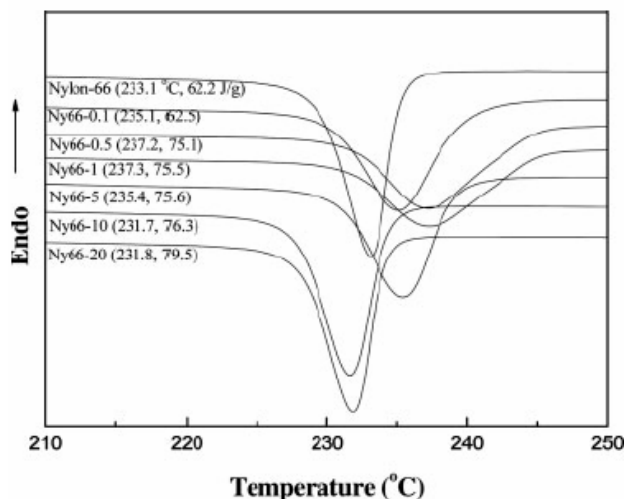


Figure 3: DSC cooling scan thermograms of nylon-66 and nylon-66/ferrite nanocomposites. Maximum crystallization temperature (T<sub>c</sub>) and heat of crystallization (ΔH<sub>c</sub>) values are indicated.

similar to that of primary nanoparticles. In addition, the morphology of ferrite/nylon-66 nanocomposites was examined with a field emission scanning electron microscope (FESEM; JEOL, JSM-6340F). Figure 2 presents the FESEM images of the surface of nylon-66-20 in film state. The ferrite nanoparticles are well dispersed in the nylon-66 without large aggregation.

The thermal properties of nylon-66/ferrite nanocomposite were investigated using differential scanning calorimeter (DSC 2010; TA instrument, Dupont) in a nitrogen atmosphere. The samples were held at 270 °C in the molten state for 5 min to eliminate the previous thermal history, and cooling–heating scan was then performed at 10 °C/min. In addition, the thermal stability was evaluated using thermogravimetric analyzer (TGA; TA Instruments, SDT2960). The heating scan was carried out to 800 °C at 10 °C/min in a nitrogen atmosphere.

The dynamic rheological properties were measured with an Advanced Rheometric Expansion System (ARES; Rheometric Scientific, Inc.) rotational rheometer. Parallel plate geometry with a diameter of 25 mm was employed. The plate gap and strain level were 1 mm and 10%, respectively. The frequency sweep tests were carried out in an oscillatory mode at 270 °C.

## 3 RESULTS AND DISCUSSION

The DSC cooling scan of nylon-66 and nylon-66/ ferrite nanocomposites is shown in Figure 3. The presence of ferrite nanoparticles less than 1 wt % increases the crystallization temperature (T<sub>c</sub>) of nylon-66 with the loading level. This indicates that the ferrite nanoparticles act as a nucleating agent, leading to a small degree of supercooling. However, further addition decreases T<sub>c</sub> with ferrite content and produces even lower T<sub>c</sub> than does pure nylon-66 at circa 1.3 °C at as high as 10 or 20 wt %. This suggests that above some critical loading level, the nanoparticles in the polymer matrix may reduce the chain mobility to such an extent that they disturb the participation of the polymer chain in the crystallizable unit because of the significantly increased interfacial area. In addition, the nanoparticles increase the heat of crystallization (ΔH<sub>c</sub>) with ferrite content because of the heterogeneous nucleation.

Figure 4 shows the effect of ferrite nanoparticles on the degradation process of nylon-66. When comparing the onset temperature (T<sub>0.1</sub>) of the degradation at which 10% degradation occurs, only Ny66-0.1 shows a slight enhancement of thermal stability by giving higher T<sub>0.1</sub> than that of pure nylon-66 at 7.3 °C. However, further incorporation of ferrite nanoparticles induces a negative effect on the thermal stability of nylon-66 matrix. This suggests that the high polarity of ferrite nanoparticles gets themselves favorably dispersed around the polar amide group in the nylon-66 chain and heat is easily transferred to the amid group because of high thermal conductivity of the

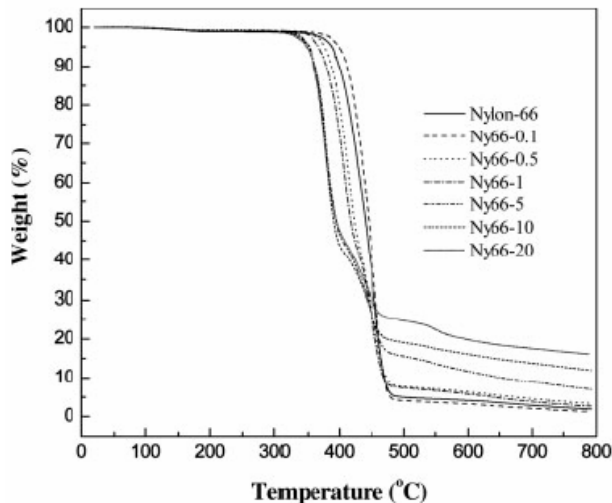


Figure 4: TGA curve of nylon-66 and nylon-66/ferrite nanocomposites.

nanoparticles. Thus, this facilitates the thermal decomposition of nylon-66 matrix at a high content of ferrite nanoparticles.

Figure 5 shows the dynamic viscosity ( $\eta'$ ) curve of nylon-66 and nylon-66/ferrite nanocomposites at 270 °C. The nanocomposites present non-Newtonian flow behavior over the frequency range examined, which is more noticeable at a higher ferrite content. The incorporation of ferrite nanoparticles more than 5 wt % increases the  $\eta'$  notably with the loading level. In particular, it produces shear thickening behavior in the low frequency. However, shear thinning is followed after the frequency, and its

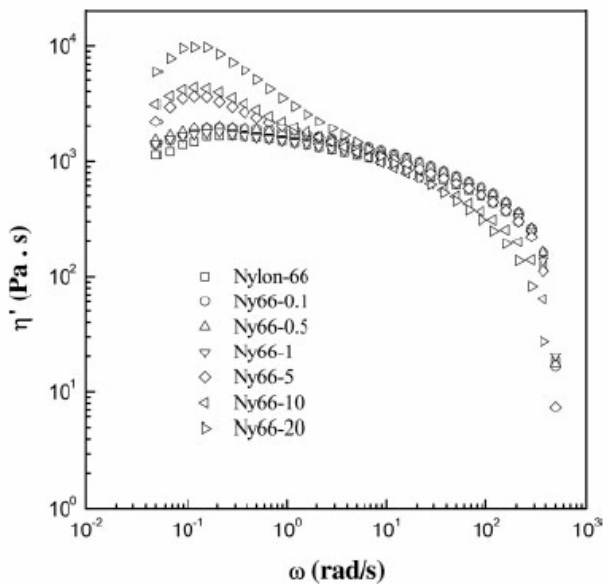


Figure 5:  $\eta'$  curve of nylon-66 and nylon-66/ferrite nanocomposites at 270 °C.

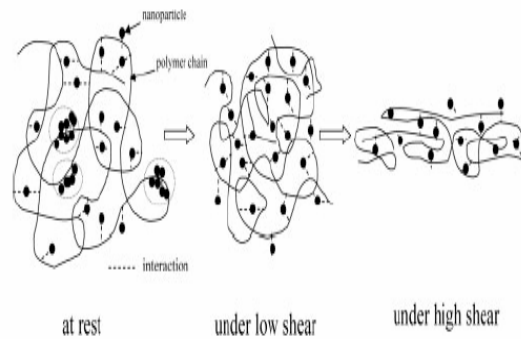


Figure 6: Schematic diagram of polymer chain in ferrite-filled nylon-66 nanocomposite systems.

degree is increased with ferrite content showing even lower  $\eta'$  than that of pure nylon-66 in the high frequency range. At a high ferrite content more than 5 wt %, the polymer chain can be easily destructed and deformed by shear.

To explain the situation in more detail we provide in Figure 6 a schematic diagram of polymer chain in ferrite-filled nylon-66 nanocomposite systems. There exists the interaction between polar polymer chain and polar nanoparticle. Thus, the ferrite nanoparticles in the matrix constrain the chain mobility, leading to an increase of the chain rigidity.[16] When low shear is applied to the systems the degree of interaction between polymer and nanoparticle is notably increased at high content by increasing the possibility to contact each other as indicated in the diagram. In addition, high shear deformation gives rise to the orientation of polymer chain, regardless of the interaction between polymer and nanoparticle.

A logarithmic plot of  $G'$  versus  $G''$ , so-called Cole-Cole plot, is shown in Figure 7. The nanocomposites containing ferrite lower than 5 wt % give a single master curve independent of the presence of ferrite. This implies that its effect is not as large as altering the molecular structure of nylon-66 matrix. However, the notable deviation from the master curve is observed from the 5 wt% loading, suggesting that high content of ferrite nanoparticle gives rise to the difference in the molecular structure.[16] In addition, the reduced slope with increase in the ferrite content indicates that the nanocomposites become more heterogeneous. [17] The slope also changes with the shear rate, giving three distinct regions, which is notable at a high ferrite content ( $\geq 5$  wt %). It is worth noting that the inflection point where the slope is changed shifts to a higher frequency with increasing ferrite content. This phenomenon can be explained that much energy is necessary to change the degree of heterogeneity because of the increased physical association within the nanocomposite systems at a high loading level.

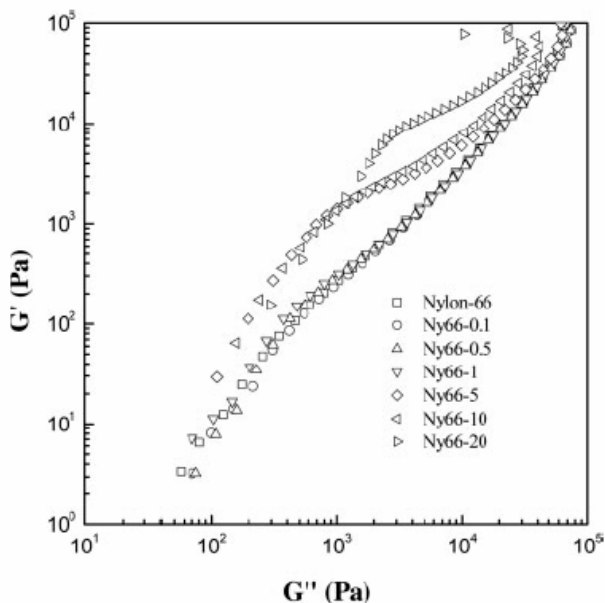


Figure 7. Logarithmic plot of  $G'$  versus  $G''$  of nylon-66 and nylon-66/ferrite nanocomposites at 270 °C.

#### 4 CONCLUSIONS

The ferrite nanoparticles acted as a nucleating agent, leading to a small degree of supercooling. However, above a critical loading level (1 wt %), the nanoparticles in the polymer matrix might restrict the chain mobility as much as disturbing the participation of the polymer chain in the crystallizable unit. This phenomenon might be ascribed to a higher degree of interaction between ferrite and nylon-66. Up to 1 wt %, ferrite nanoparticles did not have large effect on the rheological properties of nylon-66. However, the nanocomposites with more than 5 wt % ferrite displayed notable shear thickening behavior in the low frequency less than circa 0.1 rad/sec because of the increased physical association within the nanocomposite systems. After the frequency, shear thinning was followed and its degree was increased with ferrite content. This suggested that ferrite nanoparticles accelerated the orientation of polymer chain under high shear at a high content. From 5 wt % loading ferrite altered the molecular structure of nylon-66, which was proven by the deviation from the master curve in the Cole–Cole plot. This could be explained that at a low content, ferrite nanoparticles played a role in retarding the disentanglement of polymer chain under extension.

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