# 전단조건이 나일론 6/은 나노복합소재의 결정화거동에 미치는 영향

채동욱, 오성근, 김병철
한양대학교 응용화학공학부

# Effect of Shearing on Crystallization Behavior of Nylon 6/Silver Nanocomposites

Dong-Wook Chae, Seong-Geun Oh, and Byoung-Chul Kim
*Division of Chemical Engineering, Hanyang University*

## Introduction

Recently, organic-inorganic nanocomposites have attracted great interest from researchers since they frequently exhibit unexpected hybrid properties synergistically derived from two components[1]. The addition of highly dispersed inorganic nano-sized fillers permits improvement of certain properties of polymers as compared with conventional particulate composites; increase of modulus and strength, improved barrier properties, increase in solvent and heat resistance, and good optical properties[2]. Further, these improvements are achieved at very low loadings of inorganic component (1~10 wt%) as compared with conventional filled polymers, which require a high loading of the order of 25~40 wt%.

Shear induced crystallization of semi-crystalline polymers is a matter of great importance in controlling the final morphologies and properties. The importance of shear-induced structural changes in polymeric materials is much raised recently in the field of polymer processing. Processing of polymeric materials involves the application of very complex deformation histories to the polymer melt, which can modify the nucleation and crystallization behavior. A great deal of effort is devoted to elucidate the structure formation during crystallization under shear flow in polymer melt. Thus this effort makes it possible that the wide range of molecular morphologies can be altered in desired way by tuning the processing conditions, such as temperature , shear rate, and the composition of a composite.

Due to the necessity for understanding the influence of various shear environments on polymer nanocomposite systems, the rheological behavior of nanocomposites have received considerable attention over the past several years[3]. However, despite the recent progress in polymer nanocomposite technology, the

nature, origin and some unique behaviors of such nanocomposites are not well understood. Only a few studies have shown time development of crystallinity under shear. In this study, a nylon 6/silver nanocomposite was prepared via melt compounding and its crystallization behavior stimulated by shear was discussed in terms of shear rate and crystallization temperature.

## Experimental

### Preparation of nylon 6/silver nanocomposties

Nylon 6 was obtained from Kolon, Inc.(Korea). Silver was introduced as a fine powder ,whose particle size was less than 100 nm. The surface treatment of silver was carried out with stearic acid to give good dispersion to organic material. The nylon 6 pellet was dried under vacuum at 80 ℃ for 24 hrs prior to mixing. The preweighed quantities of nylon 6 and silver nanoparticles were first dry mixed by shaking them in a bag. The mixture was then melt-blended at 250 ℃ by using an internal mixer(Haake Rheomix 600). The rotor speed was 60 rpm, and mixing time was 10 min. Two differently concentrated nanocomposites were prepared with 0.5 (Ny6-Ag05) and 1 %(Ny6-Ag10) silver nanoparticles based on nylon 6 by weight .

### Measurement of physical properties

Advanced Rheometric Expansion System (ARES) (Rheometric Scientific, Inc.) was employed to measure the dynamic rheological properties. The parallel plates of diameter 25 mm were used, whose gap was 1 mm. The specimen was melted at 250 ℃ and the excess sample which occurred in gap-setting was trimmed off. This newly set specimen was relaxed for 5 min at the temperature in a nitrogen atmosphere to remove the residual stress, then quenched to the desired crystallization temperature of 190 or 200 ℃ for a time sweep measurement. The experiment was carried out at the three different frequencies 1, 3, and 5 rad/sec with a 5% strain till the value of G′ leveled off. The molten disk-shaped specimen were then taken off the plates and further used for measuring other properties such as thermal and morphological properties by DSC, X-ray diffractometer and TEM.

Wide angle X-ray diffraction(WAXD) experiment was carried out by Rigaku Denki (D/MAX-2000) with Nickel filtered CuKα radiation of 40 kV and 100 mA. Scanning was carried out on the equator in the 2Θ range from 5° to 80° at the scan speed 5°/min.

DSC 2010(TA Instruments, Dupont) differential scanning calorimeter was used to evaluate thermal properties of the nanocomposites. About 5 mg samples were

heated from 10 to 250 ℃ at a rate of 10 ℃/min in a nitrogen atmosphere and held for 5 min to eliminate the heat history. The sample was then cooled off to 10 ℃ at a rate of 10 ℃/min to obtain cooling scan thermogram

## Results and discussion

The DSC thermogram was investigated to study the crystallization behavior of nanofiller dispersed nylon 6 composites as compared with pure nylon 6 in Fig 1. As-received pure nylon 6 shows different peak form and peak temperature from the nanocomposites. In presence of silver nanoparticles the crystallization temperature of two nanocomposites is increased from 172.8 to about 186.0 ℃ and also the width of crystalline peak narrows down as compared with pure nylon 6. The dramatic increase of crystallization temperature and peak sharpness for the nanocomposites clearly brings out the strong nucleation efficiency.

Figs. 2 and 3 show the variation of G′ and η′ of the samples with time at a frequency of 3 rad/s at 190 and 200 ℃, respectively. At the early stage of experiment, both G′ and η′ are increased slowly, indicating an induction time for crystallization. Subsequently, an abrupt increase of both parameters takes place in some minutes. This phenomenon can be ascribed to the formation of crystallites probably due to the shear-induced crystallization[4]. The incorporation of silver nanoparticle gives rise to short induction time and crystallization time as compared with nylon 6. The increase of G′ and η′ in the nanocomposites represents the extent of crystallization of the melts. The number and growth rate of nucleated crystallites are greater for Ny6-Ag05 than nylon 6. However there is little difference in the rheological properties between Ny6-Ag05 and Ny6-Ag10. Fig 4. shows a variation of G′ with time for Ny6-Ag05 at 190 ℃ at three different frequencies. The induction time and crystallization time at the frequency of 3 or 5 rad/s are shorter than those at 1 rad/s. Shear flow accelerates the overall crystallization kinetics due to an increase in the nucleation rate caused by orientation of the polymer chains[5]

Fig. 5 shows XRD patterns of the nanocomposites sheared at a frequency of 3 rad/sec at 190 ℃. Two sharp diffraction peaks appear at $2\Theta$ = 19.8°(α1) and 23.4° (α2) contributed by α crystalline phase of nylon 6 irrespective of incorporation of silver nanoparticle. However, the addition of silver nanoparticle gives rise to the decrease of α1 peak and increase of α2 peak. In addition, a diffraction peak appear at around $2\Theta$=21.2° a characteristic feature of the γ crystalline phase although there isn't a clear resolution of peaks. Diffraction peaks at $2\Theta$= 38.2°, 44.4°, 64.5°, and 77.5°, characteristic peak positions of silver, are more prominent with increasing silver.

## REFERENCES


1. X. Liu and Q. Wu, *Polymer*, **43**, 1933(2002).
2. E. P. Giannelius, *Adv. Mater.*, **8**, 29(1996).
3. T. D. Fornes, R. J. Yoon, H. Keskkula, and D. R. Paul, *Polymer*, **42**, 9929(2001).
4. W. J. Yoon, H. S. Myung, B. C. Kim, and S. S. Im, *Polymer*, **41**, 4933(2000).
5. A. Nogales, B. S. Hsiao, R. H. Somani, S. Srinivas, A. H. Tsou, F. J. Balta-Calleja, and T. A. Ezquerra, *Polymer*, **42**, 5247(2001).


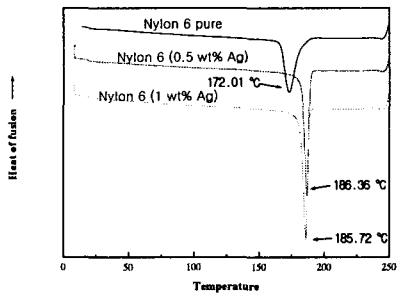


Fig. 1. DSC cooling scan thermograms

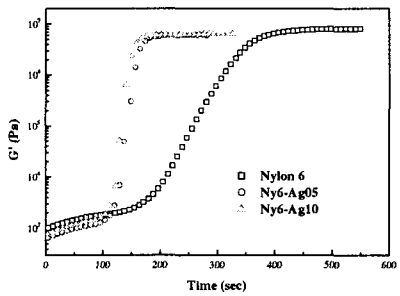


Fig. 2. Variation of G′ with time at 190 ℃ at a frequency of 3 rad/s

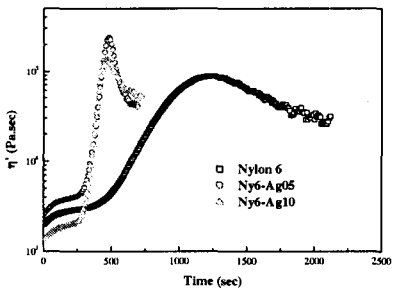


Fig. 3. Variation of η′ with time at 200 ℃ at a frequency of 3 rad/s

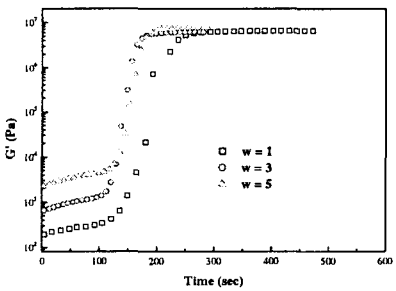


Fig. 4. Variation of G′ with time for Ny6-Ag05 at 190 ℃ at three different frequencies

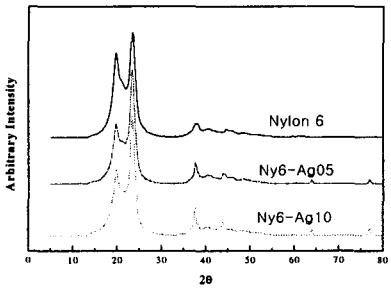


Fig. 5. WAXD patterns of Ny6 nanocomposites crystallized at 190 ℃ at a frequency of 3 rad/s