Preparation of Nylon 66/Mesoporous Molecular Sieve Composite Under High Pressure

YOSHITSUGU KOJIMA, TAKAAKI MATSUOKA, HIDEROH TAKAHASHI

Toyota Central Research & Development Laboratories, Inc., Nagakute-cho, Aichi-gun, Aichi 480-11, Japan

ABSTRACT: Nylon 66/mesoporous molecular sieve (pore diameter: 2.7 nm) composites were prepared by annealing mixtures of nylon 66 and mesoporous molecular sieve (FSM) powders under high pressures and high temperature (FSM content: 0–60 wt %; pressure: 0.5–30 MPa; temperature: 300°C; time: 1 h). X-ray diffraction and TEM measurements indicated the presence of the pores of FSM in the composite. Above 2 MPa, nylon 66 was charged in the pores of FSM. The fraction of the charged nylon 66 increased with pressure and was independent of the FSM content (pressure: 2–30 MPa; fraction of charged nylon 66: 54–66%). The infrared spectrum of the composite showed the bands based on Si—O, C—H, N—H, C=O. DSC measurement indicated that the heat of fusion of nylon 66 crystallite in the FSM pores was low compared with that of nylon 66. The composites prepared above 2 MPa were found to be superior in storage modulus to nylon 66. The modulus increased with an increase in the fraction of charged nylon 66 and the amount of FSM. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3254–3258, 1999

Key words: nylon 66; mesoporous molecular sieve; composite; high pressure; storage modulus

INTRODUCTION

Polyamide resins have been widely used as injection and extrusion molding materials, particularly for parts of automobiles and electrical goods because the molded materials have excellent mechanical properties.[1] Polyamides have been successfully reinforced by using glass fiber[1,2] and other inorganic additives such as silicate layers of montmorillonite.[3–5]

Recently, mesoporous molecular sieve with a honeycomb construction of silica has been developed.[6–8] The pore diameter of the mesoporous molecular sieve is varied in the range of below 1.5 to 3.2 nm and increased with increasing surfactant chain length. If polyamide could be charged in the pore of the mesoporous molecular sieve

(FSM), the mechanical properties would be improved.

In this study, a nylon 66/mesoporous molecular sieve composite, in which polyamide is charged in the pores, was prepared by annealing mixtures of nylon 66 and FSM powders under high pressure and high temperature above the melting temperature of nylon 66. Dynamic viscoelastic properties were measured with a dynamic viscoelastometer.

EXPERIMENTAL

Materials

Nylon 66 powder (P2020, Ube Industries Ltd, Tokyo, Japan) was used for the experiment. Mesoporous molecular sieve powder with the pore diameter of 2.7 nm (synthesized in the previous study) was used.[8] The composition of nylon 66 and mesoporous molecular sieve was carried out
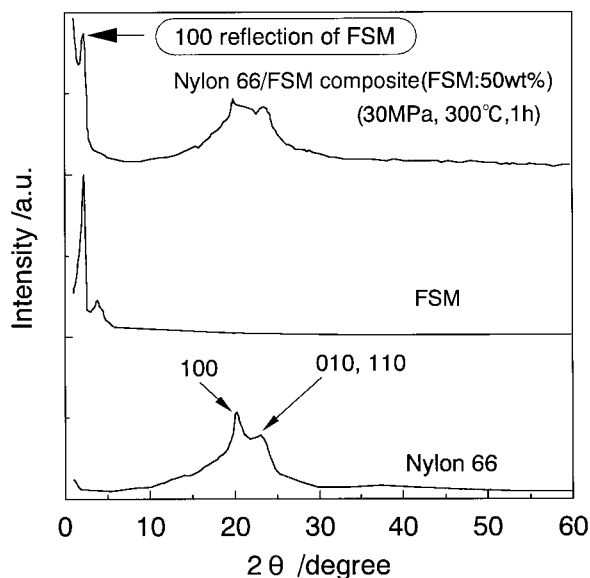
Figure 1 X-ray diffraction intensity curves of composite, FSM and nylon 66.

using a high hydrostatic pressure reactor.[9] Mixtures of nylon 66 and the mesoporous molecular sieve (FSM) powders (FSM content: 0–60 wt %) were packed into polytetrafluoroethylene cells (inside diameter: 8 mm; length: 23 or 40 mm). After closing each cell, it was introduced into the high-pressure vessel. The specimens were compressed at various pressures in the range of 0.5–30 MPa by a hand oil pump, substantially annealed at 300°C for a constant time of 1 h, with pressure transmitting medium (silicone oil). The specimens were annealed at a heating ratio of 10°C/min. After the reaction under high pressure, the products were cooled to room temperature, decompressed, and removed from the cell.

Characterization

Transmission electron micrograph was obtained with a JEOL JEM2000EX II TEM using an acceleration voltage of 200 kV. X-ray diffraction intensity curves were recorded with Cukα radiation (30 kV, 30 mA) filtered by monochrometer using Rigaku-Denki Rad-B. The aperatures of the first, second, and third slits were 0.5, 0.5, and 0.15 mm, respectively. A Fourier transform infrared spectrophotometer (Japan Spectroscopic Co., Ltd. FT/IR-5M) was used for infrared studies in the wavenumber from 4000 to 600 cm^{-1}. Specimens in powder form were mixed with KBr (0.7–0.9 mg of specimen with 200 mg of KBr), and their tablets were formed by applying pressure. Thermal prop-

erties were investigated with differential scanning calorimetry (DSC), at a heating rate of 10°C/min. The endothermic peak of the DSC thermogram was identified as the melting temperature. Dynamic viscoelastic properties were measured with a dynamic viscoelastometer VES-F from Iwamoto Seisakusho Co., Ltd. The storage modulus E' and the loss modulus E'' were determined at 10 Hz in the temperature range between -150 and $+300$°C. The specimens were heated at a rate of 2°C/min. The peak temperature of E'' was identified as the glass transition temperature. The density was calculated using the volume and the weight.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction intensity curves of the composite (FSM content: 50 wt %), FSM, and nylon 66. FSM has a 100 reflection at 2θ of about 2°.[6,8] The composite displays the 100 refection of FSM. Figure 2 shows the transmission electron micrograph of the composite prepared under 30 MPa. The dark lines with honeycomb construction of silica correspond to the intersection of FSM. We found that the pore of FSM is present in the composite. This indicates that the pore of FSM isn't collapsed at or below the pressure of 30 MPa. The unit cell of nylon 66's α-form is triclinic in shape with $a = 0.49$ nm, $b = 0.54$ nm, $c = 1.72$ nm, $\alpha = 48°$, $\beta = 77°$, $\gamma = 63°$.[10] The diffractions at 2θ of 20 and 23° are
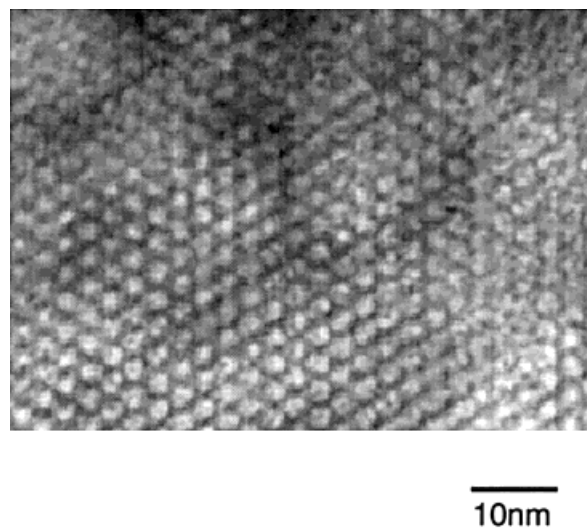

Figure 2 Transmission electron micrograph of composite (30 MPa, 300°C, 1 h).
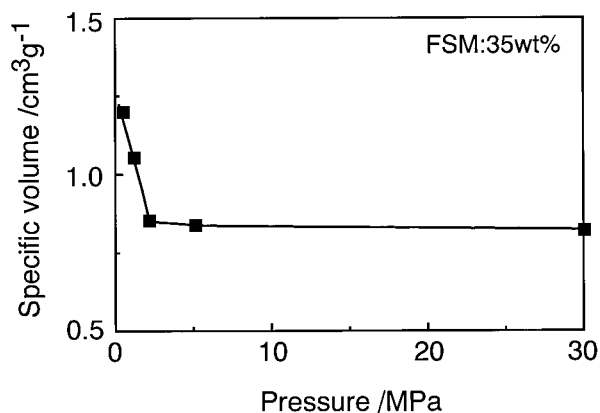
Figure 3 Influence of pressure on specific volume.

raised from 100 and 010, 110 planes of α-form of nylon 66, respectively.[1] Both samples of nylon 66 and nylon 66 in the composite have the same form of α-form.

The pressure dependence of the specific volume of the composite is shown in Figure 3. The specific volume of the composite decreases abruptly at 2 MPa, due to the insertion of nylon 66 in the pore of FSM. Above 2 MPa, the pressure dependence of the specific volume is small. It is suggested that nylon 66 was charged in the pore of FSM above 2 MPa. The fraction of charged nylon 66 X can be expressed by eq. (1).

$$X = 1 - [(V_c - 1/\rho_N)W_F - 1/\rho_F + 1/\rho_N]/V_F \quad (1)$$

where ρ_N and ρ_F are densities of nylon 66 and FSM minus the pores, respectively; V_F is the pore volume per unit of weight of FSM (cm³/g); V_c is the specific volume of the composite; and W_F is the weight fraction of FSM.

The density of FSM minus the pores ρ_F and the pore volume of FSM V_F is assumed as 2.2 g/cm³ (specific volume: 0.455 cm³/g) and 0.8 cm³/g, respectively.[8] Nylon 66 is a semicrystalline material and the densities of the amorphous and crystalline phases are 1.09 cm³/g and 1.24 g/cm³.[10] The density of normal nylon 66 is in the range of 1.13 and 1.16 g/cm³.[1] Assuming that the density of nylon 66 above insertion pressure of 2 MPa is 1.12 g/cm³ (see Fig. 4) and the pressure dependence is small, the fraction of the charged nylon 66 in FSM under 2 MPa is calculated as 54%. X increases with increasing pressure [fraction of charged nylon 66: 54–66% (FSM content: 35 wt %; pressure: 2–30 MPa)]. We found that the nylon 66 was charged in the pores of FSM. Figure 4

shows the specific volume as a function of the FSM content. The specific volume of the composite prepared under 30 MPa linearly decreases with FSM content. Using eq. (1), the fraction of the charged nylon 66 is obtained as 66% and was independent of the FSM content. The specific volume of the composite prepared under 0.5 MPa linearly increases with FSM content. The density of nylon 66 obtained at the intercept is 1.06 g/cm³ and low compared with normal nylon 66. Furthermore, the slope is larger than that of the calculated line, assuming that the fraction of charged nylon 66 is zero. This suggests the presence of pores in the nylon 66 matrix.

IR spectroscopy yields the structural information. Figure 5 shows the infrared absorption spectra of the composite prepared under 30 MPa together with FSM and nylon 66. For the composite, the bands at 3300 and 1530 cm⁻¹ indicate the N—H stretching and deformation vibrations.[10,11] The C—H stretching vibration of the composite occurs at 2940 cm⁻¹. The IR bands at 1640 and 1080 cm⁻¹ are assigned to the C=O stretching vibration and the Si—O stretching vibration, respectively. The spectrum of a partially crystalline polymer has crystalline and amorphous bands. The IR bands of nylon 66 at 936 and 1140 cm⁻¹ in Figure 5 are assigned to the crystalline and the amorphous bands.[1] The amorphous band of the composite is absent because the Si—O stretching vibration has the strong IR absorption at 1080 cm⁻¹. The absorbances of the crystalline bands for the composites prepared under 30 MPa, 0.5 MPa, and nylon 6 were standardized by the values at 1640 cm⁻¹. The relative absorbance of the composite prepared under 30 MPa is 0.087 and small compared with those of the composite pre-
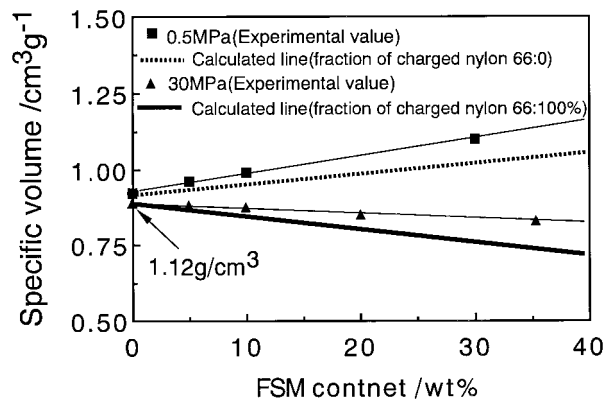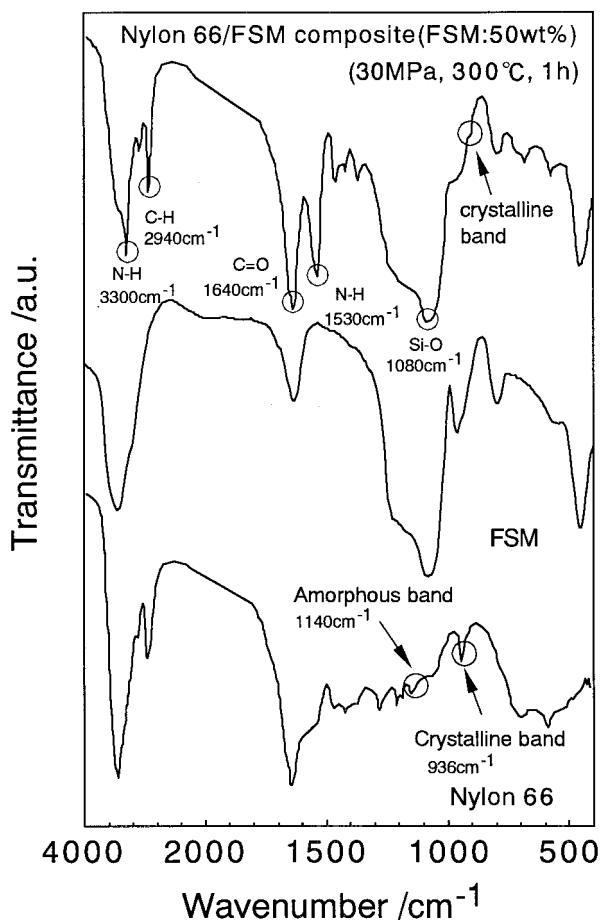

Figure 4 Influence of FSM content on specific volume.

Figure 5 Infrared absorption spectra of composite, FSM and nylon 66.

where ΔH_N and ΔH_F are the heat of fusion of nylon 66 crystallites outside and inside the pore, respectively, ρ_N is the density of nylon 66, V_F is the pore volume of FSM, and X is the fraction of charged nylon 66.

The slope S of the line in Figure 6 is given by

$$S = \Delta H_N + (\Delta H_N - \Delta H_F)\rho_N V_F X \qquad (3)$$

Substituting this into eq. (2)

$$\Delta H_F = (\Delta H_N \rho_N V_F X + \Delta H_N - S)/(\rho_N V_F X) \quad (4)$$

We can assume that the heat of fusion of nylon 66 outside the pores prepared under 30 MPa ΔH_N is 85 J/g, the density of nylon 66 ρ_N is 1.12 g/cm^3, the fraction of the charged nylon 66 X is 0.66, the pore volume V_f is 0.8 cm^3/g, and the slope S is 127 J/g. The heat of fusion ΔH_F is estimated to be 14 J/g using eq. (4). This indicated that the structural regularity of the polymer chain can be disrupted in the pores.

According to the viscoelastic behavior, the storage modulus and the loss modulus were obtained. The glass transition temperature of the composite obtained by the peak temperature of the loss modulus was 67–78°C and approximately agrees with that of nylon 66. The storage moduli at various temperatures are plotted against pressure in Figure 7. Above 2 MPa, the moduli of the composites (FSM: 35 wt %) are about twice as larger as those of ones prepared under 0.5 MPa and gradually
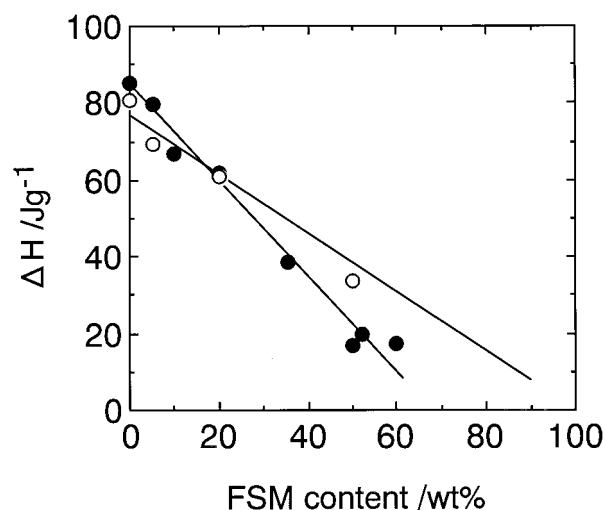
pared under 0.5 MPa (relative absorbance: 0.159) and nylon 66 (relative absorbance: 0.263). This means that the degree of crystallinity of nylon 66 decreases by charging in the pore of FSM.

DSC measurements were carried out to discuss the FSM content dependence of the heat of fusion and the melting temperature. The melting temperature was 260–270°C, and independent of the annealing pressure and the FSM content. The effect of the FSM content versus the heat of fusion of the composite is shown in Figure 6. The heat of fusion decreases with the FSM content and the straight line between the heat of fusion ΔH and the FSM content is demonstrated. The relationship between the heat of fusion of the composite prepared under 30 MPa ΔH and the weight fraction of FSM W_F is expressed as the form

$$\Delta H = \Delta H_N - [\Delta H_N + (\Delta H_N - \Delta H_F)\rho_N V_F X]W_F$$

$$(2)$$

Figure 6 Influence of FSM content on heat of fusion: (○) 0.5 MPa, fraction of charged nylon 66: 0; (●) 30 MPa, fraction of charged nylon 66: 66%.

increase with pressure. The increase in the modulus is related to the insertion of nylon 66 in the pore of FSM. Figure 8 shows the dependences of the moduli at various temperatures on the FSM content. The modulus of the composite at 25°C (FSM: 35 wt %) prepared under 30 MPa, containing a fraction of charged nylon 66 of 66 wt % is about two times that of nylon 66. The modulus of the composite was standardized by the value of nylon 66. The higher the temperature, the higher the relative modulus [relative modulus: 2.9 (100°C; FSM: 35 wt %), relative modulus: 4.7 (180°C; FSM: 35 wt %)]. The modulus of the composite at 25°C prepared under 0.5 MPa (fraction of charged nylon 6: 0) is nearly equal to that of nylon 66, but the moduli at 100 and 180°C increase a little with the FSM content [relative modulus: 1.4 (100°C; FSM: 35 wt %), relative modulus: 2.1 (180°C; FSM: 35 wt %)], as shown in Figure 8. Thus it is obvious that the modulus of the nylon 66/mesoporous molecular sieve composite increased by the insertion of nylon 66 in the pores of FSM.

CONCLUSIONS

Nylon 66/mesoporous molecular sieve (pore diameter: 2.7 nm) composites were prepared by annealing mixtures of nylon 66 and the mesoporous molecular sieve (FSM) powders under high pressures and high temperature (FSM content: 0–60 wt %; pressure: 0.5–30 MPa; temperature: 300°C; time: 1 h). Above 2 MPa, nylon 66 was charged in the pore of FSM. DSC measurement indicated that the heat of fusion of nylon 66 crystallite in the FSM pores was low compared with that of nylon 66. The composite pre-
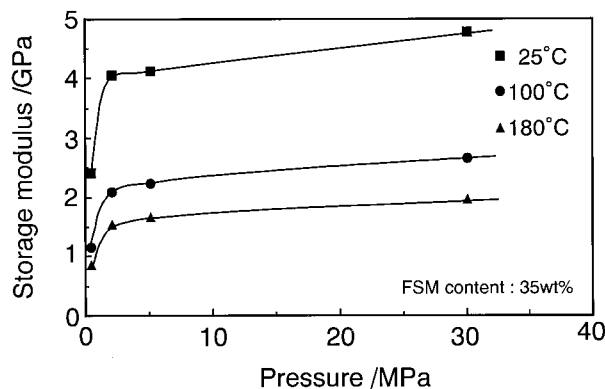

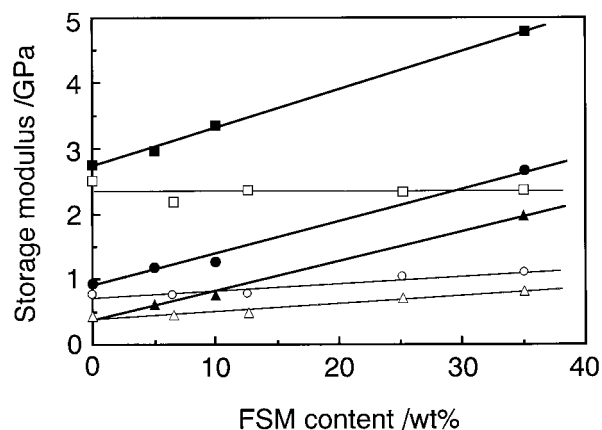**Figure 7** Relationship between storage modulus and pressure.

Figure 8 Dependence of storage modulus on FSM content: (□) 25°C, (○) 100°C, (△) 180°C (pressure: 0.5 MPa; fraction of charged nylon 66: 0); (■) 25°C, (●) 100°C, (▲) 180°C (pressure: 30 MPa; fraction of charged nylon 66: 66%).

pared above 2 MPa was found to be superior in storage modulus to nylon 66.

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