

Crystallization of Nylon 6–Clay Hybrid by Annealing Under Elevated Pressure

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SYNOPSIS

Nylon 6–clay hybrid (NCH) is a molecular composite of nylon 6 and uniformly dispersed silicate layers of montmorillonite. We found that the phase with the high melting temperature (HMT phase) in the NCH annealed under elevated pressure. The melting temperature of the HMT phase was 240°C. Nylon 6 annealed under elevated pressure did not have the HMT phase. Thus, the presence of the HMT phase was characteristic of the NCH. The relative heat of fusion of the HMT phase (heat of fusion of HMT phase/heat of fusion in the pressure annealed NCH) increased with increase in pressure. High-pressure differential thermal analysis (DTA) measurement revealed that the temperature, at which the relative heat of fusion showed a maximum value, was below about 20°C of the melting temperature of the original NCH under elevated pressure. It was considered that the nylon 6 crystallite near the melting temperature and the molecular mobility under elevated pressure were necessary to the appearance to the HMT phase. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Nylon 6–clay hybrid (NCH) is a molecular composite of nylon 6 in which silicate monolayers of montmorillonite, 1 nm in thickness and 100 nm in width, are uniformly dispersed.^{1–4} NCH is readily processed in the molten state by injection molding or extrusion molding. It is well known that high pressure above 0.3 GPa strongly enhances the rate at which polyethylene crystallizes in extended forms. Extended-chain crystal (ECC) of polyethylene is grown either by pressure-induced crystallization⁵ or by annealing of folded chain crystal near the melting temperature, as was reported by Rees and Bassett.⁶ The melting temperature and the crystallinity of the polyethylene with ECC are higher than those of folded-chain crystals of polyethylene.⁷ In the NCH annealed under elevated pressure, it is expected that the melting temperature and the crystallinity are increased due to the growing of the ECC.

In this study, the NCH was crystallized by annealing under elevated pressure above 0.15 GPa. The

effect of pressure on the crystallization of the NCH was evaluated by differential scanning calorimetry, wide-angle X-ray diffraction, infrared spectroscopy, and high-pressure differential thermal analysis.

EXPERIMENTAL

The montmorillonite is a natural clay mineral and has a cation-exchange capacity of 119 mmol/100 g. The NCH (montmorillonite content: 1.6 wt %) was synthesized by the same method described in the preceding paper.¹ The number-average molecular weight of the nylon 6 in the NCH was 15,000 as estimated from the end-group (COOH) analysis. Annealing of the NCH under elevated pressure was carried out using a piston cylinder apparatus. The NCH was packed into a polytetrafluoroethylene cell. After closing the cell, it was introduced into the cylinder with a pressure-transmitting medium (lead). The NCH was compressed at various pressures in the range 0.15–0.3 GPa through the pressure-transmitting medium by squeezing the piston into the cylinder, subsequently annealed (200–300°C) for a constant time (1 h). After annealing under elevated pressure, the specimen was cooled to room temper-

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ature, decompressed, and removed from the cell. A nylon 6 (commercial grade: 1013B, number-average molecular weight: 13,000, Ube industries, Japan) was also treated under the same conditions as for the NCH.

The thermal properties were investigated with differential scanning calorimetry (DSC) and a thermal controller SSC/580 from Seiko Instruments & Electronics, at a heating rate of 5°C/min. The endothermic peak of the DSC thermogram was identified as the melting temperature.

The crystalline structures were investigated by wide-angle X-ray diffraction. The X-ray diffraction patterns were recorded at room temperature over the range of the diffraction angle (2θ) from 10° to 40° with $\text{CoK}\alpha$ radiation (30 kV, 30 mA) filtered by a monochromator using a Rigaku-Denki Rad-B.

A JEOL Model FTIR/5M (Japan Electron Optics Laboratory) was used for infrared studies in the wavenumber from 4000 to 1800 cm^{-1} . The powdered specimen was mixed with KBr (1 mg of polymer with 200 mg of KBr) and was formed into tablets for the infrared studies by applying pressure.

High-pressure differential thermal analysis (DTA) thermograms were obtained using a Rigaku-Denki high-pressure DTA apparatus. The endothermic peak of the DTA thermogram was identified

as the melting temperature under elevated pressure. The block diagram of the apparatus is schematically illustrated in Figure 1. The apparatus was operated in the temperature range from room temperature to 400°C under hydrostatic pressure up to 1 GPa. A compensating heater functioned to hold the predetermined pressure during heating runs. Pressure measurements were performed using a Bourdon gauge (Heise gauge) and a manganin coil gauge. The pressure measured using the latter gauge was displayed directly on a digital manometer with an accuracy of ± 0.5 MPa. Low viscosity silicone oil (Shin-Etsu Chemical, KF-96-10CS or KF-96L-2CS) was used as the pressure-transmitting fluid. Data of temperature, temperature difference between specimen and reference, and pressure were recorded on a 3-pen recorder and simultaneously stored in a floppy disk of a data processor (PC-9801 DX2, NEC Corp.).

RESULTS AND DISCUSSION

DSC thermograms of the original NCH and the NCH annealed under an elevated pressure (0.3 GPa, 260°C, 1 h) are shown in Figure 2. It is well known that nylon 6 has two kinds of crystal form. One is

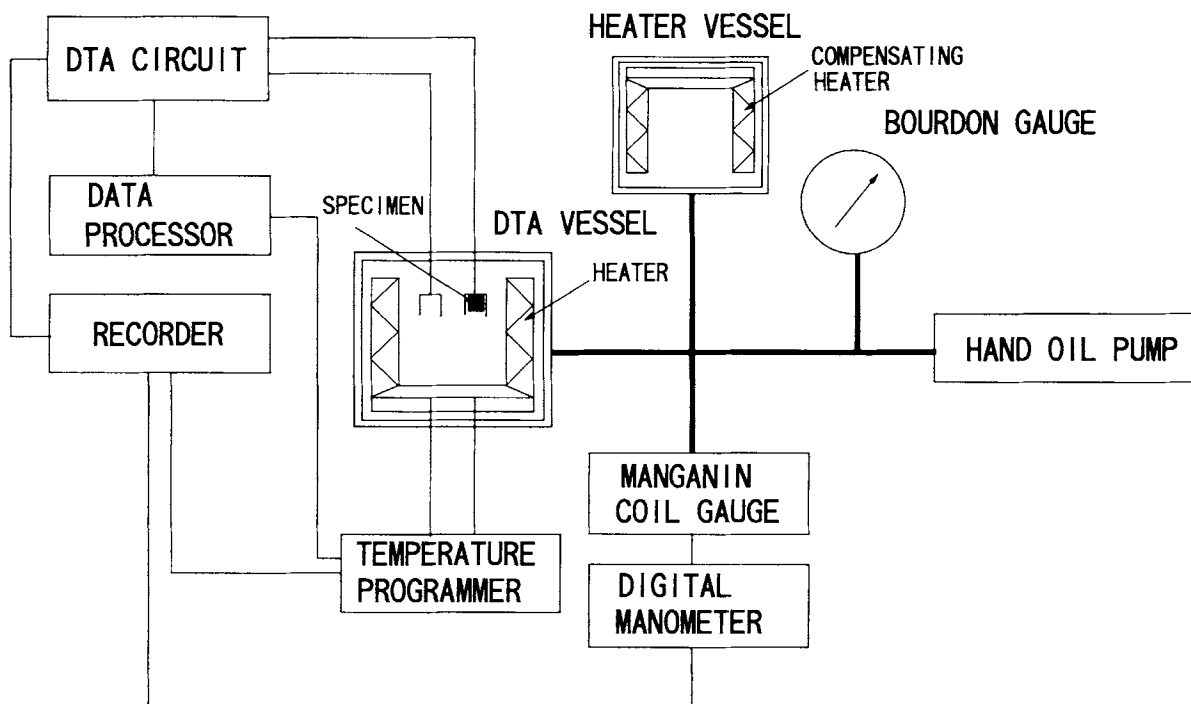


Figure 1 Block diagram of high-pressure DTA apparatus.

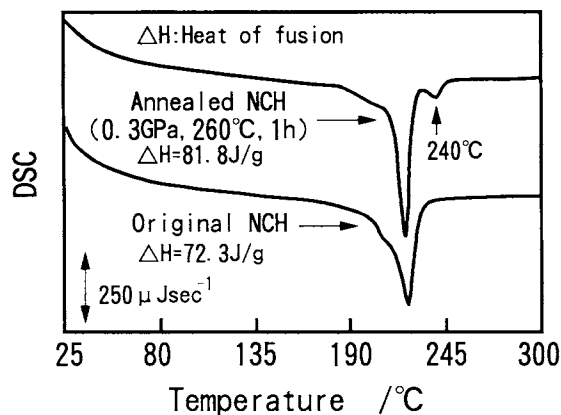


Figure 2 DSC thermograms of NCH annealed under elevated pressure (0.3 GPa, 260°C, 1 h) and original NCH.

the α -form (melting temperature $\sim 220^\circ\text{C}$),⁸ which consists of fully extended planar zigzag chains, in which adjacent antiparallel chains are joined to each other by the hydrogen bond. The other is the γ -form (melting temperature $\sim 210^\circ\text{C}$).⁸ This crystal is composed of pleated sheets of parallel chains joined by the hydrogen bond. It is noticed that a characteristic peak appears at 240°C in the NCH annealed under elevated pressure. The lower-temperature endothermic peak (223°C) and shoulder (208°C) correspond to the ordinary melting temperatures of α and γ crystals of nylon 6, respectively. Nylon 6 annealed under elevated pressure showed a single endothermic peak corresponding to the melting of the α -form (221°C), as shown in Figure 3. Thus, we found the phase with the high melting temperature in the NCH annealed under elevated pressure. We term the phase with the high melting temperature the HMT phase. The heat of fusion of the NCH and

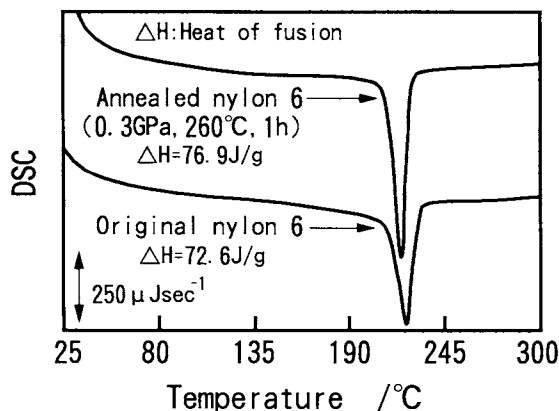


Figure 3 DSC thermograms of nylon 6 annealed under elevated pressure (0.3 GPa, 260°C, 1 h) and original nylon 6.

nylon 6 increased by annealing under elevated pressure.

The crystalline structure of the sample was evaluated from the results of wide-angle X-ray diffraction measurements. Figure 4 illustrates the X-ray diffraction patterns of the pressure-annealed NCH and the original NCH. The unit cell of the α -form is monoclinic in shape with $a = 0.956$ nm, $b = 1.724$ nm (chain axis), $c = 0.801$ nm, and $\beta = 67.5^\circ$,⁹ and that of the γ -form is orthorhombic in shape with $a = 0.482$ nm, $b = 0.782$ nm, and $c = 1.67$ nm (chain axis).¹⁰ The diffraction peaks at 2θ of 23.2° and 27.8° are raised from 200 and 002, plus 202 planes of α -crystals, and the diffraction peaks at 2θ of 12.2° and 25.0° are raised from 002 and 110, plus 020 planes of γ -crystals, respectively. Therefore, both samples had two crystalline forms of α - and γ -forms, as shown in Figure 4. After annealing under elevated pressure, the fraction of the γ -form decreased.

Figure 5 shows the infrared spectra of the pressure-annealed NCH, together with the original NCH. The differences between the two spectra were observed in the frequency range of 3400 and 3300 cm^{-1} . It was found that the relative intensity of the absorption band [intensity (3300 cm^{-1})/intensity (3400 cm^{-1})] for the original NCH changed by annealing under elevated pressure. The absorption bands at 3300 and 3400 cm^{-1} are assigned to hydrogen bonding and nonbonding N—H groups, respectively.¹¹ It is evident that the number of hydrogen bonds of N—H groups for the NCH increases by annealing under elevated pressure. This phenomenon is attributed to the fact that, upon annealing, the transformation from γ - to α -forms enhances the hydrogen-bonding formation.

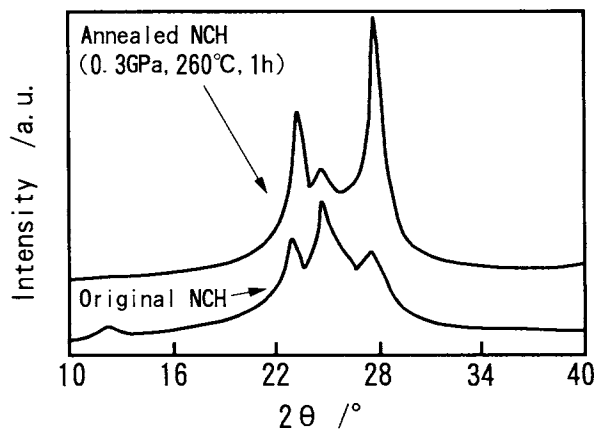


Figure 4 Wide-angle X-ray diffraction patterns of NCH annealed under elevated pressure (0.3 GPa, 260°C, 1 h) and original NCH.

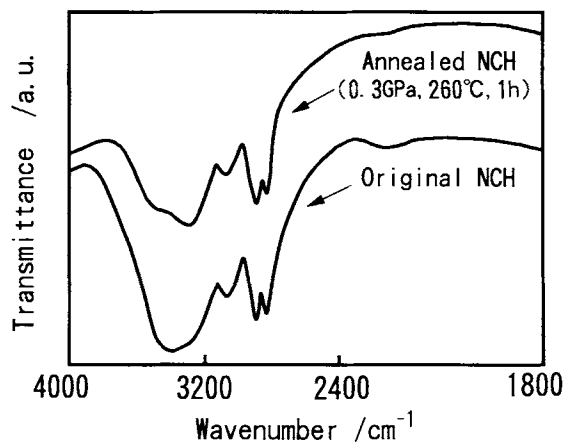


Figure 5 Infrared spectra of NCH annealed under elevated pressure (0.3 GPa, 260°C, 1 h) and original NCH.

Annealing temperature dependencies on the heat of fusion of the pressure-annealed NCH and the relative heat of fusion of the HMT phase (heat of fusion of HMT phase/heat of fusion of the pressure-annealed NCH) are shown in Figure 6. The heat of fusion increases with an increase of annealing temperature and has a maximum value around a temperature of 250°C. The relative heat of fusion of the HMT phase has the maximum value at 260°C.

High-pressure DTA measurements were carried out to discuss the temperature dependencies on the relative heat of fusion of the HMT phase and the heat of fusion of NCH. The pressure dependence of the melting temperature of the original NCH is shown in Figure 7. The melting temperature of the original NCH increases with increasing pressure and the slope decreases with pressure. A least-square fit to the pressure, P , dependence of the melting temperature, T_m , for the original NCH was tried with

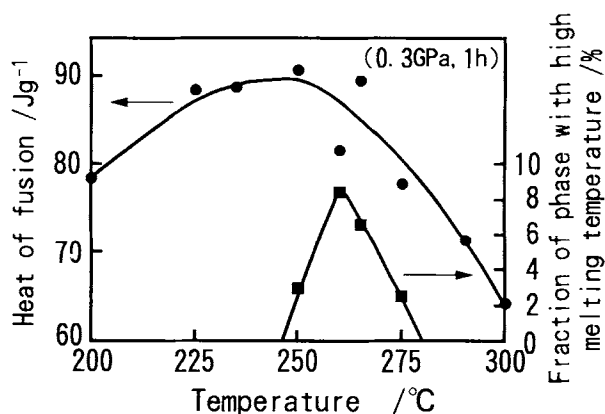


Figure 6 Heat of fusion and relative heat of fusion of phase with high melting temperature in NCH vs. annealing temperature.

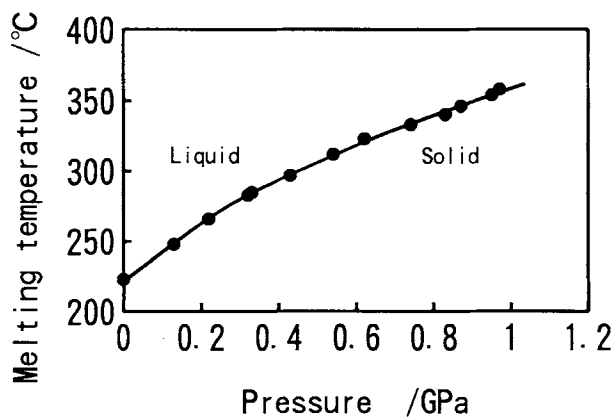


Figure 7 Phase diagram of NCH.

a second-order polynomial. We obtained the following equation with a coefficient of correlation of .999:

$$T_m = 224.3 + 199.4 P - 67.1 P^2 \quad (1)$$

From eq. (1), the melting temperature of the original NCH is determined to be 278°C at 0.3 GPa. It is revealed that the temperature, at which the relative heat of fusion of the HMT phase and the heat of fusion show maximum value, is below 20–30°C of the melting temperature under elevated pressure.

Pressure dependencies of the heat of fusion and the relative heat of fusion of the HMT phase were studied. The crystalline structure of polymer is influenced by the temperature difference ΔT between the crystallization temperature and the melting temperature.¹² Thus, the NCH specimens were annealed at ΔT of 18–24°C [melting temperature estimated from eq. (1) – annealing temperature] under various pressures. Pressure dependencies of the heat of fusion and the relative heat of fusion of the HMT phase at ΔT of 18–24°C are shown in Table I. The relative heat of fusion increases with raising pressure. The higher the pressure is, the higher the annealing temperature is. Therefore, it is considered that the presence of nylon 6 crystallite near the melting temperature and the molecular mobility under elevated pressure have an important role in the appearance of the phase with the high melting temperature. The heat of fusion is independent of pressure, and it is larger than that of the original NCH, in accordance with the X-ray diffraction patterns of the NCH annealed at various pressures. These points indicate that annealing accelerates the transformation from γ - to α -forms.

The melting temperature of semicrystalline polymer shifts to higher temperature with increasing crystallite thickness.¹³ It was reported that the HMT

Table I Heat of Fusion and Relative Heat of Fusion of Phase with High Melting Temperature in NCH vs. Pressure

Pressure (GPa)	Temperature (°C)	ΔT (°C)	Heat of Fusion (J/g)	Relative Heat of Fusion of Phase with High Melting Temperature (%)
10 ⁻⁴	200	24	78.3	0
0.15	235	18	86.4	3.6
0.30	260	18	81.8	8.6

phase of nylon 6 appeared and the crystallite size of the α -form for the chain direction was increased by crystallization in the presence of water under elevated pressure.¹⁴ This crystallization is related to the acceleration of the hydrolysis of the amide group, indicated by the decrease in the molecular weight. The nylon 6 in NCH is classified to bonding and nonbonding nylon 6. The bonding nylon 6 has an ion bonding with the minus charge of montmorillonite.¹ It is assumed that the molecular weight of the bonding nylon 6 is smaller than that of the nonbonding nylon 6, and the bonding nylon 6 partially rearranges more readily into larger crystallite of the α -form for the chain direction, which has the phase with the high melting temperature.

CONCLUSION

We found the HMT phase in the NCH annealed under elevated pressure. Pressure increased the heat of fusion of the HMT phase. Nylon 6 annealed under elevated pressure did not have the HMT phase. High-pressure differential thermal analysis (DTA) measurement revealed that the temperature, at which the relative heat of fusion of the HMT phase showed maximum value, was below about 20°C of the melting temperature of the original NCH under elevated pressure. It was considered that nylon 6 crystallite near the melting temperature in the NCH and the molecular mobility under elevated pressure were necessary for the appearance of the HMT phase.

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