Sorption of Water in Nylon 6–Clay Hybrid

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SYNOPSIS

Various nylon 6–clay hybrids, such as molecular composites of nylon 6 and silicate layers of montmorillonite and saponite, NCHs and NCHPs, respectively, have been synthesized. Sorption of water in those hybrids was measured to estimate the resistance to water permeation. The diffusion coefficient D and the partition coefficient K were obtained from the sorption curves. The resistance to water permeation of NCH was superior to that of nylon 6 because of a decrease in D. In NCHP, saponite had a smaller effect on the increase of the resistance. The diffusion coefficients in NCH and NCHP decreased with an increase in the amount of clay minerals. It was found that those diffusion coefficients were well described by the contribution of the constrained region calculated from the storage and the loss modulus at the glass transition temperature. According to the mixing law, the following equation was obtained between the diffusion coefficient D and the fraction of the constrained region C, $D = D_a(1 - C)^{1/n}$, where the values of D_a (diffusion coefficient in amorphous nylon 6) and n (morphology parameter) were 12.6×10^{-7} cm^2/s and 0.585, respectively. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Nylon 6 is a material that can be readily processed as a melt via injection molding or extrusion to yield a product having excellent mechanical properties.[1] Injection-molded nylon 6 has been widely used for, particularly, the parts of automobiles and electrical appliances. However, nylon 6 is inferior in resistance to water permeation. Rigidity will be lowered by water sorption under an environment of high humidity.[1] It is of interest to improve the resistance to water permeation of nylon 6.

We have reported the synthesis and mechanical properties of nylon 6–clay hybrids, such as molecular composites of nylon 6 and silicate layers of montmorillonite and saponite.[2,3] Injection-molded nylon 6–clay hybrids were found to be excellent in strength, elastic modulus, and heat distortion temperature compared with those of nylon 6.[3] It was expected that the presence of impermeable silicate layers in the hybrids would increase the resistance to water permeation. In this study, sorption of water in the injection-molded hybrids was measured to estimate the resistance to water permeation.

EXPERIMENTAL

Materials

Nylon 6–clay hybrid (NCH) is a molecular composite comprised of nylon 6 and uniformly dispersed silicate layers of montmorillonite.[2] Nylon 6 and the silicate layers are bonded to each other through an ionic bond. The montmorillonite is a natural clay mineral with a cation-exchange capacity of 119 meq/100 g. The NCHs had various resistances to water permeation by changing the number of silicate layers (1.9, 4.7, and 7.1 wt %). The NCHs were synthesized by the following procedures: To a beaker was dispersed 100 g of montmorillonite in 2.3 L water. Then, 51 g of 12-aminolauric acid and 24 mL of hydrochloric acid (36%) were added and the mixture was stirred for 5 min, followed by filtration. By this operation, a composite of 12-aminolauric acid ammonium ion and montmorillonite contained water (water content: 92 wt %) was prepared. Next, 814

g of ε-caprolactam, 105 g of 6-aminocaproic acid (accelerator), and the above composite (240, 610, and 1000 g) were charged into a reaction vessel. The mixture was reacted at 260°C for 5 h in N_2 atmosphere under normal pressure. After completion of the reaction, the product was cooled and subjected to milling to obtain pellets comprising NCH. We also synthesized a nylon 6–clay hybrid (NCHP, clay contents: 1.8, 3.6, and 6.6 wt %), which comprises nylon 6 and silicate layers of saponite (synthetic clay mineral with a cation-exchange capacity of 100 meq/100 g), in the same manner as that of NCH.

Nylon 6 (commercial grade, 1013B, Ube Industries Ltd.) was used as a reference specimen. Those specimens were molten at 250°C and injected into the mold at 60°C by an injection-molding machine PS40E2ASE from Nissei Plastic Industrial Co. Injection-molded NCH and nylon 6 plates of the following dimensions were used for characterization and sorption: length 175 mm, width 20 mm, and thickness 3 mm, with a restricted region in the middle of 50 mm long and 10 mm wide.

Characterization

Transmission electron micrographs were obtained with a JEOL JEM-200CX TEM using an acceleration voltage of 200 kV. The heat of fusion was obtained with a DSC SSC/580 from Seiko Instruments & Electronics Ltd. The specimens were heated at a rate of 5°C/min. The density of the specimen was measured with an electric densitometer ED120T from Mirage Trade Co. The weight in air and in water was measured and the density was calculated from these values. Dynamic viscoelastic properties were measured with a dynamic viscoelastomer VES-F from Iwamoto Seisakusho Co. 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 of E'' was identified as the glass transition temperature. The fraction of the constrained region was calculated from E' and E'', to be described later.

Sorption Experiments

Sorption experiments were done to estimate the resistance to water permeation. The diffusion coefficients and the partition coefficients of water were obtained from the sorption curves. Sorption experiments of the water were carried out by the following procedures: The molding materials were dried in an oven at 50°C for 24 h. After this processing, they were kept in deionized boiling waters for a fixed time, then blotted quickly between sheets of paper to remove the excess water. The amount sorbed was calculated from the increase of the weight of the materials.

RESULTS AND DISCUSSION

Figure 1 compares the transmission electron micrographs of sections of injection-molded NCH and NCHP. The dark lines are intersections of sheet silicate of 10 Å thickness. An X-ray diffraction peak on the (001) plane of the silicate layers could not be obtained for NCH and NCHP.[3] NCH and NCHP are molecular composites of nylon 6 and silicate layers of clay minerals, which are oriented to the flow direction. The average lengths of a face of the montmorillonite and saponite were 1000 and 500 Å, respectively. NCH, NCHP, and nylon 6 had the crystal of the γ-form.[3] The perfectly crystalline phase of the nylon 6 γ-form has a heat of fusion of 213 J/g.[4] The heat of fusion was used to calculate the crystallinity. The crystallinity thus estimated is shown in Figure 2 as a function of the clay content. It should be noted that the crystallinity of nylon 6 in NCH and NCHP is a little lower than that of nylon 6 and that the crystallinity is independent of the clay content.

It is well known that the sorption curve is represented by a relationship between the amount of water sorbed in the specimen M_t and the square root of time divided by the thickness. The sorption curve shows a linear line at the initial stage, followed by a saturated curve.[5] Figure 3 shows sorption curves of water by NCH and nylon 6. We estimated the resistance to water permeation from the water sorption for 30 min.

Figure 4 shows the resistance to water permeation of the nylon 6–clay hybrid. The resistance of NCH containing 4.7 wt % of montmorillonite is about half that of nylon 6. NCH has excellent resistance to water permeation. The resistance increases with increase in the clay content. The nylon 6–clay hybrid (NCHP) comprising nylon 6 and silicate layers of saponite also had better resistance to water permeation compared with that of nylon 6, but the value was lower than that of NCH. A semicrystalline polymer has a lower permeability than that of the amorphous polymer.[6] The presence of crystallite or other impermeable particles within a diffusion medium lowers the overall rate of transport. The higher the amount of impermeable filler, the lower both the diffusion coefficient and the partition coefficient.
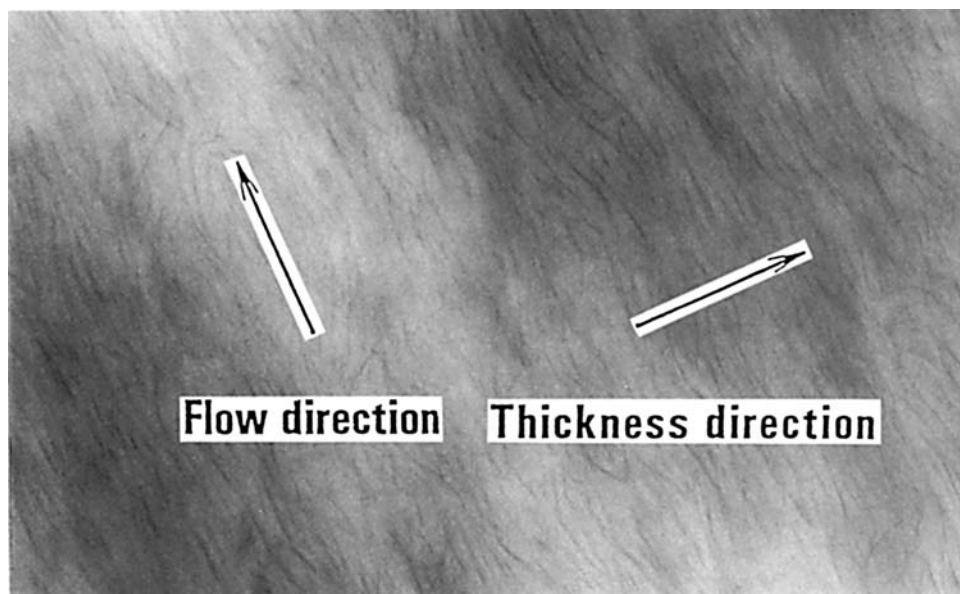
(A) NCH(montmorillonite:4.7wt%) — 1000Å
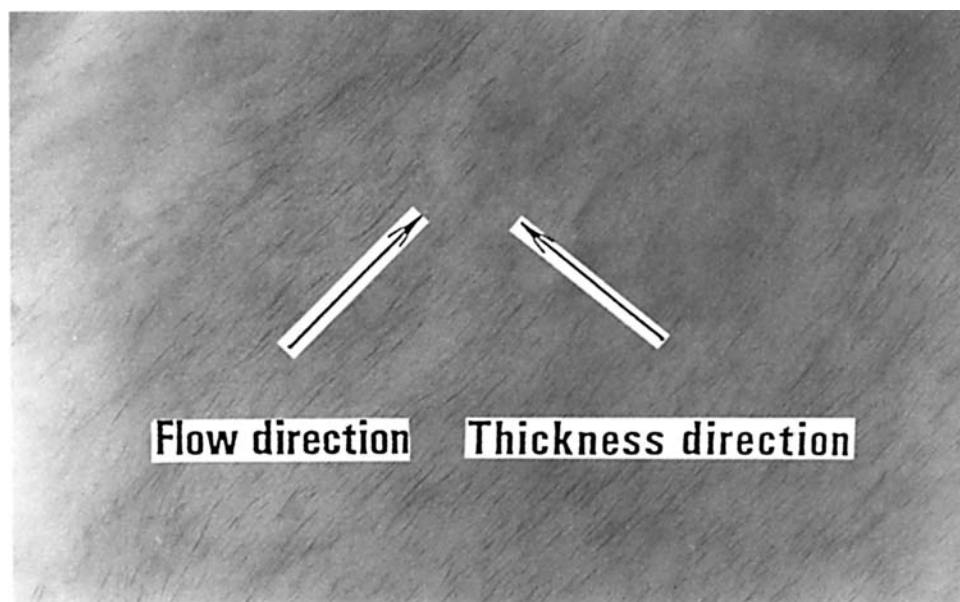
(B) NCHP(saponite:3.6wt%) —— 1000Å

Figure 1 Transmission electron micrographs of sections of injection-molded nylon 6–clay hybrids.

The partition coefficient K was defined as the volume fraction of water contained in a unit volume of materials at an equilibrium state and is estimated by the following equation:

$$K = (M_s - M_d)/(M_s - M_d + M_d/\rho) \qquad (1)$$

where M_s and M_d are the weights of a specimen at equilibrium and dry state, respectively, and ρ is the
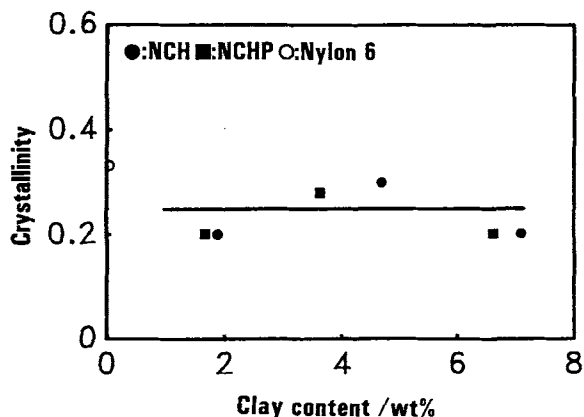
Figure 2   Crystallinity of nylon 6–clay hybrid.

L:average length of silicate layers

Figure 4   Resistance to water permeation of nylon 6–clay hybrid.

density of the specimen. In eq. (1), the density of water was assumed to be 1.0 g/cm^3. K is plotted against the clay content in Figure 5. It is indicated that K is much less than unity and the K's of NCH and NCHP were about the same value as that of nylon 6. K increases with an decrease in clay content, approaching the value of nylon 6 at a clay content of 0. The diffusion coefficient was estimated from sorption data at the early stage using

$$M_t/M_\infty = (4/\sqrt{\pi})(1/\Delta x)(Dt)^{1/2} \qquad (2)$$

where Δx is the thickness of the material, and M_t and M_∞, the amount of water sorbed in the material at time t and after an infinite time, respectively. The diffusion coefficients thus obtained are shown in Figure 6. As the figure shows, the diffusion coefficients decrease with an increase in the amount of montmorillonite and saponite. The diffusion coefficient D in NCH was lower than that in NCHP.
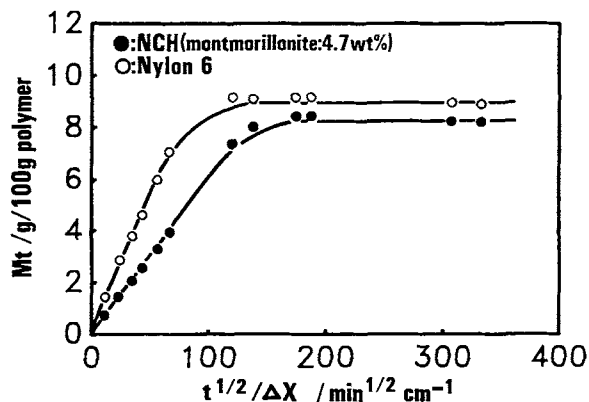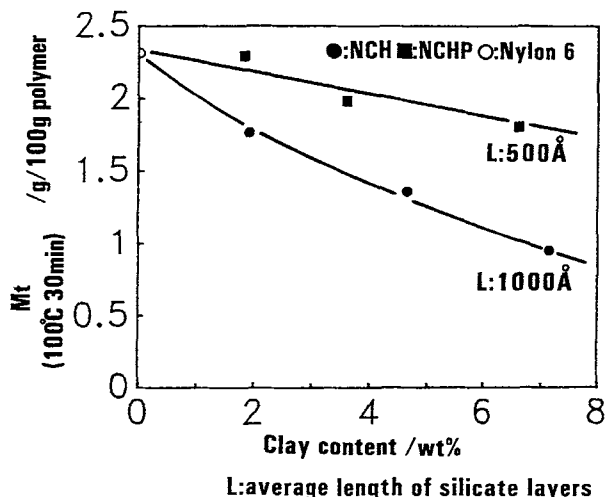
The excellent resistance to water permeation of the NCH is caused mainly by the decrease in D compared with nylon 6. A dispersion of impermeable filler and crystallite decrease the diffusion coefficient by increasing the average path length required to transport the specimen.[6,7] The average path length also depends on the size and shape and arrangement of crystallite and filler.[7] We may estimate the average path length using a concept of the constrained region obtained by the viscoelastic method.

The fraction of the constrained region in NCH can be obtained in the following manner: According to the linear viscoelastic behavior, the relationship among the energy loss fraction W, the storage modulus E', and the loss modulus E'' is given in the form[8,9]

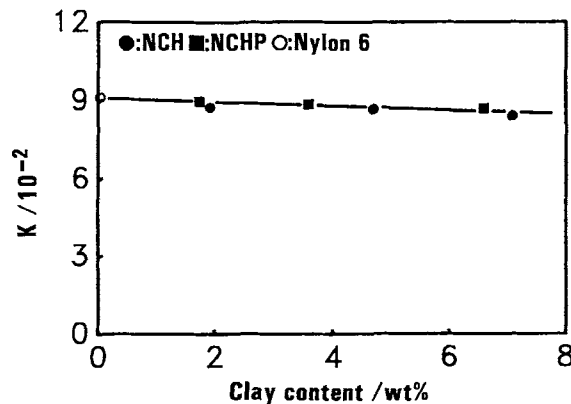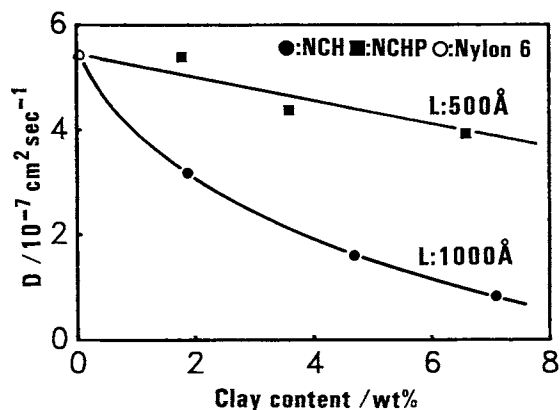**Figure 3**   Sorption curves of water.

Figure 5   Dependence of partition coefficient K on clay content.

**Figure 6**   Dependence of diffusion coefficient D on clay content.

$$W = \pi E''/(\pi E'' + E') \quad (3)$$

The energy loss fraction W at the glass transition temperature increases with the decrease in the crystallinity.[10] Then, the energy loss fraction W of NCH at the glass transition temperature is expressed by the dynamic viscoelastic data in the form

$$W = \frac{(1 - C)}{(1 - C_o)} W_o \quad (4)$$

where C is the fraction of the constrained region, $(1 - C)$ is the fraction of the amorphous region; and subscript o denotes nylon 6. Equation (4) is rearranged as follows:

$$C = \frac{W}{W_o}(1 - C_o) \quad (5)$$
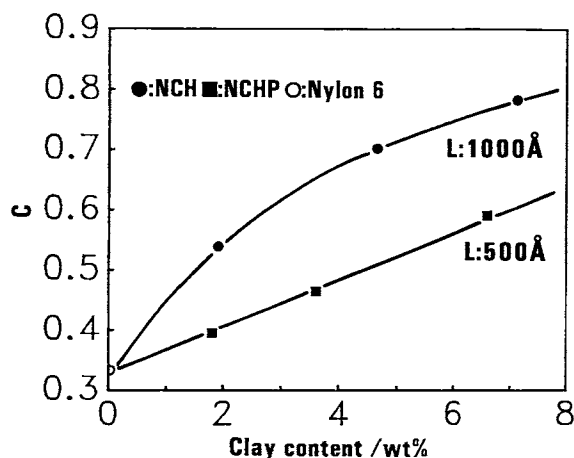
Figure 7   Fraction of constrained region C vs. clay content.

where the energy loss fraction at the glass transition temperature $(54-63°C)$[3] is obtained at 10 Hz, and W_o and C_o is 0.249 and 0.333 (crystallinity of nylon 6 obtained by DSC), respectively. The fraction of the constrained region C of NCH can then be estimated from eq. (5). Figure 7 shows the fraction of the constrained region C as a function of the clay content. C increases with an increase in clay content. The fraction of the constrained region in NCH is higher than the value in NCHP. Therefore, C depends on the length and content of the silicate layers. The crystallinity of nylon 6 in the hybrids is a little lower than that in nylon 6. It is considered that the crystallinity in the hybrids is not effective in increasing C. We have shown that the silicate layers have face orientation in the hybrid. Thus, it could reasonably be assumed that another factor to increase the constrained region in the hybrid is the face orientation of the silicate layers. The diffusion coefficient D is plotted against the C calculated using eq. (5) for various NCHs and NCHPs in Figure 8. D increases inversely with increasing C. It is noted that the diffusion coefficient is well described by the contribution of the constrained region.

For a two-phase system, the diffusion coefficient is represented by the mixing law.[11] The relationship between the diffusion coefficient D and the fraction of the constrained region C is assumed as the following expression:

$$D^n = (1 - C)D_a^n + CD_c^n \quad (6)$$

where D_a and D_c are the diffusion coefficients in the amorphous region and constrained region, respectively. n is a morphology parameter and changes from -1 to 1. It is assumed that D_c is much smaller than is D_a; eq. (6) approximately becomes eq. (7):
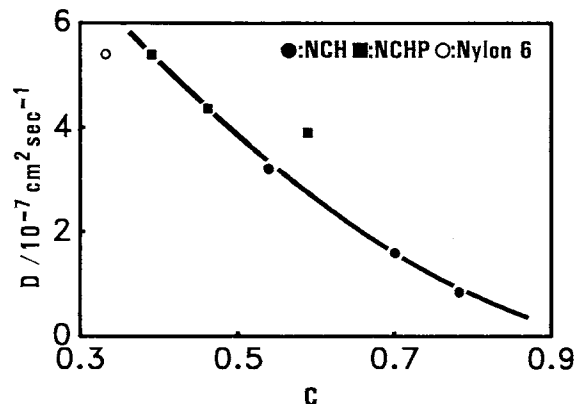
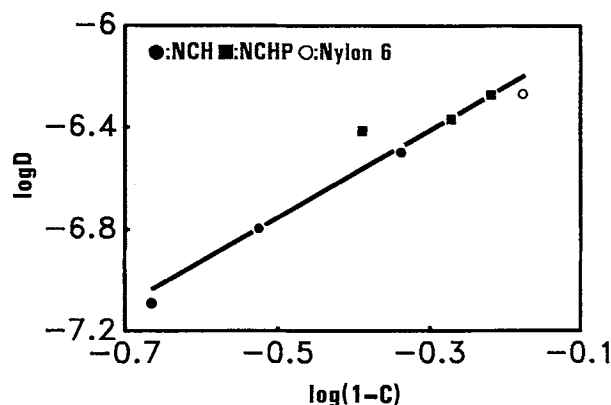**Figure 8**   Diffusion coefficient D vs. fraction of constrained region C.

Figure 9 Relation between log D and log$(1 - C)$.

$$D = D_a(1 - C)^{1/n} \qquad (7)$$

Equation (7) shows that the relation between log D and log$(1 - C)$ should be linear, and this relation is demonstrated in Figure 9. We found the linear relation between the logarithm of D and the logarithm of $(1 - C)$ and that the values of D_a and n are estimated as 12.6×10^{-7} cm^2/s and 0.585, respectively. Thus, the diffusion coefficient in the hybrid is represented by the mixing law. We can calculate the diffusion coefficient from the fraction of the constrained region by the equation.

CONCLUSION

NCH has excellent resistance to water permeation because of a decrease in the diffusion coefficient compared with that of nylon 6. The diffusion coefficient decreased with increase in the length and content of the silicate layers. The diffusion coefficient was well described by the contribution of the constrained region calculated from the storage and the loss modulus at the glass transition temperature. Furthermore, we obtained the relation between the diffusion coefficient and the fraction of the constrained region.

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