Thermal and Mechanical Properties of Nylon6-clay Hybrids

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1. INTRODUCTION

Recently, attention has been paid to the nanocomposites in the field of polymeric composites. The nanocomposites are expected to have excellent properties owing to the dispersed phase has nano order dimension. Montmorillonite is a clay having layer structure and its silicate monolayer has nano order dimension. In order to obtain nanocomposites, the use of the intercalation of the clay is one of the useful methods. By using this method, Nylon6-clay hybrid (NCH) has been developed. The silicate layers in NCH are supposed to be well dispersed in the PA6 matrix. The preparation and the structure of NCH can be seen in another papers[1-5]. It has been reported that NCH has good mechanical properties, for example, high modulus, high distortion temperature. Although the structure and properties of isotropic NCH have been studied, those of anisotropic drawn NCH have not been studied yet.

In this work, the structure and properties of NCH including drawn samples have been investigated using mainly X-ray scattering methods.

2. EXPERIMENTAL

2.1 Materials

Two NCH samples with 2wt% and 5wt% clay contents and one nylon6 (PA6) sample were supplied by Ube Kosan. NCH2 and NCH5 indicates 2wt% and 5wt% clay content samples, respectively. From these pellet samples, we obtained extruded strands by using a flow tester (Shimazu). The extruded strands were further drawn and then annealed using the zone-drawing apparatus shown in Fig.1. Furthermore, NCH films were also used in this work.

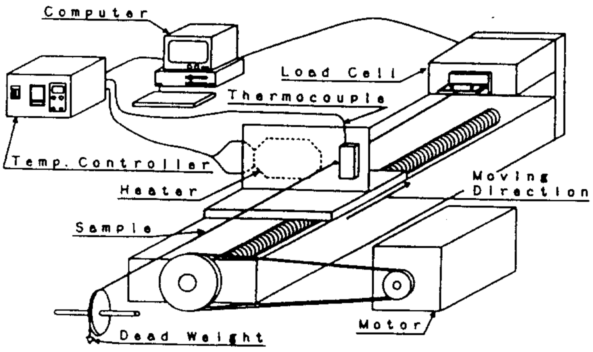

Fig.1 Schematic diagram of zone-drawing apparatus.

2.2 Measurements

Polarized optical microscope, DSC, Wide angle X-ray (WAXD) apparatus and small angle X-ray (SAXD) apparatus were used to estimate the structure of NCH. The absorption of water by NCH was also estimated.

3. RESULTS AND DISCUSSION

3.1 Structure of NCH

SAXD photographs were taken to the extruded NCH strands. In spite of clay content, there is a sharp streak of intensity on equator, although the streak cannot be seen in the PA6 strand. This means that the streak is attributed to the clay, the clay has anisotropic dimensions and that the clay is oriented to the extruded direction. WAXD photographs were also taken to extruded NCH strands. The reflection from clays can be seen around the beam-stopper. It also indicates the uniaxial orientation of clay layers. Although the crystallites of nylon6 have γ-form in spite of existence of clays, PA6 sample shows no special crystal orientation and instead, NCH shows preferred orientation. This means that the formation of crystallites is affected by the existence of clay layers. That is, in the case of NCH, it is found that the fiber axis of the crystallites is perpendicular to the extruded direction. Furthermore, it should be noted that the layers of clay are oriented along the extruded direction under gravity only, although the PA6 crystallites are not oriented. WAXD and SAXD photographs were taken to the zone-drawn NCH strands. The crystallites are oriented and α-form crystallites can be seen. SAXD shows that the streak on equator is wider by drawing. This may imply that layer of clay becomes thinner with drawing. In other words, it is thought that silicate monolayers are not well dispersed but form very small size of cluster in the original NCH strands.

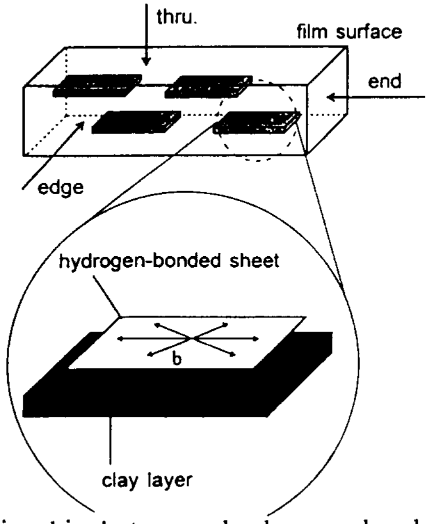

Fig.2 Geometrical relationship between clay layer and nylon6 crystallite.

In order to investigate the relation between the geometry of clay layer and that of nylon6 crystallites in detail, the structure of rolled films has been studied. SAXD photographs were taken to the rolled NCH films. In the case of incident X-ray beam being through direction, a streak of intensity cannot be seen on equator. However, a strong intensity can be seen in the case of the incidence from edge and end directions. This means that the surface of clay layer is parallel to film surface. WAXD photographs were also taken to the rolled NCH films. Although PA6 shows no orientation of crystallites, NCH shows preferred orientation of crystallites. From the reciprocal picture of the WAXD patterns of NCH, we concluded that the hydrogen-sheets are formed being parallel to the clay surface. From the discussion, the geometrical relationship between the clay layer and PA6 crystallites can be obtained. The result is shown in Fig.2

The effects of annealing on the crystal structure is investigated. Two rings can be seen in PA6. This implies that the crystal structure of PA6 can be easily transformed from γ- to α-form by annealing. However, the crystallites of NCH does not exhibit such a transformation. This means that there is a strong interaction between clay layer and PA6 crystallites in NCH.

Although the thermal properties are also studied by DSC, the results will be showed in the conference.

3.2 Zone-drawing Process

Lateral surfaces of zone-drawn NCH samples were observed by optical microscope. The NCH sample kept at room temperature shows voids formation during the drawing process. However, PA6 does not shows the voids. This means that migration of water is difficult during the drawing process of NCH sample. That is, the migration is obstructed by the clay layers in the NCH. In order to ascertain this conclusion, we measured the absorption behavior of water of NCH. From the measurement, we found that this conclusion is right.

Table 1 Young's Modulus of Various Samples

Sample	Young's modulus (GPa)
NCH5 (UD)	3.917
NCH2 (UD)	2.968
PA6 (UD)	2.081
NCH5 (UDA)	4.176
NCH2 (UDA)	3.385
PA6 (UDA)	2.630
NCH5 (ZD)	7.748
NCH2 (ZD)	5.989
PA6 (ZD)	5.955
NCH5 (ZDA)	8.073
NCH2 (ZDA)	7.254
PA6 (ZDA)	7.192

UD: undrawn ZD: zone drawn
UDA: annealed UD ZDA: annealed ZD

3.3 Mechanical Properties

Table 1 shows the mechanical properties of extruded samples, zone-drawn (ZD) and zone-drawn-annealed (ZDA) samples; the samples used were well dried. Although the modulus of NCH is higher than PA6, it is found that the drawn samples do not show a remarkable increase of modulus by introducing clay.

4. CONCLUSION

1. There is a interaction between clay layer and PA6 crystallites. Namely, hydrogen-sheets are formed parallel to clay layer and the interaction hinders the transition of crystallites from γ to α.
2. The clay layer hinders the migration of water.
3. The modulus of samples is remarkably increased with a small amount of clay in the case of undrawn isotropic samples. However, the drawn sample does not show a marked increase of modulus with clay content.

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