An attempt to prepare a layer-type complex of clay and carbon

Much work has been published on the layer-type complexes of clay and organic compounds e.g. [1]. Some investigators have extended this work to prepare clay–polymer complexes e.g. [2, 3]. In the carbon field other investigators have thermally decomposed organic polymers to give carbon material with desirable properties [4]. Both facts, we thought, suggest that the layer-type complex of clay and carbon may be prepared by heat-treating the clay–polymer complex, and a complex of this kind may have interesting properties, in view of the properties of clay and carbon. This letter reports the thermal decomposition behaviour of the layer-type complex of montmorillonite clay and α-naphthylamine. Details of the structure and properties of the resulting complex will be reported later.

Raw montmorillonite (particle size: 2 μm) was converted into the cation form with lithium (Li-mont) and a self-supporting film was prepared from it. The preparation procedure followed is reported by Yamanaka *et al.* [5]. In order to prepare the complex, 0.3 g of the self-supporting film was soaked in $50\,\mathrm{cm}^3$ of 0.4 N aqueous solution of α-naphthylamine(NA) hydrochloride, $C_{10}H_6NH_2 \cdot HCl$, at 80° C for 24 h. After soaking, the self-supporting film was washed with acetone to remove NA from its surface. To polymerize the NA monomer, the film was subjected to γ-radiation (12 mrad) in a sealed glass tube, followed by heat-treatment at 200° C for 1 h. The film was

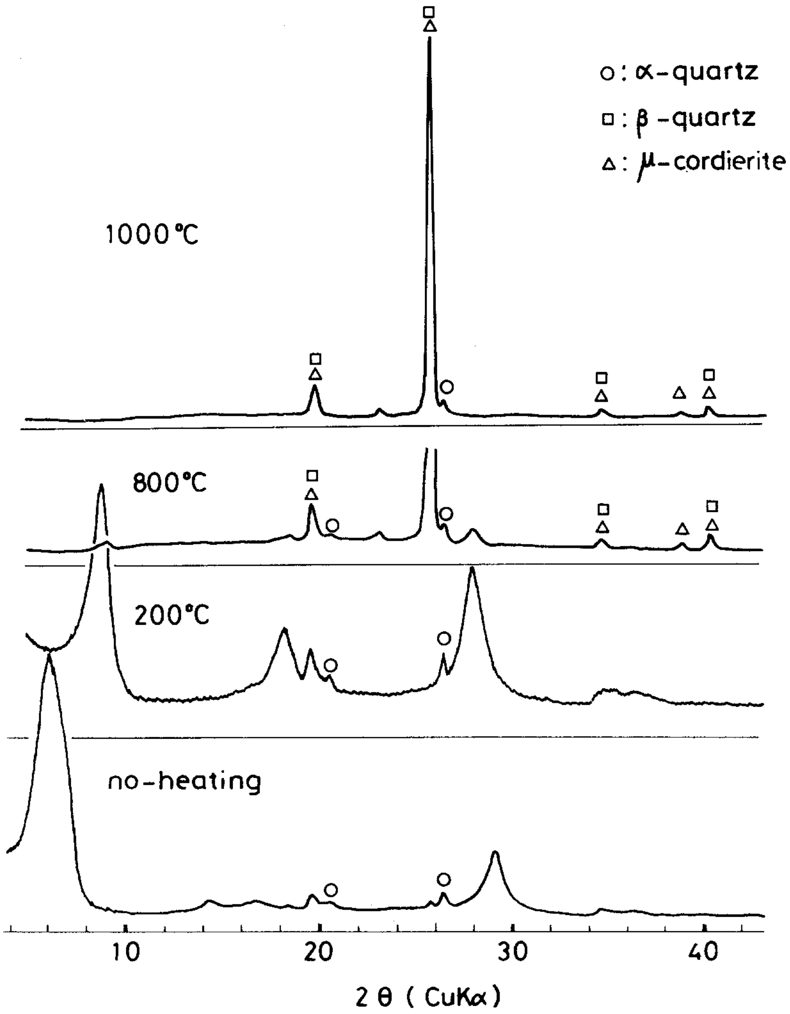

Figure 1 Change in X-ray diffraction profiles of Li-mont with heat-treatment.

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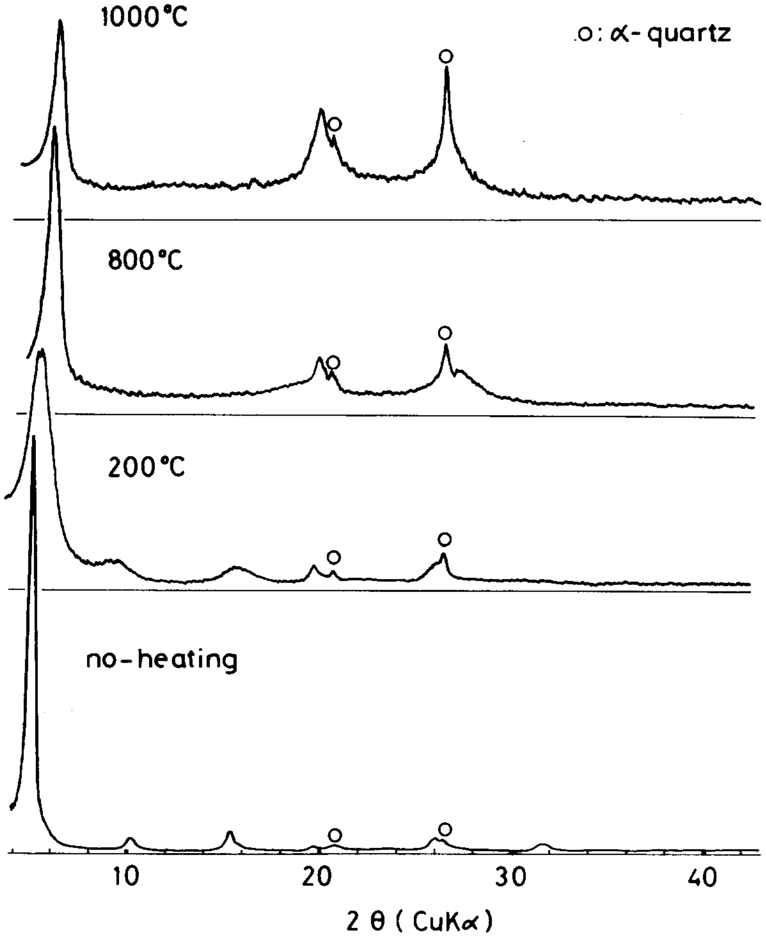

Figure 2 Change in X-ray diffraction profiles of the Li-mont–NA complex with heat-treatment.

taken out of the tube and heat-treated at higher temperatures under a nitrogen atmosphere. Li-mont was also heat-treated.

Figs. 1 and 2 show changes in X-ray diffraction profiles of Li-mont and the Li-mont–NA complex after heat-treatment. Table I shows the basal spacing values of these samples. The basal spacing of Li-mont decreased from 14.5 to 10.1 Å on heating at 200° C as a result of dehydration. The basal spacing continued to decrease, though only slightly, to 9.6 Å on heat-treatment up to 600° C. At 800° C, the layered structure of Li-mont decomposed to β-quartz and μ-cordierite.

TABLE I Basal spacings of Li-mont and the Li-mont–NA complex

Heat-treatment temperature (° C)	Li-mont spacings (Å)	Li-mont–NA spacings (Å)
no-heating	14.5	17.3
200	10.1	16.4
800	–*	14.5
1000	–*	14.3

*The layer structure was destroyed.

The basal spacing of the Li-mont–NA complex was 17.3 Å, this value is larger than that of Li-mont heated to 200° C by 7.2 Å. After γ-radiation and heating to 200° C, the spacing decreased to 16.4 Å. The most interesting feature of this work is that the Li-mont–NA complex retains the layer-type structure even after heating to 1000° C, as can be seen in Fig. 2. Its basal spacing is nearly equal to that of Li-mont with no heat-treatment. Elemental analysis of the 1000° C Li-mont–NA complex gave the following results; 15 wt % C, 0.3 wt % N (atomic ratio N/C = 1/55). Compared with the atomic ratio of N/C = 1/10 for NA, the ratio of N/C for the 1000° C sample is very small. These results suggest that after heat-treatment at 1000° C, NA decomposes to give a layer consisting mainly of carbon. At present, we have no data on the thermal decomposition of the Li-mont–NA complex at higher temperatures. Considering the phenomenum reported in this letter, it seems that it would be possible to prepare a layer-type complex of clay and carbon.

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Small-angle X-ray scattering from polybutene-1 films crystallized from a highly extended melt

In an experimental analogue to many industrial processes, Petermann and Gohil [1] have produced very thin (0.1–0.2 micron) polymer films under elongational strain rates of more than 10^4sec^{-1}. The microstructure of these films is thus of considerable technological importance. As is the case in most materials science research, it is essential to characterize such films with a variety of physical techniques. These films are sufficiently thin to permit transmission electron microscopy (TEM), and the results of such an investigation have been reported previously [1]. In this companion paper, we present results of a small-angle X-ray scattering (SAXS) investigation of the same films.

Phase contrast TEM micrographs of polybutene-1 (PB-1) show a fibrous microstructure with the fibrils oriented along the draw direction [1]. (See [2] for a description of the method). The chain and fibril axes coincide. The fibril spacing is approximately 200 Å, while the fibril diameter is approximately 100 Å. No lamellar overgrowths on the fibrils were observed for any annealing conditions.

Dark-field $(h\,k\,0)$ TEM micrographs, also shown in [1], reveal an alternating dark–light contrast along the fibrils. The mean periodicity of this contrast is ~ 300 Å. Whether this dark–light contrast reflects an orientation or a density variation cannot be determined from TEM alone. In the present work, SAXS was used to study the same films. SAXS is sensitive only to electron density fluctuations, and hence should be useful in identifying the nature of the dark-field contrast alternation along the fibrils. The method also provides a quantitative evaluation of fibril dimensions.

PB-1 materials were supplied by Chemische Werke Marl. Four materials, of viscosity average molecular weights 5.54×10^5, 8.02×10^5, 10.32×10^5 and 30.0×10^5, were used. Films, approximately 1000 Å thick and 5 cm wide, were prepared by drawing from a molten film on a microscope slide held at 132° C as described in [1]. Adhesion of the film to the slide causes the drawing region to be highly localized.

The experiments were performed using the ORNL 10-m SAXS camera [3]. This instrument includes a 6 kW rotating anode X-ray source (CuKα radiation), a graphite monochromator, pinhole collimation and a two-dimensional position sensitive proportional counter. Data were collected using the instrument in its highest resolution geometry, with a specimen-to-detector distance of 5.15 m and an angular resolution of approximately 0.5 mrad.

The most useful information available from SAXS from these specimens relates to (1) density modulation along the fibre direction and (2) the diameters of the fibrillar units. As we already know the approximate diameters of the fibrils from the TEM investigation, the principal atten-