Microhardness of sintered poly(4-hydroxybenzoate) and poly(2-hydroxy-6-naphtoate) homopolymers: Influence of pressure and morphology

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In recent years much scientific attention has been focused on the structure and physical properties of thermotropic liquid crystalline copolyesters of 2-hydroxy-6-naphtic acid (HBA) with 4-hydroxybenzoic acid (HNA). The homopolymers poly(4-hydroxybenzoate) (PHBA) and poly(2-hydroxy-6-naphtoate) (PHNA) have been investigated to a lesser extent due to their difficult processability. High molecular weight PHBA was first synthesized by Economy *et al.* [1] and commercialized under the tradename Ekonol. The nature of the thermal transitions [2–5], crystal structure [2, 6–10] and synthesis of PHBA have been reported [11, 12]. On the other hand, since its development in 1983, the amount of published work on PHNA has been comparatively small [13–15], emphasizing mainly the similarities and differences with PHBA. Direct evidence of the trans-esterification reactions that take place in a mixture of PHBA and PHNA under given conditions of pressure and temperature has also been provided [16].

PHNA and PHBA are obtained in powder form, which can be further fabricated by sintering at temperatures above 400 °C for a short time before the onset of degradation [17]. Depending on the synthesis method, both materials show very different morphologies: fibrous, columnar or needle-like single crystals called whiskers or slab-like polycrystalline aggregates [12, 14]. Such whiskers may be of interest as reinforcing fibres for other matrix polymers such as Nylon-6 [18].

The purpose of this letter is twofold. Firstly, it reports on an investigation of the surface mechanical properties of cold sintered homopolyesters as a function of applied pressure, using the microhardness technique. A point of interest was to discover the influence of crystal morphology on the final properties, taking into account the few available reports on the sintering of semi-crystalline thermoplastics [19]. Secondly, the above results and the results obtained by extrapolation to high pressures are compared with the mechanical properties of compression moulded materials at 400 °C. A study of the microhardness of the series of copolyesters P(HBA/HNA) will be the object of a separate paper [20].

Microhardness is a measure of the local resistance of the material surface to plastic deformation. This mechanical property has been proved to be sensitive

to the microstructural changes occurring, both in the amorphous and crystalline phases [21, 22]. Furthermore, microhardness is directly related to the macroscopic mechanical properties of the material [21–23]. Consequently, it is an appropriate technique for evaluating the mechanical properties of these systems and their dependence on crystal morphology.

Samples of PHNA and PHBA were synthesized at the University of Hamburg under several reaction conditions leading to different crystal morphologies. Details of the synthesis and characterization can be found elsewhere [11, 12, 14]. The powder samples were cold sintered for 10 min at pressures ranging between 0.19 and 0.93 GPa. Pellets of thickness ~1 mm were finally obtained. Some of the samples were subsequently compression moulded (100 MPa) at 400 °C for 3 min. This temperature is above the first transition of both materials at ~350 °C but below the melting point in the mesophase (~450 °C) where degradation becomes important.

Micro-indentations were produced at room temperature using a square based diamond. Microhardness, H , applied force, F , and diagonal length of the indentation, d , are related through the following equation:

$$H = K \frac{F}{d^2} \quad (1)$$

where K is a geometric constant equal to 1.854. Loads of 0.25, 0.49, 0.98 and 1.96 N were applied. A loading cycle of 0.1 min was used. The length of the impression was measured with an eyepiece micrometer up to $\pm 1 \mu\text{m}$.

X-ray diffraction (XRD) patterns at room temperature of the two homopolymers with different crystal morphologies were recorded using a 40 kV and 140 mA source. Crystallinity was calculated from the total scattering area after subtraction of the estimated non-crystalline scattering halo. The microhardness of PHNA and PHBA samples in the different morphologies was measured at room temperature for each pressure applied to the material in the sintering process.

Fig. 1 shows the indentation load F as a function of the square of the indentation diagonal d for PHNA and PHBA homopolymers sintered at three different pressures. The slope of the straight lines in Fig. 1 is proportional to the microhardness value according to

Figure 1 Indentation load plotted against the squared indentation diagonal for sintering pressures of (a) 0.19, (b) 0.56 and (c) 0.93 GPa. Upper row, PHNA; lower row, PHBA.

Equation 1. It can be observed that for PHNA samples, the microhardness corresponding to a needle-like morphology is higher than that corresponding to a slab-like morphology. For PHBA, the microhardness increases in the following order: columnar whiskers, slab-like crystals and fibrous whiskers. XRD revealed that for PHNA the crystallinities of the samples with slab-like and needle-like morphologies were 0.53 and 0.64, respectively. The broadening of the crystalline reflections also showed a higher degree of crystal perfection in the latter. This result is in agreement with the wide angle X-ray spectroscopy (WAXS) diffraction data and calorimetric results published by Schwarz and Kricheldorf [14]. From these results one could attempt to establish a correlation between the degree of crystalline perfection and the microhardness value. However, for the three investigated PHBA morphologies it is observed that the higher microhardness values correspond to the sintered fibrous whiskers which, according to the WAXS results, show the lowest crystallinity of the series.

Fig. 2 shows the plot of microhardness as a function of $1/P$ for the two homopolymers and their different crystal morphologies. The microhardness values increase linearly, as a first approximation, with increasing applied pressure, P , as a consequence of a more effective intergranular packing. The intersection of each linear plot with the H -axis yields an extrapolated value of the microhardness at a theoretical infinite pressure of the sintering process, $1/P=0$. These values are, respectively, 174 and 146 MPa for the needle-like whiskers and the slab-like crystals of PHNA, and 146, 172 and 217 MPa for the columnar whiskers, the slab-like crystals and the fibrous whiskers of PHBA. As mentioned above, there is no correlation between the microhardness values and the crystallinity content or coherent crystal size of the materials. Other factors, such as particle morphology, may have a determinant role in

Figure 2 Microhardness as a function of the reciprocal value of the sintering pressure. (∇ , $\circ$), PHBA; ($\blacktriangle$, $\bullet$), PHNA; ($\blacktriangle$), needle-like or columnar whiskers; (∇), fibrous whiskers; ($\circ$, $\bullet$), slab-like aggregates.

defining sintering behaviour. Reducing surface area is the principal driving force in the sintering process, hence finely divided powders with high surface area would be expected to sinter more rapidly [19]. It is worth mentioning that the above microhardness results were measured after the applied load was removed from the surface. Results obtained when the material is under load showed much lower surface mechanical values, indicating an $\sim 50\%$ elastic recovery for the indentation diagonal length of the sintered materials.

Temperature is a further parameter that should increase the efficiency of the diffusion process during sintering. For this purpose the microhardness of the compression moulded samples was examined. The obtained microhardness values, measured at room temperature, were 191, 171 and 170 MPa for those

samples obtained from the columnar whiskers, the slab-like crystals and the fibrous whiskers of PHBA, and 310 MPa for the PHNA sample originally in its slab-like morphology. It is noteworthy that these values are much higher than the extrapolated ones to infinite pressure in Fig. 2, after correction of the elastic recovery, suggesting that the sintering process at room temperature is not sufficient to induce a molecular diffusion similar to that occurring at moderate pressure when heating the sample above its first transition temperature. In the latter process, the initial morphology of the crystallites is lost, and the microstructure (crystallinity and crystal size and perfection) determines the final value of microhardness.

Furthermore, we have measured the microhardness of the compression moulded PHBA samples as a function of loading time under the indenter. The results are shown in Fig. 3. The time dependence of the hardness under the indenter follows a law of the type [21]:

$$H = H_{0.1}t^{-k} \quad (2)$$

where $H_{0.1}$ is the hardness value at a given reference time (0.1 min) and the slope k of the straight lines in Fig. 3 provides a quantitative measure of the rate of creep under the indenter. It was observed that the creep constant, k , decreases with crystallinity, ranging from 2.4×10^{-2} for the columnar whiskers to 3.7×10^{-2} for the fibrous ones. This result is consistent with the fact that creep is favoured in those materials with a less well-developed crystalline structure.

Finally, we wish to point out the remarkable mechanical properties of PHBA and PHNA, particularly, as compared with other conventional polymers. We have found a microhardness value for PHNA as high as 310 MPa, while typical values for polyethylene and poly(ethylene terephthalate) are, respectively, 80 and 200 MPa.

Figure 3 Log-log plot of the microhardness as a function of indentation time for PHBA compression moulded materials. (Δ), Needle-like or columnar whiskers; (∇), fibrous whiskers; ($\circ$), slab-like aggregates.

In conclusion, it is shown that both the sintering pressure and the morphology of micro-crystals are factors that directly affect the surface mechanical properties of sintered thermotropic homopolyesters. Compression moulding at high temperature yields materials with the best mechanical properties, depending on overall structure and crystallinity rather than morphology.

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