# Mechanical model on polyethylene blends as revealed by microhardness

J. MARTINEZ-SALAZAR, F. J. BALTÁ-CALLEJA
*Instituto de Estructura de la Materia, CSIC, Serrano 119, Madrid-6, Spain*

The increasing interest in composite materials has led in recent years to many attempts to relate their mechanical behaviour to that of the constituent phases. To this end several theoretical developments have concentrated on the study of the elastic modulus of two-component systems [1–3]. Specifically, the application of composite theories to relationships between elastic modulus and microstructure admittedly applies for semicrystalline polymers exhibiting distinct crystalline and amorphous phases [4]. Furthermore, the elastic modulus has been shown to be correlated to microhardness (MH) for lamellar polyethylene (PE) [5]. MH has been suggested, in fact, to be also an adequate property to describe a semicrystalline polymer as a composite material consisting of alternating stiff and compliant elements [6]. Application of this concept to lamellar PE poses, nevertheless, certain difficulties. Firstly, this material has a complex microstructure which requires sophisticated methods of analysis involving the calculation of volume fraction of crystallized material, crystal shape and dimensions, crystalline perfection, etc. Secondly, it is impossible to separate the two phases to measure the single mechanical properties. Hence only limiting values for the MH of the crystals ($H_c$) and for the disordered phase ($H_a$) have been, so far, tentatively estimated and a parallel arrangement for the MH of lamellar polyethylene (PE) has been suggested [6]. Thus, no direct evidence for the $H_c$ and $H_a$ values of the single components is available.

The object of the present study is, firstly, to investigate the MH of a model system composed of varying mixtures of two PE types with well differentiated hardness values in such a way that the experimental hardness data derived can be compared with predictions of the various component arrangements. On the other hand, the MH measurement of these polyblends at high temperature can furnish a direct information on the hardness value of the disordered phase. The mechanical characterization of these blends is also of evident interest from the viewpoint of the production of new materials with novel properties.

Solution crystallized mixed polyblends of high density (HD) and low density (LD) ($3CH_3/100CH_2$) PE with $M_w \sim 50 \times 10^3$ have been prepared in various composition ranges. The samples were crystallized from the melt in two modes: (a) by slow cooling ($0.2°C\,min^{-1}$) and (b) by quenching, to room temperature. The intimate mixture of the two molecular species has been indicated by the decrease observed in the crystallization temperature of the linear component with the increasing proportion of the branched polymer [7]. Wide angle X-ray diffraction analysis reveals, in addition, that the branch molecules do not incorporate within the linear polymer crystals [8]. This result is also confirmed by the presence of two peaks in the thermograms of the samples [7]. The MH was measured using a Leitz tester with a square pyramidal indenter. The MH has been calculated from the residual projected area according to $MH = K(P/d^2)$, $d$ being the length of the impression diagonal, $P$ being the contact load applied and $K$ being a geometrical factor equal to 18.54. A loading cycle of 0.1 min was used. Loads of 0.25 and 0.5 N were employed to investigate the instant elastic contribution. For MH measurements at high temperature a heating stage was designed. The temperature was calibrated using a thermocouple located at the tip of the diamond. A temperature variation smaller than $1°C$ was detected instantly when the diamond penetrates into the polymer surface.

In what follows examples are given in which a model is used to predict quantitatively the MH of PE blends. Fig. 1 shows, for the materials slowly crystallized from the melt (curve A), the linear decrease of the hardness of the linear polymer with increasing concentration of the branched
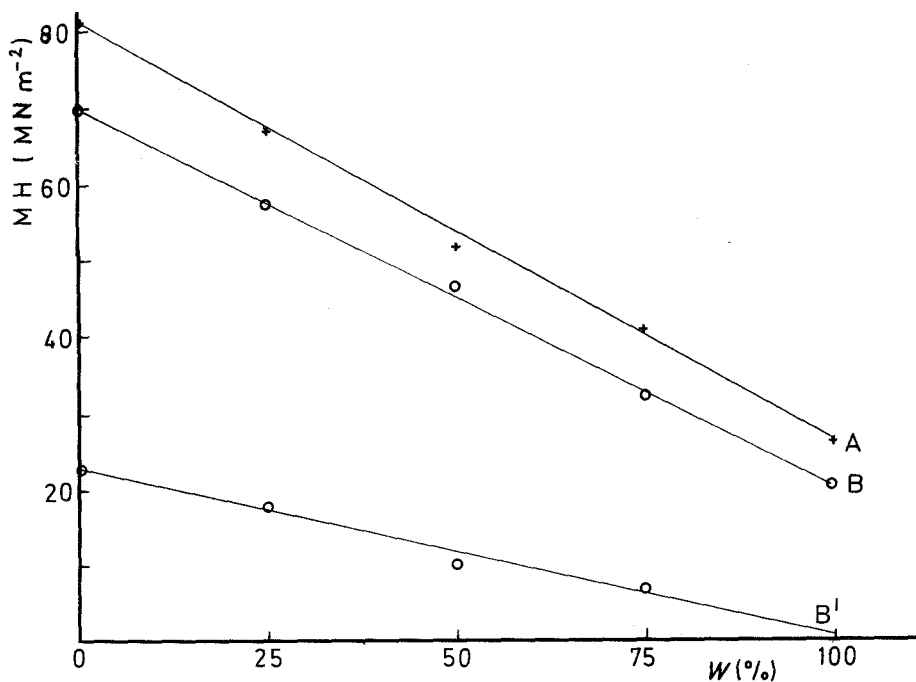
*Figure 1* Microhardness of melt crystallized blends of HD and LDPE as a function of increasing wt. concentration of the latter component. Curve A, slowly cooled crystallized samples, curve B quenched material measured at room temperature, and curve B', quenched material measured at 110° C.

material from $80\,MN\,m^{-2}$ down to $30\,MN\,m^{-2}$ for 100% of (LD) component. A similar linear behaviour is obtained for a quenched material (curve B). The MH values are, however, smaller (70 and $25\,MN\,m^{-2}$ for the HD and LD components, respectively) owing to the smaller thickness of the crystals of both components [9]. The addition of MH for this system composed of two types of crystals, LD and HD, follows the expression $H_{blend} = H_1 w + H_2(1 - w)$, which is immediately identified as a parallel composite model, where $H_1$ and $H_2$ are the hardness values of the two independent components and $w$ is the weight concentration of the LDPE component. This emphasizes the validity of a distinct phase microhardness for these PE blends. This is probably due to the above mentioned molecular segregation at a crystal level. The hardness for the blends measured at high temperature shows substantially lower values. This is a consequence of a decrease in the chain packing within the crystals [6, 10]. The decrease in MH for the quenched samples measured at high temperature (110° C) is linear too, showing a lower slope. This is due to the fact that the rate of hardness-decrease is proportional to the crystallinity. Hence, the HD component contributes to a faster MH decrease than the LD

component. At the temperature where the LD component melts (110° C) the hardness value for 100% LDPE, obviously, cannot be measured experimentally. However, it can be extrapolated. This extrapolation yields a value for the hardness of amorphous PE of $\sim 0.5\,MN\,m^{-2}$. Such a value is in consonance with estimated data of branched material extrapolated to the hardness of amorphous PE at room temperature [6].

In conclusion, microhardness is shown to be a promising technique for the microstructural investigation of polyblends of known composition and can provide information on the level of structural segregation. In particular, the present study confirms that the hardness of the studied PE blends can be explained in terms of a parallel simple additive system of two independent components $H_1$ and $H_2$. Finally, the hardness of the amorphous phase turns out to be of the order of $0.5\,MN\,m^{-2}$ yielding a ratio $H_c/H_a \sim 200$ for melt crystallized linear PE.

## References

1. R. G. C. ARRIDGE, "Mechanics of Polymers" (Clarendon Press, Oxford, 1975) p. 98.
2. R. HILL, *J. Mech. Phys. Solids* **1** (1963) 357.
3. J. L. KARDOS and J. RAISONI, *Polym. Eng. Sci.* **15** (1975) 183.
4. E. H. ANDREWS, *Pure Appl. Chem.* **39** (1974) 179.
5. J. MARTINEZ-SALAZAR and F. J. BALTÁ-CALLEJA, *J. Mater. Sci.* **18** (1983) 1077.
6. F. J. BALTÁ-CALLEJA, J. MARTINEZ-SALAZAR, H. CACKOVIĆ and J. LOBODA-CACKOVIĆ, *ibid.* **16** (1981) 739.
7. J. MARTINEZ-SALAZAR, E. LÓPEZ CABARCOS and F. J. BALTÁ-CALLEJA, Proceedings of the 16th EPS Conference on Macromolecular Physics, Bruges, 1984.
8. J. MARTINEZ-SALAZAR, unpublished results.
9. F. J. BALTÁ-CALLEJA, *Colloid Polym. Sci.* **254** (1976) 258.
10. J. MARTINEZ-SALAZAR and F. J. BALTÁ-CALLEJA, to be published.