

Microhardness Studies of PMMA/Natural Rubber Blends

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ABSTRACT: The microhardness, H , of PMMA/natural rubber blends, prepared following the solution method has been investigated by means of the microindentation technique. Hardness changes are correlated with the variation of the glass transition temperature. The influence of temperature and degree of deformation on H were additionally examined. The inclusion of rubber particles in the PMMA matrix is shown to soften the blends. The variation of the micromechanical property at the phase boundary of polymer/rubber particle has been studied. Results reveal that H

drastically drops at the interphase. In the case of the drawn materials, the indentation anisotropy (ΔH) is shown to gradually increase with the draw ratio, where ΔH is found to be higher for the PMMA/rubber blend than for the original PMMA. This result is explained by the higher orientation of the PMMA molecules near the periphery of stretched rubber particles. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 205–210, 2004

Key words: hardness; rubber; blends

INTRODUCTION

Owing to its transparency, poly(methyl methacrylate) (PMMA) is often used in applications that require good optical properties. However, its brittleness manifests itself as a limiting factor for being used in the automotive industry.¹ A significant improvement in the toughness of PMMA and other glassy polymers is obtained by combination of a discrete amount of rubbery like modifier particles to introduce soft domains into the matrix.^{1–3} Methods for the preparation of such a rubber-toughened PMMA, that have been reported in the literature, include emulsion polymerization and mechanical blending.^{2–8} In these studies, the morphology and mechanical properties of these materials have been discussed. However, as far as we know, data regarding the micromechanical properties of PMMA/natural rubber (NR) blends are missing. Therefore, in the present study, blends were prepared through physical mixing of natural rubber with PMMA by the

solution method. Despite the fact that these two polymers are immiscible and cannot be properly compatibilized to make homogeneous blends, the inclusion of a small amount of NR into PMMA makes it possible to study the mechanical and thermal properties of these modified new materials. A further attempt of mechanical reinforcement of the PMMA/NR blends can be achieved by stretching the samples above the glass transition temperature.

The microindentation test has become a popular technique due to its simplicity and to the fact that it provides valuable information about the morphology and mechanical properties of polymeric materials.⁹ The indentation method has been also successfully employed to investigate the glass transition temperature of polymers.¹⁰ The effect of the processing parameters of polyolefins blends on the properties of injection molded parts was studied by microhardness.¹¹ Microindentation tests have also been performed on composites of carbon fibers embedded in thermoplastic and thermoset matrices.¹² Recently, microindentation appears as a promising tool for micromechanical and microstructural investigation of polymer blends.^{13,14} For instance, it has been found that increasing the ethylene-co-propylene rubber content into isotactic polypropylene lowers the hardness value by 30–40%.¹³

The aim of the present study is to investigate the hardness value of both PMMA and PMMA/NR blends as a function of temperature and degree of deformation. Furthermore, the influence of the phase boundaries on the mechanical properties, as studied by microindentation, has been examined.

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EXPERIMENTAL

Materials

Blends of PMMA/NR were prepared by the solution method. PMMA was produced from the monomer MMA (Merck, Germany) by the radiation polymerization technique using a dose of 0.8 kGy of γ -rays from a Co^{60} source. Natural rubber latex, having a total solid content of 35%, was supplied by Forest Industries Corporation, Bangladesh. NR films were prepared from concentrated latex, which was single centrifuged with a Saito Separator Ltd., Japan. Thereafter, these films and PMMA were separately dissolved in toluene (Merck, Germany) and the two solutions were mixed together in different proportions. From the physical appearance of the solution, it was observed that the increase of the rubber component gave rise to inhomogeneous solutions even after long stirring times using a magnetic bar. Solution blends having a PMMA/NR content in the range 100/0–95/5 were made and poured on leveled glass dices to produce the films by evaporation.

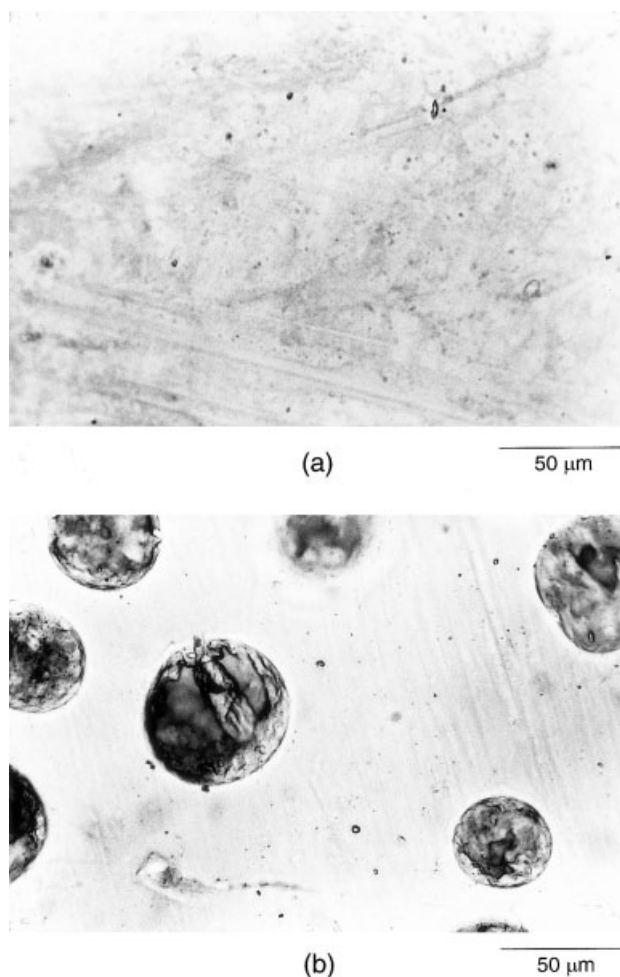


Figure 1 Surface morphology using an optical microscope, (a) original PMMA, and (b) PMMA/NR (97/3) blend.

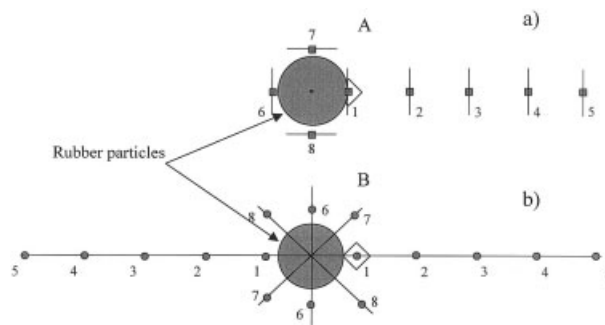


Figure 2 Schematic representation of the H measurement near rubber particles, (a) indentation taken at different distances from the center of a spherical rubber particle A, and (b) indentation taken at symmetric points on both sides of the particle B.

Techniques

The blended films containing a small NR content (~ 3 wt %) are inhomogeneous, as revealed by the optical micrographs (Leitz, Laborlux 12 Pol, Germany) of the material surface as shown in Figure 1. The inclusion of rubber in PMMA results in globule- or spherical-like particles of various sizes that are nonuniformly dispersed throughout the samples regardless the concentration. Furthermore, the rubber has the tendency to form a wider phase when its proportion in the solution is more than 3 wt %.

The microindentation hardness (H) was measured from the residual impression of a Vickers square-based diamond indenter after an indentation time of 6s. Loads of 98, 147, 245, and 490 mN were used to derive a load-independent value of H . The H -value in MPa was estimated using: $H = kp/d^2$, where d (mm) is the indentation diagonal, p (N) the applied load and k a geometric factor equal to 1.854.¹⁵ The indentation method neither can be used in the original NR films nor in the rubber particles included in the blends due to the strong elastic recovery. Accordingly indentations were only made on the PMMA matrix of the PMMA/NR blends. Ten indentations were made for each load and the H -values, for the original PMMA and the blends (1–5 wt % NR), were determined within an error of $\pm 3\%$.

In addition, the H variation (for one single load) at different distances from the center of an isolated spherical rubber particle was measured. The procedure for the measurement is schematically illustrated in Figure 2. Hardness values are obtained at various points around two rubber particles (A and B) by measuring only the diagonal length along the drawn straight lines. In the case of particle A, a hardness value was calculated for each single indentation using a load of 147 mN at various distances from the center of the spherical particle. In the case of B, an average microhardness value was determined from each pair

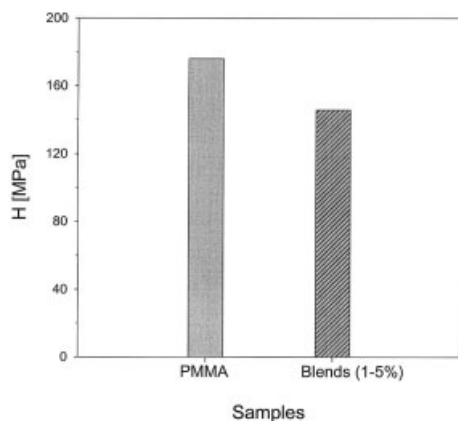


Figure 3 Comparison of H -values for PMMA and the average value for the blends.

of indentations carried out at symmetric points on both sides of the particle.

To follow the change of microhardness with temperature, a hot stage that can be controlled between room temperature and 573 K was used. The samples were mounted on the stage, and the H -value was measured using a load of 490 mN in the temperature range of 293–365 K. From these measurements, the glass transition temperature (T_g) of each sample was determined after calibrating the temperature at the surface. The T_g value of the samples was also determined by differential scanning calorimetry (DSC) using a heating rate of 20 K/min.

Because PMMA is both hard and brittle, the plastic deformation of a narrow strip of the material cannot be easily performed at room temperature. Thus, two samples (PMMA and 3 wt % blend) were stretched at temperatures above T_g . Before deformation, nearly equidistant 0.2 mm ink-lines perpendicular to the drawing direction were made onto the surface of each strip. The draw ratio (λ) was estimated as the ratio of the distance between ink-marks before and after the drawing with the help of a micrometer attached to the indenter microscope. On stretching, two necks developed in opposite directions. The steepness of the neck gradually becomes smaller with increasing draw ratio. After drawing, the samples were cooled down to room temperature, keeping them in a taut state between the clamps. H -values parallel (H_{\parallel}) and perpendicular (H_{\perp}) to the stretching direction at different draw ratios were measured.

RESULTS AND DISCUSSION

Influence of natural rubber content on the microhardness

Figure 3 shows the H -value of PMMA in comparison with the average H -value of the blends with a rubber-content in the range 1–5 wt %. As mentioned above, an

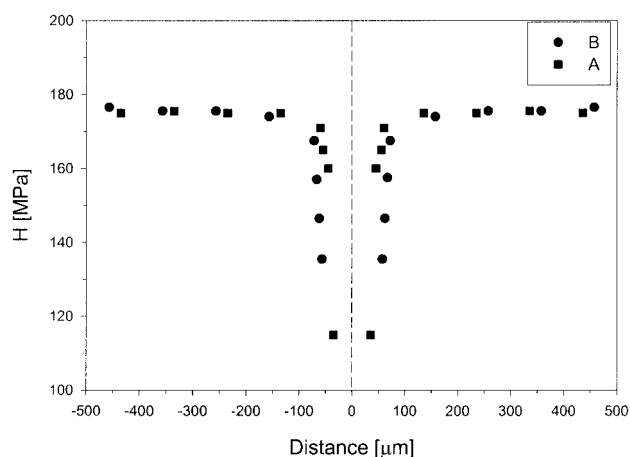


Figure 4 Variation of H with distance from the center of a rubber particle as described in Figure 2.

average value of H for blends is taken, because they all show similar hardness values due to the irregular distribution of rubber particles. It is evident that there is a hardness decrease in the case of the blends. How-

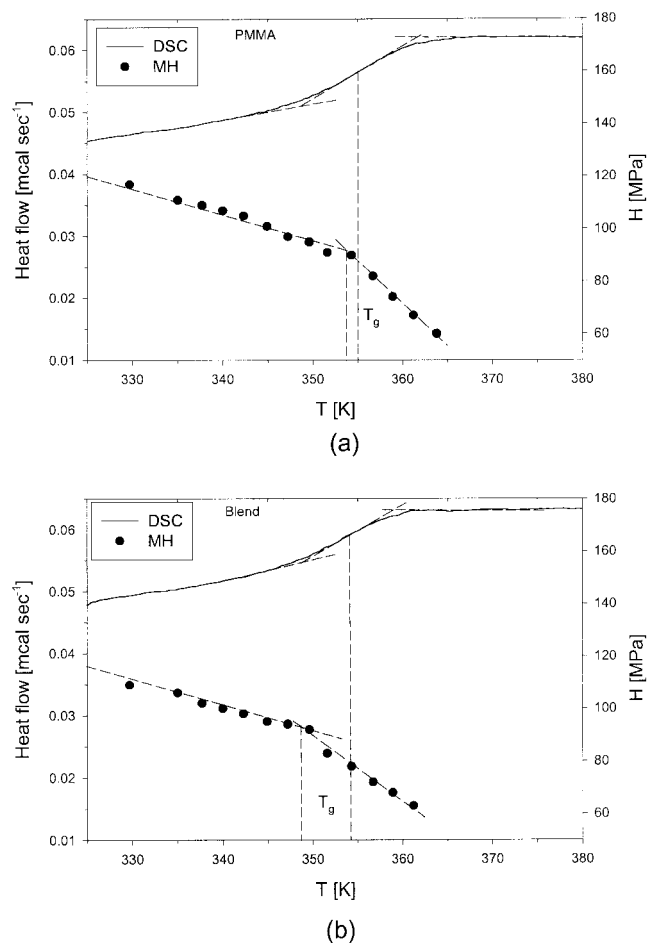


Figure 5 Comparison of T_g as measured by DSC and H techniques for (a) PMMA and (b) blend.

ever, the mechanical properties of the blends depend on those of PMMA, because the matrix is absorbing most of the stress and energy when the material is under load.

Considering the radial symmetry of the particles, the H -values measured as a function of the distance to the center of one of the particles (see Fig. 2) are represented in Figure 4. Here the variation of H is plotted as a function of distance from an average reading at two symmetric points, in the case of B, and single reading, in the case of A. The diameters of the A and B particles were about 70 and 66 μm , respectively. The two plots for A and B render the same tendency for the hardness variation observed. The lowest value of H is found in both cases at the closest point to the center of the particles. The H -values increase with distance up to a plateau, which corresponds to the value of the PMMA matrix. The steep increase of microhardness

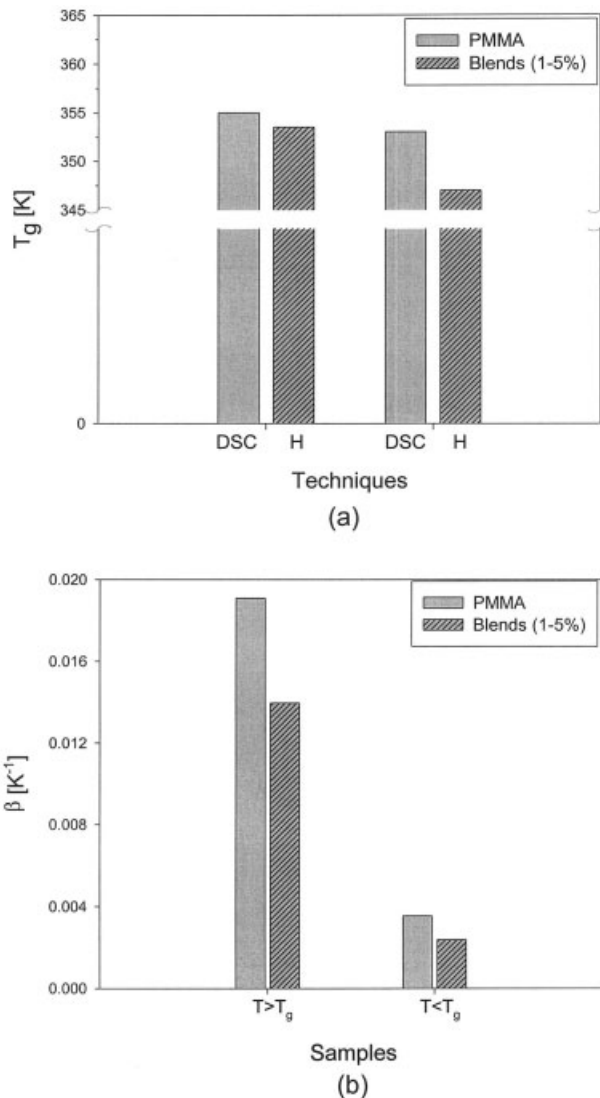


Figure 6 Average T_g values and coefficient of thermal softening, β for (a) PMMA and (b) blend.

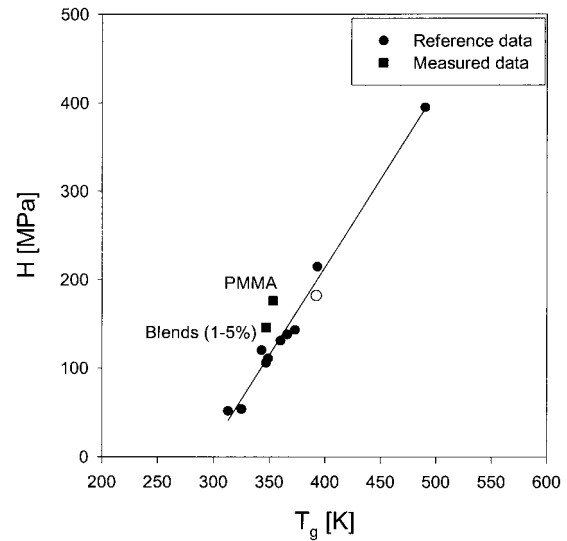


Figure 7 Relationship between room temperature-measured H and T_g . The circles correspond to the data of ref. 14 and the squares indicate the data of the samples investigated in the present study.

from the periphery of rubber particles to about 25 μm outwards denotes a weak interface of the rubber particle with the matrix.

Effect of T_g on microhardness

It is interesting to compare the T_g determined by measuring the thermal variation of microhardness with the corresponding DSC runs of PMMA and blends [Fig. 5(a) and (b)]. Hardness conspicuously decreases with T and the T_g value can be easily traced from a bend in the H - T plot. For DSC, the T_g value is derived from the midpoint of the step transition found. The T_g values derived from both techniques are represented in a bar diagram [Fig. 6(a)]. It can be observed that the glass transition temperature of both samples characterized by the two techniques shows a slight difference. The apparent discrepancies in the obtained T_g values could arise from several factors. However, the main reason is that DSC is a thermosensitive method, whereas the T_g measurement using the microhardness is a quasi-static method, i.e., the higher heating rate of DSC increases the transition temperature.¹⁰ On the other hand, the values of the coefficient of thermal softening, β , for the samples below and above T_g are represented in Figure 6(b). These data were calculated from the relation: $H = H_o \exp[-\beta(T - T_o)]$, where H_o is the hardness at a given reference temperature T_o and H is the hardness corresponding to T .⁹ For both temperature ranges, the value of β is lower for the blends than for PMMA. This means that the H -value at T_g for the blends is practically the same as that for PMMA that started at much higher value at room temperature.

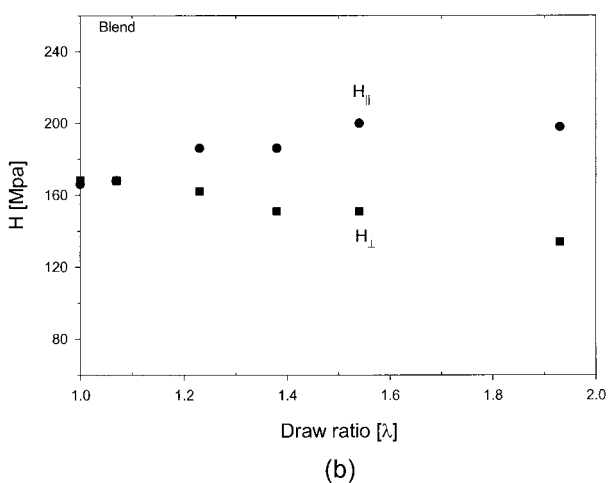
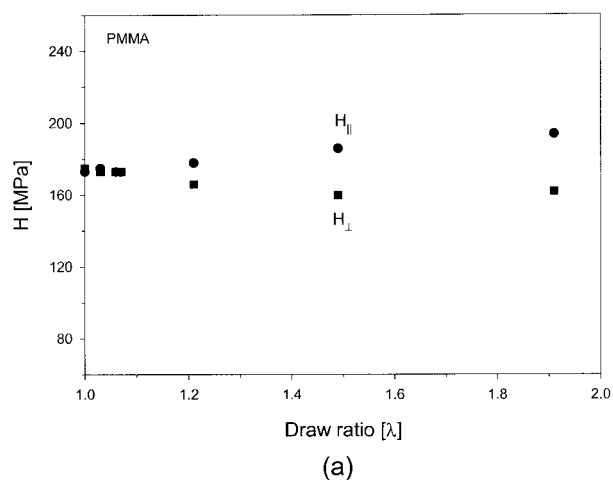


Figure 8 Change of H as a function of draw ratio, λ , for: (a) PMMA, and (b) blend.

The H measured values with reference to T_g of PMMA and the blends are compared in Figure 7 with results investigated earlier for other polymers.¹⁶ The measured values fit reasonably well the plot of the reference data following a straight line. However, the value of $T_g = 393$ K (open circle) of another PMMA sample represented in this graph is much higher than that (filled squares) of PMMA produced by the radiation polymerization method. This discrepancy could arise from the different molecular weight of the two PMMA samples, the one used in our case being notably lower.

Indentation anisotropy

Figure 8 illustrates the H variation with increasing draw ratio for PMMA and for the blend with 3 wt % rubber. At $\lambda \approx 1$, both materials exhibit isotropic behavior and, as a result, no change of $H_{||}$ and H_{\perp} values is found at all. For deformations larger than $\lambda \sim 1.2$, in both samples one sees the occurrence of striations,

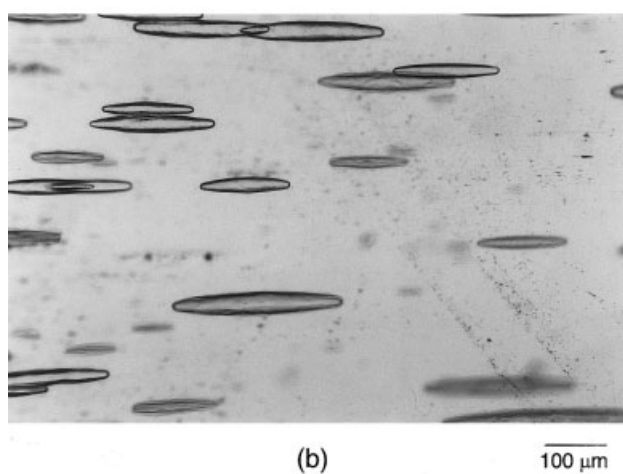
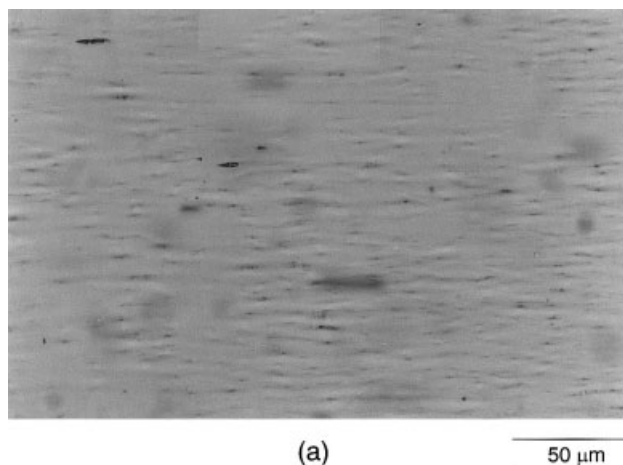


Figure 9 Surface structure at the maximum draw ratio: (a) PMMA (dark-field image with higher magnification), and (b) blend with 3 wt % rubber (bright-field image with lower magnification).

which are only observable in a dark field image as shown in case of the former [Fig. 9(a)]. Highly stretched NR particles, like ellipsoids, are found in the

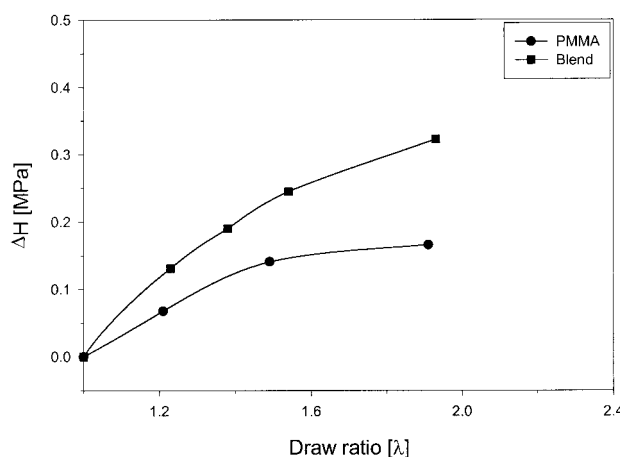


Figure 10 Variation of ΔH as a function of λ .

latter [Fig. 9(b)]. From the anisotropic shape of the NR particles in Figure 9(b) a local deformation ratio of approximately 2.8 can be derived. It is noteworthy that this local ratio is slightly higher than the overall deformation measured ($\lambda \approx 2$). As a result of the high anisotropy of the oriented structure, which increases with λ , a conspicuous anisotropic shape of the indentation arises. During indentation, the material under the compressive stress is uniformly deformed. However, after load removal two well-defined H -values emerge for $\lambda > 1.2$. One hardness value (largest) can be derived from the indentation diagonal parallel to the orientation direction. The second one (smallest) is derived from the diagonal perpendicular to it. The former value corresponds to an instant elastic recovery of the oriented material in the draw direction. The latter value defines the plastic component of the uniaxially deformed systems. Figure 10 shows the increase of the indentation anisotropy $\Delta H = 1 - (d_{\parallel}/d_{\perp})^2$ with λ showing a final leveling-off tendency for $\lambda > 1.5$. It is noteworthy that the ΔH value of the blend is much higher than that of PMMA at higher draw ratios. This may arise from the higher orientation of the peripheral PMMA molecules by the shrinkage of the rubber molecules. In practice, the elongated rubber particles act as the fibers in a reinforced composite material for which the material becomes stronger in the direction of the ellipsoid.

CONCLUSIONS

1. The microhardness of PMMA/natural rubber blends conspicuously diminishes with the inclusion of a small amount of rubber particles (1–5 wt %).
2. The micromechanical properties of the material abruptly decrease at the interface of PMMA–matrix/rubber particle.
3. The microhardness study of these blends as a function of temperature permits accurate detec-

tion of the glass transition temperature of the material. The addition of rubber particles into the matrix induces a sharp decrease in T_g . The hardness decrease can be correlated to the observed T_g decrease.

4. The mechanical deformation of the blends gives rise to an indentation anisotropy that increases with draw ratio. Results indicate that anisotropy of the blends is higher than that of the PMMA matrix due to the higher orientation of the peripheral PMMA molecules at the rubber particles.

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