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STRUCTURE-MICROHARDNESS RELATIONSHIP IN SEMI-INTERPENETRATING POLYMER NETWORKS

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ABSTRACT

Two series of single-phase, semi-interpenetrating polymer networks (semi-IPN) based on the same linear polyurethane and two different heterocyclic polymer networks (HPN), respectively, were characterized by the room-temperature microhardness (H) measurement. It is shown that the H -value linearly increases, both, with the mass content of the stiffer component (HPN) and with the glass transition temperature of a semi-IPN. The latter dependence can be justified on the assumption that the excess enthalpy of the glass with respect to a hypothetical melt state is a measure of the yield strength of the glassy quasilattice.

INTRODUCTION

According to the experimental evidence accumulated in the last years the microhardness technique (H) has proven to be highly sensitive to morphological features of semi-crystalline polymer materials (degree of crystallinity, size of microcrystals, etc) /1-5/. Large-scale structural heterogeneities are, however, believed to be absent in amorphous (glassy) polymers (e.g., /6/). Thus, the observed spread of the experimental H values found in different glassy polymers ought to be explained in terms of the different intrinsic chain stiffness and average interchain packing values which are characteristic for each amorphous polymer.

Single-phase, two-component polymer blends (PB) and interpenetrating polymer networks (IPN) are a convenient choice to study the effect of local environment on the microhardness value. However, the tendency of both, PBs and full-IPNs to incipient microphase separation /7, 8/ arises as a possible limiting factor. In this respect, the appropriate combination of chemically similar linear and cross-linked components to produce a homogeneous semi-IPN seems more promising.

The aim of the present study is to examine the dependence of composition upon microhardness of two series of semi-IPNs based on the same linear polyurethane (LPU), and of two different heterocyclic polymer networks (HPN), respectively. From small-angle X-ray scattering, calorimetry and dynamic mechanical analysis data, both semi-IPN series can be regarded as essentially homogeneous, single-phase systems in the interval of compositions studied /9-11/ (sample LPU/HPN = 50/50 of the second series of semi-IPNs, in which the miscibility of components is not complete /10/ represents an exception).

EXPERIMENTAL

Materials

A linear polyurethane (LPU) from 4,4'-diphenylmethane diisocyanate and oligomeric butylene glycol adipate (molar mass 1000 g/mol) is the common first component in both semi-IPN series (Fig. 1a). The second component (heterocyclic polymer network, HPN) is either the trimerized dicyanic ether of Bisphenol A (DCE) in the semi-IPN-1 series, or a 60/40 (by weight) copolymer of the DCE and of the epoxy oligomer (DCE/EO) in the semi-IPN-2 series (HPN-1 and HPN-2, respectively, see Fig. 1b).

The synthesis of semi-IPN-1 and semi-IPN-2 was described in detail elsewhere [9-11]. Therefore, only the essentials need to be reported here. The monomeric DCE (or the DCE/EO prepolymer) was dissolved in a 15 % solution of the LPU in cyclohexanone and the solution was cast at room temperature on the glass slides treated with dimethyldichlorosilane. The films obtained were heated at 423 K to remove the solvent. The cross-linking reaction of the HPN was initiated by a storage during 5 hours at 423 K and completed by a subsequent post-cure at 453 K during 3 hours.

Techniques

A Leitz Tester equipped with a square-based diamond indenter was used for the microhardness (H) measurements. The H values were calculated from the standard equation [1], H [MPa] = kS , where S is the slope of the straight-line plot of the residual projected indentation area A [m²] = d^2 vs. the contact load applied P [N], d [m] is the diagonal length of the impression, and $k = 1.854$ is the geometrical factor. In a loading cycle of 0.1 min the loads of 0.5, 1.0 and 1.5 N were used. For each point, at least 3-5 measurements were averaged. The

correlation coefficients and the standard deviations for the linear A vs. P fits obtained are within the limits of 0.96-0.98 and 1.2-2.3, respectively.

RESULTS AND DISCUSSION

Dependence of microhardness upon composition

Fig. 2 illustrates the gradual increase of the density ρ measured at room-temperature for the semi-IPN-1 series with mass fraction w of the corresponding cross-linked component. In contrast, a ρ decrease with w is observed for the semi-IPN-2 series. The rather large “overshoot” of the ρ values for HPN-1 suggests the existence of a lower molecular packing density in the HPN-2 (cross-linked DCE/EO oligomer) as compared to HPN-1 (neat DCE network). The deviation of ρ from the linear additivity on the ρ vs. w plot (i.e., the negative excess volume of mixing) for the semi-IPN-1 series suggests the occurrence of a strong interaction between the two components.

As reported elsewhere /9-11/, the initial (approximately linear) slow decrease of the storage moduli E' with temperature for all studied samples in the solid state, below the glass transition temperature T_g , is followed by a faster, non-linear drop by over two decades in a relatively narrow temperature interval near T_g . The room-temperature values of E' and T_g (corresponding to the maxima on the mechanical loss tangent vs. T plots at the driving frequency of 3 Hz) /9-11/ are also collected in Table 1.

The E' values for each semi-IPN show an increase with w (Table 1). The plot of E' vs. the volume fraction ϕ of cross-linked component (Fig. 3) exhibit for both semi-IPNs, series a nearly linear increase within the experimental error. The E' -value for the semi-IPN-2 at

$\varphi \approx 0.50$ shows, however, a remarkable deviation from the general trend. This discrepancy is clearly the result of an unusually steep slope b' of the E' vs. T plot below T_g for this sample (Table 1). It is likely that the incomplete miscibility of components in this sample could be responsible for this anomaly [10].

The above results together with the gradual increase of T_g with w (Fig. 4) are qualitatively consistent with the earlier claim [9-11] of a predominant single-phase state of each semi-IPN. The obtained higher T_g value of HPN-2 as compared with HPN-1 (Table 1) is somewhat unexpected in view of the difference in molecular packing density referred to above (Fig. 2). Apparently, the looser molecular packing (larger free volume fraction) of the former is overbalanced by its higher chain stiffness.

As can be seen from Table 1 and Fig. 5, the microhardness H of each semi-IPN series gradually increases with the mass fraction w of the stiffer, cross-linked component (HPN). This behavior could be reasonably approximated by the following empirical equation (broken line in Fig. 5) :

$$H[\text{MPa}] = -120 + 400 w \quad (1)$$

It can be easily verified (Table 1) that eq. (1) only applies for solid samples with T_g values above room temperature (i.e., the temperature of measurement $T' \geq 300$ K).

Influence of the glass transition temperature

The linear increase of H with T_g (see Fig. 6) can be expressed by the following equation :

$$H[\text{MPa}] = -460 + 1.51 T_g . \quad (2)$$

This expression is similar to the one obtained for amorphous polymers containing single bonded main chains /12/. The empirical correlation (eq 2) can be substantiated by the following qualitative considerations. The basic condition for the microhardness measurement is the formation of an irreversible indentation at the polymer surface. This condition can be met if only the local compressive stress under the indenter is well in excess of the macroscopic yield stress σ_y of the polymer. According to Tabor this is explicitly expressed in the equation predicted by the theory of plasticity /13/ :

$$H \approx 3\sigma_y \quad (3)$$

According to current concepts /14/, the inelastic (irreversible) deformation of an amorphous solid (glassy) polymer above the σ_y starts by a breakdown of a rigid glassy quasilattice followed by a cooperative rearrangement of structural units ("plastic flow"). Within this context, a small volume element of the glassy polymer under the indenter is assumed to be "forced" by a plastic flow mechanism into the state of a hypothetical melt at $T' \ll T_g$. As illustrated in Fig. 7, this is equivalent to an exothermal transition from the high-energy glassy state (h_{glass}) into the low-energy melt state (h_{melt}). The heat liberated during this transition (i.e. $\delta h = h''_{melt} - h''_{glass}$ in the glassy state at $T' \ll T_g$) can be looked as another measure of the strength of a glassy quasilattice, alternative to the σ_y .

Thus, assuming $\sigma_y \sim \delta h$, one derives from equation 3

$$H \approx C' \delta h \approx C' \langle \Delta c_p \rangle (T' - T_g), \quad (4)$$

where C' is a numerical parameter, and $\langle \Delta c_p \rangle = c_{p, melt} - c_{p, glass}$ is the mean difference between the specific heat capacities of a polymer in the melt and in the glassy state, respectively, in the temperature interval between the measurement temperature T' and T_g /15/.

Combination of equations (4) and (2) leads to:

$$H = -1.51 (304.5 - T_g), \quad (2a)$$

it is easily seen that these two equations are identical assuming $C' \langle \Delta c_p \rangle = -1.5$ MPa and $T' = 304.5$ K (room temperature). A constancy of the product $C' \langle \Delta c_p \rangle$ implies either the constancy of each one of both terms, or the inverse proportionality between them. The accuracy of the calorimetric data available /9-11/ is unfortunately insufficient to decide between both alternatives. The observed scatter of experimental data on the plot of hardness vs T_g (Fig. 6) suggests, nevertheless, that the product $C' \langle \Delta c_p \rangle$ in equation 4 may not have a fixed value.

An additional source of scatter could be the dependence of T_g on the mechanical and/or thermal history of a given sample. As can be inferred from the schematic diagram in Fig. 7, the value of the T_g (hence, the excess enthalpy Δh at T') of a given polymer sample will be higher, the higher the rate of cooling of the equilibrium melt at the same pressure, or the higher the densification pressure at the same cooling rate. This effect, however, is not expected to be of major importance. In fact, the elimination of the previous thermal history (by heating to 470 K, isothermal storage for 15 min. and subsequent spontaneous cooling to room temperature during about 10 hours) has no appreciable effect on the microhardness of some of the samples of the semi-IPN-2 series (cf. Table 1 and Fig. 6).

CONCLUSIONS

The empirical correlation between microhardness and glass transition temperature of single-phase, semi-interpenetrating polymer networks can be theoretically justified on the assumption that the excess enthalpy of a glass with respect to a hypothetical melt state is an

alternative measure of the yield strength of a glassy quasilattice. It is believed that this approach may prove also applicable to other single-phase, binary or multi-component polymer systems.

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REFERENCES

1. F.J. Balta Calleja, *Trends Polym. Sci.*, **2**, 419 (1994).
2. F.J. Baltá Calleja and C. Santa Cruz, *Acta Polymerica*, **47**, 303 (1996).
3. F.J. Baltá Calleja, L. Giri and .H.G. Zachmann, *J. Mater. Sci.*, **32**, 1117 (1997).
4. L. Giri, Z. Roslaniec, T.A. Ezquerro and F.J. Baltá Calleja, *J. Macromol. Sci. Physics*, **B 36**, 335 (1997).
5. F.J. Baltá Calleja, L. Giri, G.H. Michler and I. Naumann, *Polymer*, **38**(23), 5769 (1997).
6. "Organization of Macromolecules in the Condensed Phase", *Faraday Disc.*, No. 68 (1979).
7. D. R. Paul and S. Newman (eds.), *Polymer Blends*, Academic Press, San Diego (1978).
8. L.H. Sperling. *Interpenetrating Polymer Networks and Related Materials*. Plenum Press, New York (1981).
9. A. Bartolotta, G. Di Marco, M. Laniza, G. Carini, G.D. Angelo, G. Tripodo, A. Fainleib, E.A. Slinchenko and V.P. Privalko, *J. Adhesion*, **64**, 269 (1997)
10. A. Bartolotta, G. Di Marco, M. Laniza, G. Carini, G.D. Angelo, G. Tripodo, A. Fainleib, E.A. Slinchenko, V.I. Shtompel and V.P. Privalko, *Polymer Eng. Sci.*, 1998 (in press).
11. A. Bartolotta, G. Di Marco, G. Carini, G.D. Angelo, G. Tripodo, A. Fainleib and V.P. Privalko, *J. Non-Cryst. Solids*, 1998 (in press).
12. S. Fakirov, F.J. Baltá Calleja and M. Krumova, *J. Polym. Sci. Polym. Phys.* (in press).
13. D. Tabor, *The Hardness of Metals*, Oxford C. Press (1951).
14. Z.H. Stahurski, *Prog. Polymer Sci.*, **22**, 407 (1997).
15. V.P. Privalko, *Molecular Structure and Properties of Polymers*, Khimia, Leningrad, 1986 (in Russian).

FIGURE CAPTIONS

Fig. 1. Chemical formulae of: a) linear and b) cross-linked components of semi-IPNs.

Fig. 2. Mass fraction dependence of density for semi-IPN-1 (triangles) and semi-IPN-2 (squares).

Fig. 3. Volume fraction dependence of storage modulus (same symbols as in Fig. 2).

Fig. 4. Mass fraction dependence of glass transition temperature.

Fig. 5. Plot of microhardness versus w before and after heating up to 470 K (opened and filled symbols, respectively).

Fig. 6. Plot of microhardness versus glass transition temperature for the semi-IPN series.

Fig. 7. Schematic diagram showing the variation of enthalpy vs. temperature for a glassy polymer.

Fig. 1 a

Common component 1 :

linear polyurethane (LPU) from 4,4'-diphenylmethane diisocyanate and oligomeric butylene glycol adipate (molar mass 1000g/mol)

Component 2 :

Semi-IPN 1: heterocyclic polymer network (HPN-1) from trimerized dicyanic ether of bisphenol A (DCE)

Semi-IPN 2: heterocyclic polymer network (HPN-2) from 60/40 (by wt) copolymer of the DCE and of the epoxy oligomer (DCE/EO)

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6

Fig. 7

Table 1

Glass transition temperatures and room-temperature properties of semi-IPNs

Sample	$E' /$ GPa	$10^3 b' /$ GPa K ⁻¹	$\rho /$ g cm ⁻³	$T_g /$ K	$H^a) /$ MPa
<u>semi-IPN-1</u>					
HPN-1/LPU :					
0/100	0.083	6.95	1.241	280	
30/70	0.425	5.78	1.314	310	2.5/...
50/50	1.060	2.47	1.336	325	24.9/...
100/0	1.592	1.30	1.384	465	241.7/...
<u>semi-IPN-2</u>					
HPN-2/LPU :					
20/80	...	...	1.231	...	5.6/...
50/50	1.811	5.50	1.224	390	107.6/122.6
75/25	1.377	4.50	1.214	420	221.6/232.6
100/0	1.936	6.91	1.207	500	249.0/234.3

^{a)} Before heating/after heating