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Mechanical properties of poly(vinyl chloride)–poly(acrylonitrile-co-butadiene) blends with modulated structure

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By solution-casting we prepared poly(vinyl chloride)–poly(acrylonitrile-co-butadiene) blends with a modulated structure (a co-continuous two-phase structure with periodic distance of a few micrometres or less). Mechanical properties of the film specimens were investigated by the uniaxial tensile test combined with small-angle light scattering. A 50:50 plastic–rubber blend has a high initial modulus which is close to that of the rigid plastic. Nevertheless, it can deform to a large extension ratio up to 6. It cannot immediately recover to its original length after the stress–strain test, i.e. residual strain in the stress–strain curve persists. However, after release from the instrument the film gradually shrinks to its original length at room temperature. After strain recovery the film shows a stress–strain curve almost identical to the original. It seems that the stretched film healed simply by resting at room temperature. Based on the light-scattering studies, a helical spring model is derived for the two-phase system with modulated structure, exhibiting the characteristic mechanical properties mentioned above. The spring model interprets well the dependence of Young's modulus on the blend composition and the periodic distance of the modulated structure.

1. Introduction

Most pairs of dissimilar polymers are immiscible. Mechanical mixing and solution-casting of immiscible polymers generally result in a blend with two-phase morphology having irregular shape and size of domains. We recently found that, by regulating the rate of solvent evaporation, solution-casting yielded a regularly phase-separated structure with a periodic distance of a few micrometres or less [1, 2]. Characteristic features of the structure are periodicity and dual connectivity of phases (see Fig. 1a). This characteristic morphology is similar in appearance to the structure formed by spinodal decomposition [3]. Actually we interpreted the development of the characteristic morphology in terms of spinodal decomposition during the solution-casting of ternary polymer solutions. Further, it was verified by kinetic studies of phase separation in the ternary solution by using a temperature-drop procedure instead of the concentration-jump corresponding to solution-casting [4]. Here we call this structure "modulated structure" for convenience to describe the morphological features of unique periodicity and a high level of phase connectivity.

We believe that our studies mentioned above presented a new way to prepare blended materials with a modulated structure for various polymer pairs. So far, the formation of modulated structure in polymer blends has been limited to the thermally induced phase separation of two-component polymer systems having LCST (lower critical solution temperature) and UCST (upper critical solution temperature) type phase diagrams [5, 6]. From the above results we can expect a much wider possibility of designing new materials. In this sense, we are interested in the mechanical properties of polymer blends with modulated structure, especially in the relationship between properties and the co-continuous two-phase character in modulated structure. Most interesting may be the properties of a blend comprising a plastic–rubber combination.

In this paper we investigate the tensile stress–strain behaviour of poly(vinyl chloride)–poly(acrylonitrile-co-butadiene) blends with modulated structure. In order to understand the structure–property relationship, we undertook the simultaneous measurements of stress–strain curve and small-angle light scattering. Based on the results, we construct a simple mechanical model to describe an interesting strain recovery phenomenon and the dependences of Young's modulus on blend composition and on the periodic distance of the modulated structure.

2. Experimental procedure

2.1. Polymer specimens

Poly(vinyl chloride) (PVC) was a commercial polymer. Nicavinyl SG 1100, supplied by the Hishinichi Co. Ltd, Tokyo, Japan ($M_n = 76000$, $M_w = 160000$). Poly(acrylonitrile-co-butadiene) (NBR) was JSR

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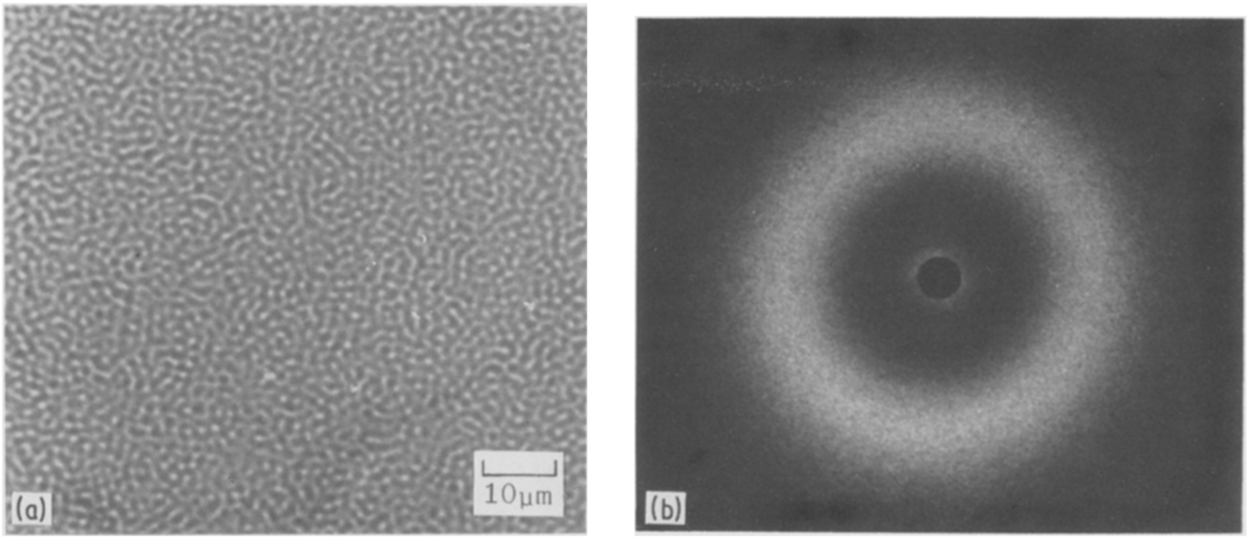

Figure 1 (a) Light micrograph of a solution-cast film of 50 : 50 PVC/NBR blend. (b) V_V light scattering from the blend film.

N240S supplied by the Japan Synthetic Rubber Co. Ltd, Tokyo, Japan; 26 wt % acrylonitrile, M_n = 120 000, M_w = 340 000. These molecular weights were estimated by gel permeation chromatography calibrated with polystyrene standards.

2.2. Blend preparation

PVC and NBR were dissolved at 8 wt % of total polymer in tetrahydrofuran. The solution was poured into a shallow glass dish with a flat glass cover. The depth of solution in the dish was ca. 2 mm. The rate of solvent evaporation was controlled by adjusting the gap between the cover and dish (the faster the evaporation of solvent, the smaller was the periodic distance of the modulated structure) [2]. After the polymer concentration had passed 90 wt % and the rate of evaporation had slowed, the concentrated solution was further dried under a vacuum of ca. 10^{-4} mm Hg for 10 h. The structure of the dried film was observed under a light microscope.

2.3. Measurements

Tensile stress–strain measurement was carried out on a Toyo Balkwin UTM-II-20 under a constant rate of elongation, 100% min^{-1}, at 23° C. Changes in the small-angle light scattering pattern from the film specimen with stretching were observed by a photographic light-scattering technique similar to that of Stein and Rhodes [7]. An incident beam from an He–Ne gas laser of 632.8 nm wavelength, polarized parallel to the stretching direction, was applied vertically to the film specimen. The V_V (parallel polarized) scattering patterns were recorded at appropriate intervals during stretching.

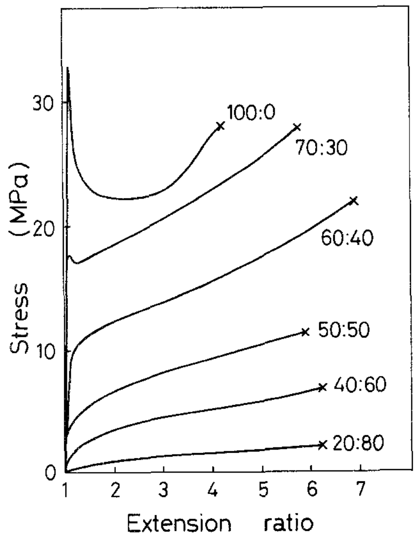

Figure 2 Stress–strain curves of PVC–NBR blends with various compositions.

3. Results and discussion

Fig. 1a is a typical example of a light micrograph of the cast film of 50 : 50 (by weight) PVC–NBR. A highly interconnected two-phase morphology with uniform domain size, i.e. a modulated structure, is seen in the micrograph. Similar two-phase micrographs were observed for all specimens in this paper. Fig. 1b shows a V_V light-scattering pattern from the cast film. The ring pattern indicates no preferred orientation of the structure in the plane parallel to the film surface. The Bragg spacing from the peak angle of the ring pattern corresponds to the periodic distance in Fig. 1a. The change in scattering profile with stretching is then expected to deliver information on structural changes in the two-phase morphology.

Fig. 2 shows the stress–strain curves of a series of blend specimens with modulated structure, differing in blend composition but similar in periodic distance (ca. 1.5 μm). It is noted that all specimens can deform to large extension ratio up to around 6, even for a PVC-rich specimen. The initial modulus depends on the blend composition, as replotted in Fig. 3. The smooth variation in the modulus–composition curve is quite different from that of a two-phase system with dispersed particles in a matrix, but rather similar to that reported for an interpenetrating polymer network system [8]. This phenomenon may be closely related to the co-continuous nature of the modulated structure, as will be quantitatively discussed later.

Fig. 4 shows stress–strain curves of 50 : 50 PVC–NBR blends with different periodic distances. Although

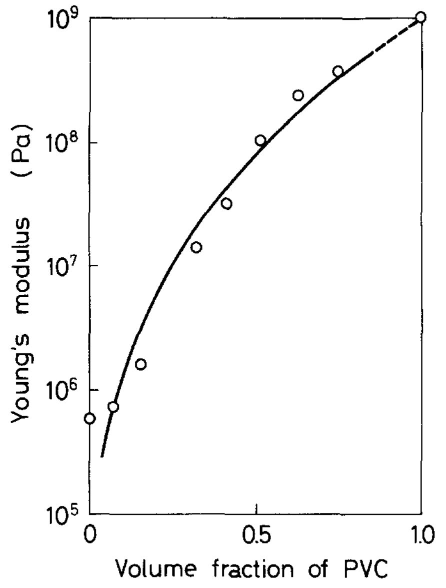

Figure 3 Young's modulus as a function of blend composition. Solid curve is from Equation 4.

the stress at high extension ratio depends on the periodic distance (the smaller the periodic distance, the higher is the stress), the initial modulus is constant, regardless of the difference in periodic distance.

Fig. 5 shows the stress–strain behaviour of a 50 : 50 PVC–NBR blend with periodic distance $1.5\,\mu m$. As shown in Figs 2 and 3, the blend has a high initial modulus which is close to that of the rigid plastic; nevertheless, it can deform to a large extension. It cannot immediately recover to its original length after the stress–strain testing, i.e. residual strain in the stress–strain curve persists as shown by the open circles. However, after release from the instrument, the film specimens gradually shrink at room temperature to their original lengths. After almost complete strain recovery, a film shows a stress–strain curve approximately identical to the original. It seems that the stretched film was healed, or in other words self-repaired, simply by resting at room temperature. The rate of healing is shown in Fig. 6. This strain-recovery behaviour may also be intimately related to the co-continuous nature of the modulated structure.

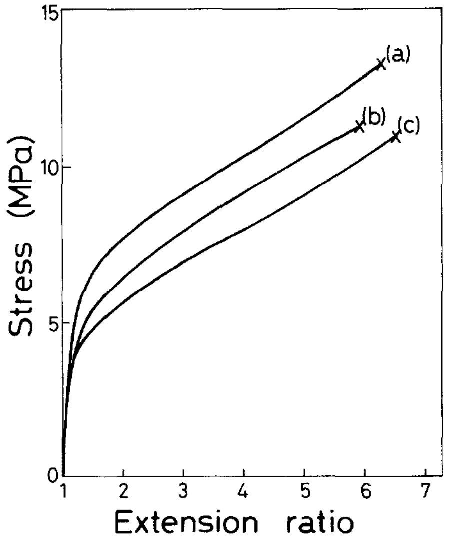

Figure 4 Stress–strain curves of 50 : 50 PVC–NBR blends having different periodic distances: (a) $0.68\,\mu m$, (b) $1.19\,\mu m$, (c) $1.54\,\mu m$.

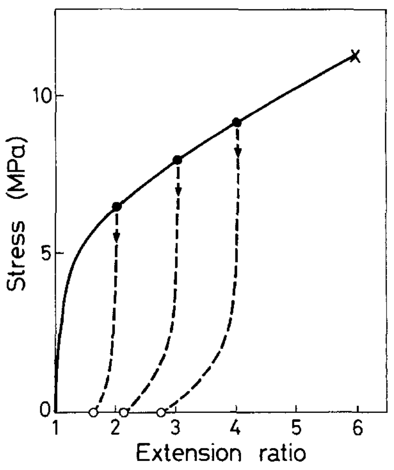

Figure 5 Stress–strain curves of 50 : 50 PVC–NBR blends at 20° C. Residual strains, indicated by open circles, are gradually recovered after specimens are released from the instrument.

In Fig. 7 is shown the change of V_V scattering pattern with extension ratio for the same specimen as in Fig. 6. The letters attached to the patterns correspond to those along the stress–strain curve. The pattern deforms from a ring to an ellipse with extension. In other words, the peak position in the meridional direction (||; parallel to the stretching direction) shifts to smaller angles, while that in the equatorial direction (⊥: perpendicular to the stretching direction) shifts to larger angles. From the peak shift in each direction one can estimate the change in periodic distance in each direction with bulk deformation by using the Bragg relation. The results are demonstrated in Fig. 8.

Fig. 8 suggests that, in the regime of small extension ratio at least, we are able to discuss the stress–strain behaviour in terms of the affine deformation of modulated structure when bulk entension ratio is α, microscopic extension ratio is

α in // direction (shown by broken line in Fig. 8) and
$\alpha^{-1/2}$ in ⊥ direction.

The deviation from the affine deformation at large extension ratios may be attributed to a local imperfection in the modulated structure, e.g. a non-uniformity

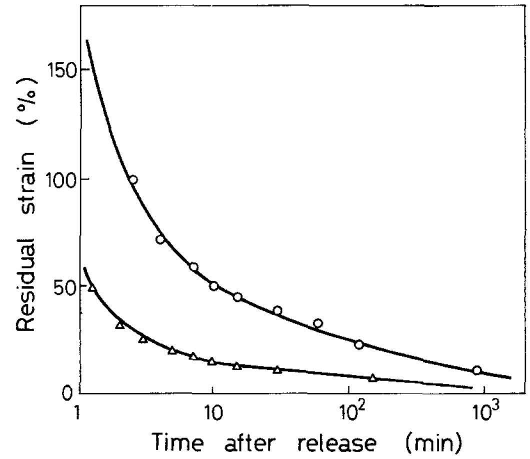

Figure 6 Strain recovery after releasing from instrument in the tensile test in Fig. 5: (○) from extension ratio 3, (△) from extension ratio 2.

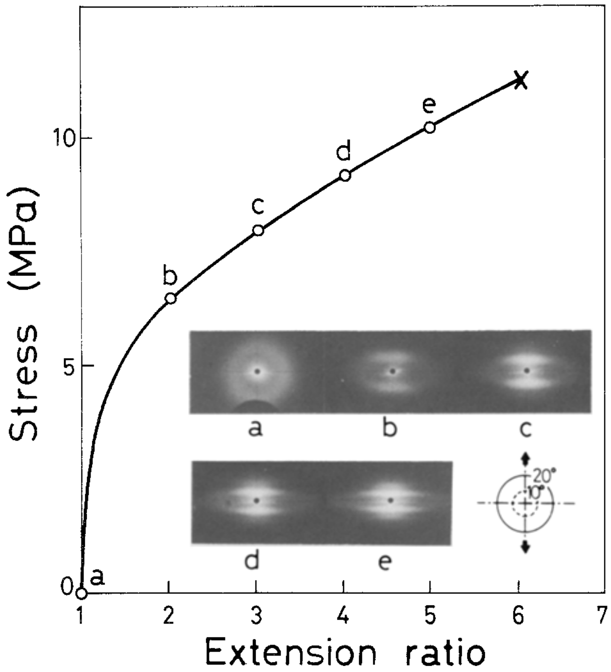

Figure 7 V_V light-scattering patterns from the film specimens (50 : 50 PVC–NBR blend) at various stretched states, indicated by the same letters as those along the stress–strain curve.

in the periodic distance and a partial interruption of the co-continuous structure, both of which induce localized intenal strain at particular points rather than a uniform strain throughout the specimen. The differences between the stress–strain curves in Fig. 4 may be also due to local imperfections in the modulated structure. However, we are not able to proceed with further argument on the structure–property relationship in the large-strain range without quantitative knowledge of the imperfections of structure.

On the other hand, we may proceed with a quantitative discussion of the stress–strain behaviour in the small-strain range in relation to the change in the modulated structure, as mentioned above. A helical spring model is shown in Fig. 9. This model comes simply from the graphical fitting shown in the same figure, demonstrating schematically the continuous and periodic characters of the rigid (PVC) phase. In this illustration, we omitted to draw another spring for the rubbery (NBR) phase shown by the dotted region, because the stress contribution of this rubber spring to the overall stress is very small in comparison to that of the rigid spring, and it is neglected in the stress analysis.

Here, the helix diameter ($2R$) corresponds to the periodic distance of the modulated structure and the diameter of the round rod (d) is related to the volume fraction of rigid phase (ϕ) by

$$\phi = \frac{\pi}{4}\left(\frac{d}{a}\right)^2 \tag{1}$$

where a is the diameter of the mandrel surrounding the whole spring (see Fig. 9) and $\tan \alpha \fallingdotseq 0.5$ is assumed for the modulated structure.

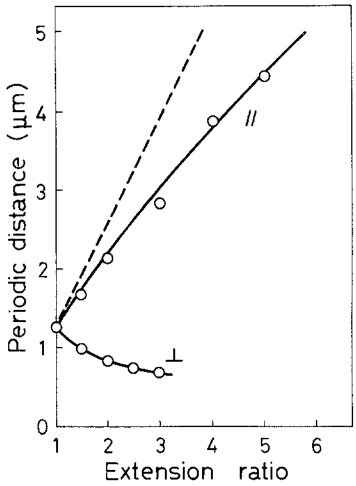

Figure 8 Periodic distances in the // and ⊥ directions, as a function of the extension ratio of the bulk specimen. Broken line indicates affine deformation.

When the helical spring is elongated by an axial load F, the deflection δ is approximated (see for example [9]) by

$$\delta = \frac{64FR^3n}{Gd^4} \tag{2}$$

where n is the number of coils of the spring and G is the shear modulus of the material (PVC). Then, Young's modulus of the spring, E, is given by

$$E = \frac{F}{\pi R^2}\frac{L}{\delta} = \frac{Gd^4L}{64\pi R^5 n} \tag{3}$$

where L is the length of the undeformed spring.

Since n is inversely proportional to R and $2R = 2a - d$.

$$E \propto \left(\frac{d}{R}\right)^4 \propto \left[\left(\frac{\pi}{\phi}\right)^{1/2} - 1\right]^{-4} \tag{4}$$

Equation 4 tells us that E depends on ϕ but it is not a function of R. This is nothing but an interpretation of the results in Fig. 4; the initial modulus does not depend on the periodic distance of the modulated structure in the case of a fixed blend composition. The calculated ϕ dependence of E is shown by a solid line in Fig. 3, where the proportionality constant in Equation 4 is fitted to be 5.85×10^8 Pa for $\phi = 0.5$.

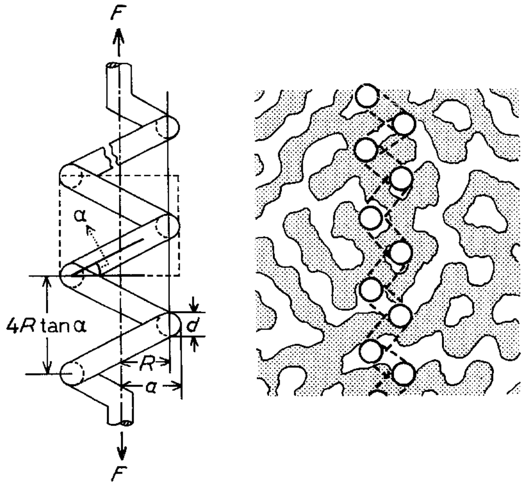

Figure 9 Helical spring model and schematic illustration of modulated structure.

Agreement between the experimental and the calculated curves is fairly good.

4. Concluding remarks

We have successfully interpreted the R and ϕ dependences of Young's modulus of a polymer blend with modulated structure by employing a simple helical spring model. As far as the ϕ dependence is concerned, our result from Equation 4 is similar to that of Davies' equation [10]:

$$E^{1/5} = E_1^{1/5}\,\phi_1 + E_2^{1/5}\,\phi_2$$

where subscripts refer to the two phases. It may be a natural consequence, because both take into account the co-continuous character of the two-phase system.

In the spirit of the helical spring model, the bulk deformation of the two-phase system with modulated structure is assumed to induce a shear deformation of the rigid phase (not an elongational one). So, the rigid phase is expected to be highly deformable. Hence, it may result in a high elongation at break.

The strain-recovery behaviour in Figs 5 and 6 may correspond to a shrinkage of the elongated helical spring. Of course, it should be a time-dependent process, since the spring has to shrink in the viscoelastic (NBR) matrix.

Finally we would like to stress that the preparation of a modulated structure implies a design of two-phase structure so as to obtain the shear deformation mode of the rigid phase.

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