Supermolecular Structures in Blends of Polypropylene and Ethylene–Propylene Rubber

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INTRODUCTION

Much attention has recently been focused on research into the mechanical and optical properties of polymer blends because of the relative ease with which many of their physical properties can be greatly modified. Investigations of the properties of polypropylene (PP) and ethylene–propylene rubber (EPR) blends have already been the subject of several publications.[1,2] The aim of this work is to determine the effect of blend composition and the method of obtaining films on the formation of supermolecular structural elements and to determine changes in the dimensions of these elements brought about by external deformation forces.

EXPERIMENTAL

The polypropylene (PP) and ethylene–propylene rubber (EPR) used in this research were industrial products. Polypropylene, in the form of a powder, was purified by washing with ethanol. EPR was purified by acetone extraction for 24 hr. The products obtained in this way were carefully dried. PP and EPR blends of known composition containing 0–50% EPR by weight were obtained by dissolving both polymers in xylene at 130°C. The solution was poured into methanol to precipitate the polymer and then filtered, washed with water and methanol, and finally carefully dried. Films of 0.08 to 0.1 $\sqrt{\text{mm}}$ thickness were obtained by pressing the different blends between two 1-mm-thick polished chrome–steel plates. The films were obtained by two different cooling methods: (a) fast cooling, whereby the sandwiched film was immersed in water at room temperature, and (b) slow cooling, whereby the sandwiched film was cooled in air. Samples obtained in this way were characterized by density measurements.

The densities determined were 0.88–0.90 g/cm³ for the samples of 0–50% EPR.

The dimensions of spherulites in all the films were studied by the small-angle light-scattering method elaborated by Stein.[3] The light source used in conjunction with a goniometer system is described in previous publications.[4,5]

Independently, the ratio of crystalline parts to randomly oriented parts

was determined.   Thus, Rayleigh's factor $R^{\perp}$ for μ equal to both 90° and 45° for scattered light was measured according to the method proposed by Keijzers and co-workers.[6]   Since the analyzer was perpendicular to the scattered rays, the respective equations proposed by Keijzers can be simplified.   Thus, the dependence of $R^{\perp}{}_{\mu=90°}$ and $R^{\perp}{}_{\mu=45°}$ on U may be obtained. The shape factor U is given by the following equation:

$$U = \frac{4\pi R}{\lambda} \sin \frac{\theta}{2}$$

here $2R$ denotes the spherulite diameter.   Integration of the area under $R^{\perp}$ versus U plots gives the fraction of ordered and randomly oriented parts, for total scattered light intensity.

The dependence of the relative extension l/l_0 on stress N was studied in quasi-stationary conditions, at different temperatures, on different PP samples containing relatively small amounts of EPR, i.e., 0% (pure PP), 10%, and 20% EPR.   The effect of external deformation forces on spherulite shape was estimated by determining the extension ratio λ_s with stress N. The λ_s values were determined using the method proposed by Gasparyan and co-workers.[7]

This method consists in determining the value of angle μ corresponding to the intensity maximum of the experimental H_v scattering pattern at a given angle $\theta_{\max,0}$.   Angle $\theta_{\max,0}$ is related to the absolute intensity of the scattered light in the H_v pattern obtained for undeformed spherulithes, and the following equation is valid:

$$\lambda_s{}^2 + \lambda_s = tg^2\mu.$$

RESULTS AND DISCUSSION

Different supermolecular structures are present in films with different EPR content.   For large EPR content, the spherulites being formed are irregular.   Figure 1 shows the dependence of the spherulite radius R on composition for quickly and slowly cooled films.   It follows from Figure 1 that the largest spherulites are present in both films containing 10% EPR. Figure 2 shows the dependence of the ratio of light-scattering intensity $I_c{}^{sp}$, from ordered parts (spherulites) and light-scattering intensity from randomly orientated parts, $I_c{}^{ro}$ on the EPR content.   From this figure it follows that in fast cooled films, the ordered phase content decreases quickly at first with increasing EPR content and slows down when the EPR content exceeds 20%.   In slowly cooled films, the ordered phase content does not decrease regularly.   The largest-size spherulites ($R = 5.7$ μ) are found in the slowly cooled (10% EPR) film.

The dependence of stress N on λ_s and on l/l_0 was confined to films containing no EPR (pure PP) or 10% and 20% EPR, obtained by the slow- and fast-cooling processes.

The deformations of samples were investigated at 22°, 31°, 37°, and 42°C.   The results obtained are shown in Figures 3, 4, 5, and 6.   Parts of
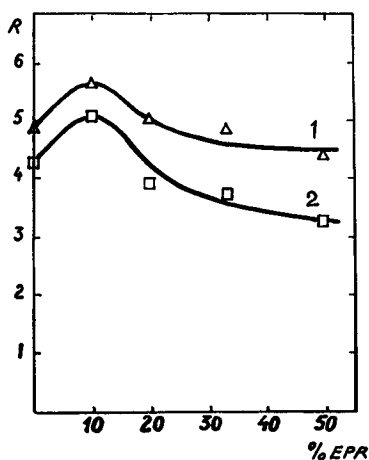
Fig. 1. Dependence of spherulite radius R on EPR content: (1) slow-cooled film; (2) fast-cooled film.
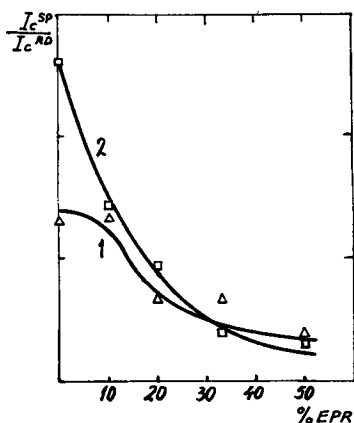

Fig. 2. Dependence of $I_c{}^{sp}/I_c{}^{ro}$ on EPR content: (1) slow-cooled film; (2) fast-cooled film.

the curves of the functions $N = f(\lambda_s)$ and $N = f(l/l_0)$ were approximated by linear sections. The general shapes of these plots are not different in principle from those obtained for pure polymers, i.e., for monocomponent systems. The relations $N = f(l/l_0)$ and $N = f(\lambda_s)$ were, however, somehow different for films obtained by the slow- and fast-cooling method thus they will be discussed separately.

Films Obtained by Slow-Cooling Process

Plots of $N = f(l/l_0)$ at constant temperature for slowly cooled films show that breaks occur at quite small values of l/l_0. The value of N at which a break occurs decreases with increasing EPR content. The slope of the first linear part of the 10% EPR curve is slightly greater than for the same part
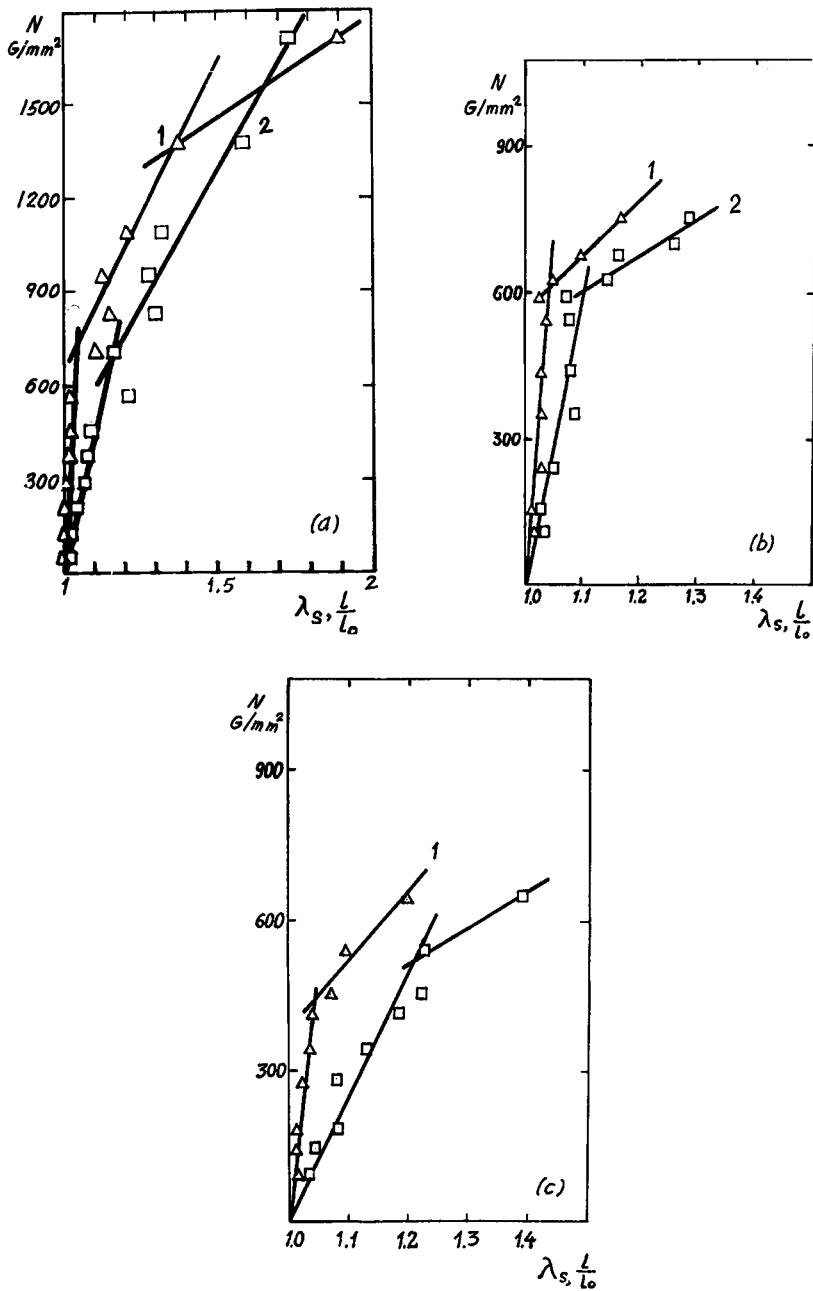
Fig. 3. Dependence of stress N on λ_s and on l/l_0 for slow-cooled films, at 22°C: (1) function $N = f$ (l/l_0); (2) function $N = f$ (λ_s); (a) pure PP; (b) PP + 10% EPR blend; (c) PP + 20% EPR blend.
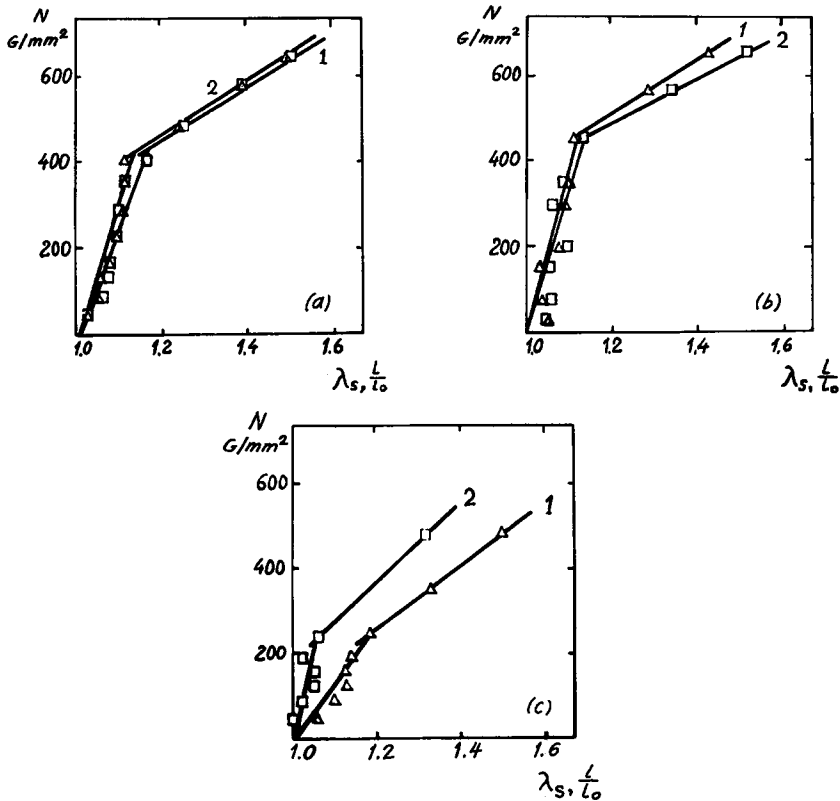
Fig. 4. Dependence of stress N on λ_s and on l/l_0 at different temperatures for films containing 20% EPR obtained by slow-cooling process: (1) function $N = f(l/l_0)$; (2) function $N = f(\lambda_s)$ (a) 31°C; (b) 37°C; (c) 42°C.

of the pure PP curve. (Fig. 3a,b,c). At greater EPR content, this slope has a smaller value. It appears that the film with 10% EPR, obtained by the slow-cooling process, is less elastic than the pure PP film. This is connected with the presence of larger spherulites in this film than in pure PP. Plots of the function $N = f(\lambda_s)$ obtained from studies of slowly cooled films of different composition have the same character as those above, i.e., there appears a definite break at stress values near those in the plots of $N = f(l/l_0)$. This proves that the first deformation phase is connected with spherulite distortion.

The comparison of the plots $N = f(l/l_0)$ and $N = f(\lambda_s)$ for samples of the same EPR content, measured at different temperatures, shows that the slope of the first curve sections exhibits a slow decrease with temperature increase. The stress values, corresponding to the limit of elasticity, decrease with temperature increase, for all the samples with rather high EPR content (20%) (Fig. 4a,b,c).
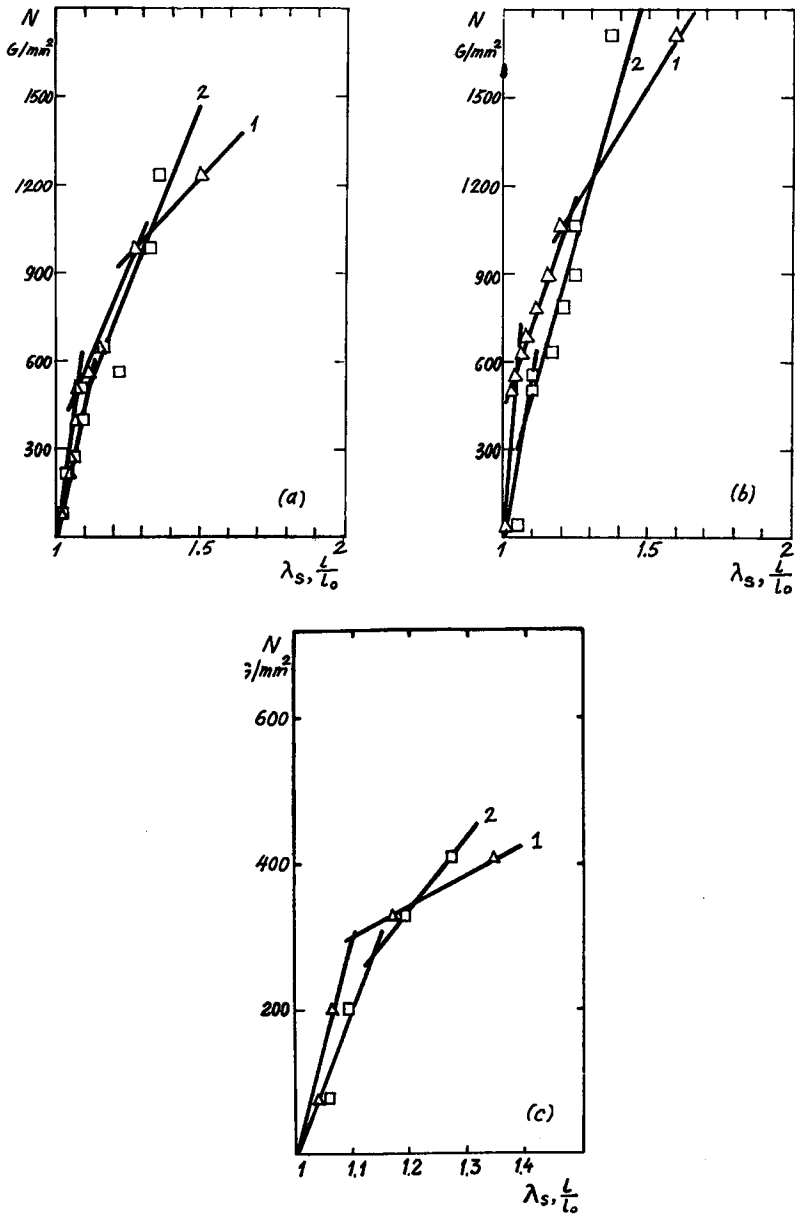
Fig. 5. Dependence of stress N on λ_s and on l/l_0 for fast-cooled films, at 22°C: (1) function $N = f\,(l/l_0)$; (2) function $N = f(\lambda_s)$ (a) pure PP; (b) PP + 10% EPR; (c) PP + 20% EPR blend.

Films Obtained by Fast-Cooling Process

At constant-temperature measurements, the plots of the functions $N = f(l/l_0)$ and $N = f(\lambda_s)$ describing the properties of films obtained_by fast-
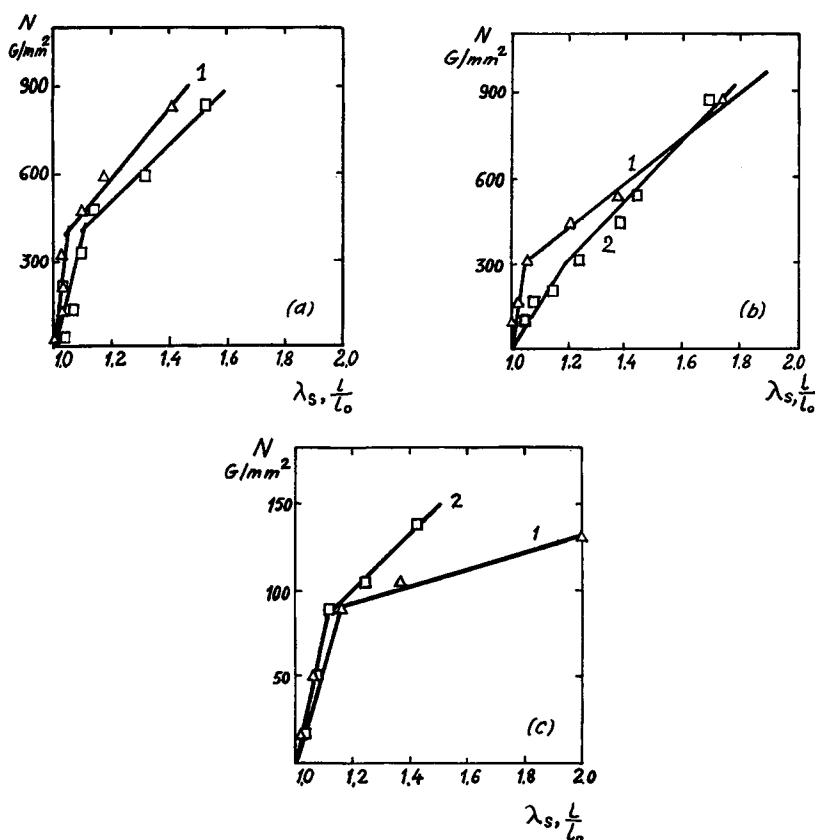
Fig. 6. Dependence of stress N on λ_s and on l/l_0 at different temperatures for films containing 10% EPR obtained by fast-cooling process: (1) function $N = f(l/l_0)$; (2) function $N = f(\lambda_s)$ (a) 31°C; (b) 37°C; (c) 42°C.

cooling process are in general similar to those discussed above (Fig. 5a,b,c). The films containing 10% EPR show at 22°C the best mechanical properties in accordance with the data published by Onogi and co-workers.[1,2] The greatest value of stress N at which the breaks in the curves $N = f(l/l_0)$ and $N = f(\lambda_s)$ occur were found for films with 10% EPR. When the temperature is raised to 31°C, the mechanical properties of the pure PP films and those with 10% EPR are similar; but a still higher temperatures, the EPR content causes the investigated materials to flow.

A comparison of the mechanical behavior of samples with the same EPR content measured at different temperatures leads to the following observations: Similarly to the films obtained by the slow-cooling process, the films of pure PP show only small changes with temperature increase. The influence of increasing the temperature is most pronounced for the films containing 10% EPR, contrary to the results obtained for slow-cooled samples (Fig. 6a,b,c).

CONCLUSIONS

The structural and mechanical studies described in this work concern blends with low EPR content in which the PP spherulites are formed; therefore this system cannot be discussed in terms of phase changes. The blend is not a molecular dispersion; at low EPR content, PP is a continuous phase of high crystallinity in which the EPR particles are embedded. As follows from Onogi's work,[1,2] in which dynamic viscoelasticity as function of temperature and PP–EPR blend composition, stress–strain curves, as well as orientation function were studied, the phase inversion occurs in the blend when the EPR content exceeds 50%. However, even at low EPR concentration in the system, the crystallization of PP is influenced by the EPR content and leads to changes of initial Young's moduli for crystalline deformation and macroscopic deformation. The low EPR content also influences the temperature dependence of both these initial Young's moduli as well as the size of the supermolecular structures obtained by the slow- and fast-cooling processes in which the samples were prepared.

The density of the blends was a linear function of the polypropylene content according to the assumption that the volume of a blend is the sum of the volumes of its components. This result was also found by Onogi.[1,2] There are, however, some differences between the density values for samples obtained by the slow- and fast-cooling process. This is due to the different density of the PP component. PP is the dominant component of the blends which crystallize in larger spherulites by the slow-cooling process, leading to higher density as compared with samples obtained by the fast-cooling method. The differences between calculated and measured densities are largest for the samples containing 10% EPR because the spherulites being formed are largest by the slow- as well as by the fast-cooling process (Fig. 1), which is due to the crystallization of PP promoted by the small EPR fraction. In this way, the results of x-ray diffraction studies of Onogi[1,2] were confirmed by direct morphologic studies.

The Young's modulus which was determined from the initial slope of the stress–strain curves of the macroscopic deformation $[N = f(l/l_0)]$ decreases slowly with the increase in EPR content (from 6000 to 900 g/mm^2). The Young's modulus determined from the initial slope of the $N = f(\lambda_s)$ curve, which corresponds to spherulite deformation, is more dependent on the blend composition; it also decreases gradually with increase in EPR content, but faster than that calculated from the $N = f(l/l_0)$ curve (from 10,000 to 600 g/mm^2).

The mechanical properties of PP–EPR blends with low EPR content and low deformation are mainly related to the mechanical properties of spherulites. This conclusion follows from the generally similar course of the $N = f(l/l_0)$ and $N = f(\lambda_s)$ curves and the rather small difference in Young's moduli calculated from the initial slopes of these curves. Because the films obtained by slow cooling contain larger and more perfect spherulites, the dependence of their mechanical properties on temperature is less pronounced

than for films prepared by fast cooling.   This result is clearly confirmed by the behavior of films containing 10% EPR and by the course of the function $I_c{}^{sp}/I_c{}^{ro}$ versus blend composition (Fig. 2), which shows a large fraction of ordered phase content for this composition.   Fast cooling leads to somewhat smaller spherulites, but still the overall ordered phase content is rather high; thus, the films containing 10% EPR show high Young's moduli for spherulites and smaller moduli when they are calculated from the measurements of macroscopic deformation.

The above results show that the introduction of small amounts of EPR into PP improves the mechanical properties associated with extension of the films, owing to a change in morphologic structure which is dependent on the rate at which the blend melt was cooled.

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