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INVESTIGATIONS OF THE CRYSTALLINITY OF PA-6/SPS BLENDS BY X-RAY DIFFRACTION AND DSC METHODS

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Abstract—An X-ray diffraction procedure for the crystallinity of polymer blends determination was verified by comparison with the DSC method. Crystallinity of polyamide 6/sulfonated polysulfone (PA-6/SPS) blends was investigated using X-ray and DSC methods. A good consistency of the results was observed. Both methods showed the same trends in the variations of crystallinity as a function of blend composition. © 1997 Elsevier Science Ltd

INTRODUCTION

Crystallinity is one of the most important parameters of the two-phase, lamellar model of polymer structure. It is defined as the ratio of the mass of crystalline phase to the total mass of the polymer. The physical and mechanical properties of polymers are profoundly dependent on the crystallinity, and various methods have been elaborated to determine this parameter.

Most frequently, the wide angle X-ray diffraction (WAXS) method is used. The method is based on the assumption that it is possible to separate the scattered intensity contributions arising from crystalline and amorphous regions. Several procedures have been elaborated to derive the degree of crystallinity from the scattered X-ray intensity distribution. They may be divided into two groups, the relative [1–3], and the absolute ones [4–11]. For the former, an index is assigned to a sample by comparing its diffraction pattern with those of crystalline and amorphous "standards". The samples of the highest and the lowest crystallinities are taken as "standards". The disadvantage of this procedure is that the indices cannot be compared between different laboratories or different polymers. The absolute procedures are based on the fact that the intensity of X-rays scattered over all angles by a given assemblage of atoms is independent of their state of order [12–14]. For, if the intensities scattered by the crystalline and amorphous regions can be separated, the degree of crystallinity may be calculated as the ratio of the integral intensity coming from crystalline regions to the integral intensity scattered by the whole sample.

Determination of the crystallinity of polymer blends is more complicated than in the case of a "pure", semicrystalline polymer. A direct resolution of a diffraction pattern of a blend into individual crystalline peaks and an amorphous part is uncertain in most cases, particularly when peaks arising from the components of the blend overlap considerably. A new procedure for the determination of the crystallinity of polymer blends was proposed in Ref. [15]. This procedure has been employed successfully for several types of polymer blends and copolymers.

This work aims to compare the crystallinity values obtained by means of the X-ray procedure mentioned above with the results obtained with the traditional DSC method. The measurements were performed for two-component blends of polyamide-6 with sulfonated polysulfone (PA-6/SPS).

EXPERIMENTAL

Sulfonated polysulfone (SPS) was synthesized using the method of Brousse [16], i.e. sulfonation of polysulfone with chlorosulfonic acid in a dichloroethane environment. The starting polysulfone, Udel P-1700, was a commercial product of Union Carbide with reported number-average and weight-average molecular masses of 30,500 and 45,000, respectively. The sulfonation level was 22 mol%, as determined by the NMR method [17]. Polyamide-6 with a viscosity-average molecular mass of 24,000 was supplied by ZWS "Stilon" Works (Gorzów Wielkopolski, Poland).

The blends PA-6/SPS containing from 10 to 50% SPS were prepared by mixing 7% solutions of the component polymers in *m*-cresol at suitable volume fractions. After shaking for 48 hr, the deposits were precipitated from the solutions by means of dehumidified methanol. The deposits were dried at 65–78°C for 6.5 hr in an ordinary dryer, and then for 72 hr at 110°C in a vacuum dryer. PA-6 was obtained in the same way from 7% solution in *m*-cresol.

Wide angle X-ray scattering (WAXS) investigations were made by means of a HZG-4 X-ray diffractometer employing the symmetrical reflection method of registration. We used a copper target X-ray tube operated at 30 kV and 30 mA. Diffraction curves were taken in the range from 5° to 55° with a step of 0.1°. X-Rays were monochromised using the Ross double filter method. The samples were powdered and pressed in a sample holder.

Experimental X-ray diffraction patterns were subject to the correction procedure including: monochromisation according to Ross; correction for the polarization factor; normalization of the integral experimental intensities by comparison with the integral theoretical intensities calculated from the atomic scattering factors; subtraction of the incoherent Compton scattering. All the calculations were made using prepared computer programs.

Differential scanning calorimetry (DSC) measurements were performed using a PL DSC calorimeter made by Polymer Laboratories Ltd (Epsom, U.K.). The calorimeter was calibrated using an indium standard ($\Delta H_m = 28.46$ J/g, $T_m = 429.99$ K). The samples of mass 9–11 mg were heated in the calorimeter at the rate $\beta = 20°C/min$, in the range from 25 to 270°C in nitrogen flowing at 1 cm^3/min. The rate of heating was chosen as 20°C/min for two reasons: (i) "pure" PA-6, as well as PA-6 contained in the blends, heated at small rates shows so-called multiple melting; (ii) at higher rates ($\beta > 20°C/min$) the conductivity between the sample and sample holder drops abruptly resulting in errors in calculated ΔH_m values.

CALCULATIONS

The main problem met in the investigation of the crystallinity of a polymer blend by means of X-ray diffraction is the necessity of separation of the scattered intensity contributions arising from crystalline and amorphous regions of the blend. It can be done using the method proposed by Hindeleh and Johnson [11]. However, directly resolving the diffraction pattern of a blend into amorphous and crystalline parts, an unequivocal solution frequently can not be obtained because of overlapping of the contributions from blend's components. For this reason, at the first step, in order to perform such a separation in the most reliable way, the diffraction pattern of the blend should be resolved into the contributions coming from each particular component. Next, such contributions can be resolved more easily into crystalline and amorphous parts, and the crystallinity of components as well as the total crystallinity of the blend can be calculated.

The blends PA-6/SPS dealt with in this work are composed of polymers which differ considerably in respect to their chemical composition and supermolecular structure in the solid state. Polyamide-6 is semicrystalline, while sulfonated polysufone is completely amorphous. WAXS patterns of these polymers in the "pure", non-mixed state are shown in Figs 1 and 2. Chemical compositions of both components are shown in Fig. 3. Taking into account the differences mentioned above and the resulting incompatibility of PA-6 and SPS, it may be supposed that their miscibility is negligible.

Thus, the blends may be considered as physical ones, with clearly separated regions formed by individual components. The volume fraction of transition layers is very low, and may be omitted.

Bearing in mind that one can assume that the components of the blend scatter the incident X-rays independently of each other and that the shape of the scattered X-ray intensity contribution arising from SPS (which is completely amorphous) is the same for all the blends investigated, independent of their composition (weight fraction of components). In other words the ratio S of the scattered intensity coming from SPS contained in a blend to the intensity of "pure" SPS sample is the same at each particular scattering angle. Obviously, such ratios are different

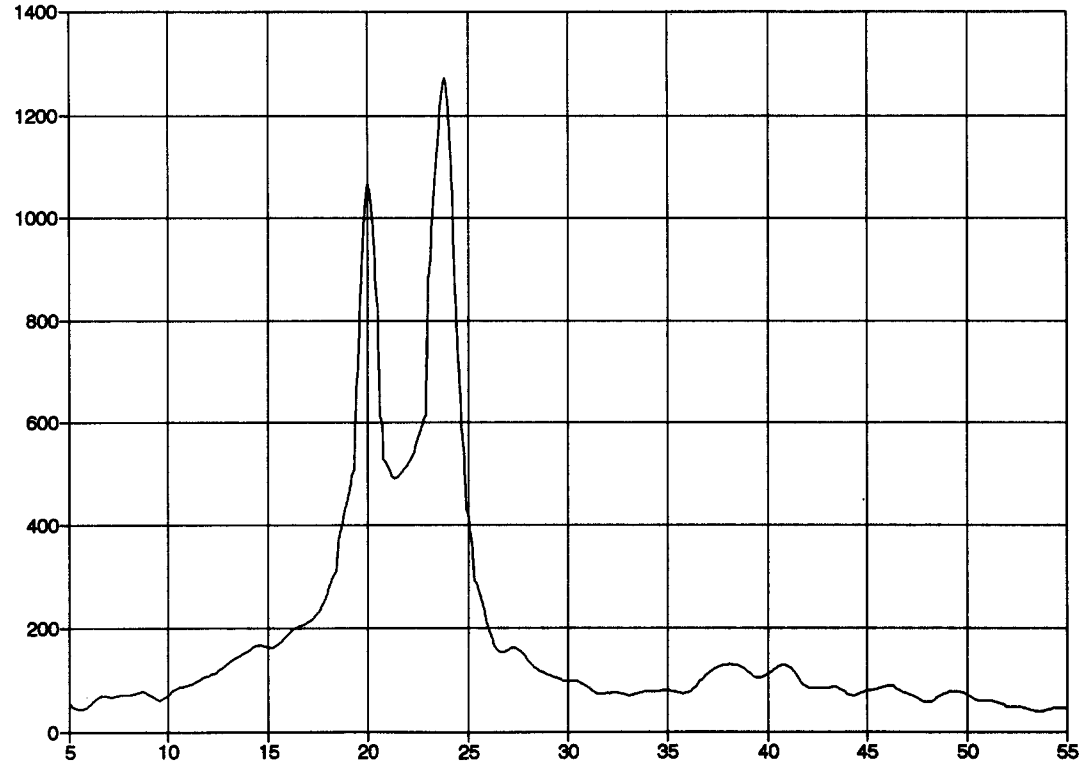

Fig. 1. Diffraction curve for "pure" polyamide (PA-6) sample.

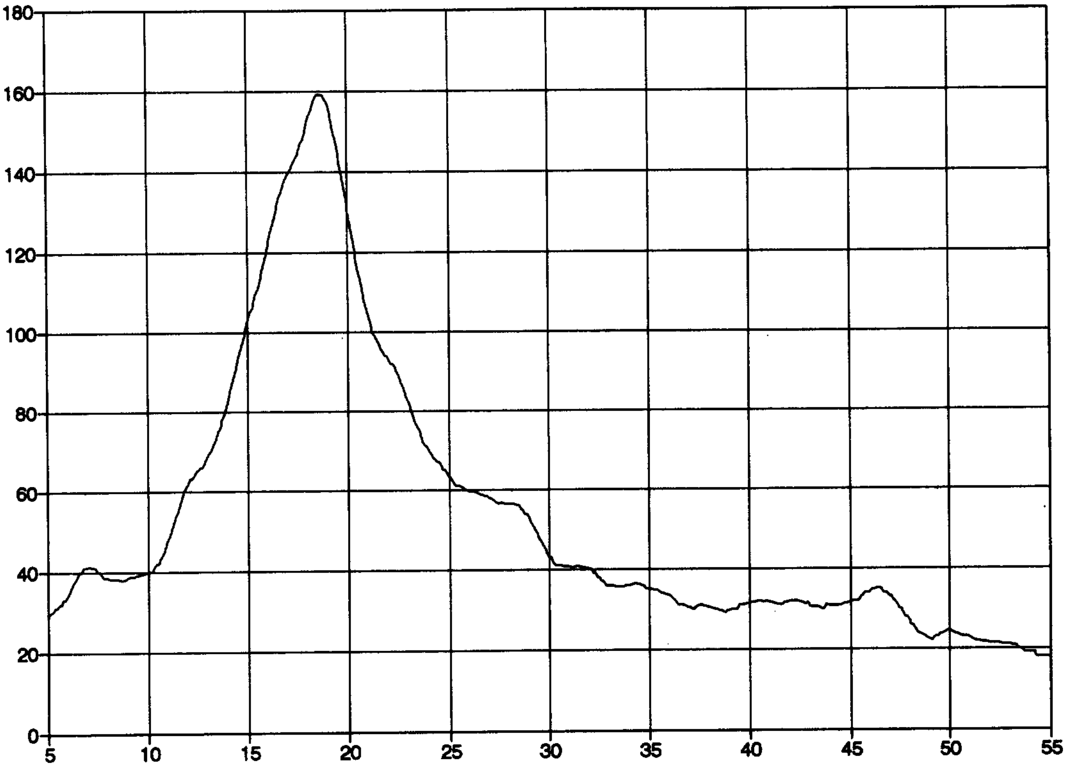

Fig. 2. Diffraction curve for "pure" sulfonated polysulfone (SPS) sample.

for different blends, but for a given blend, the ratio remains constant in the whole registration range.

Knowing the ratio S, which will be called the "scaling factor" later, the intensity contribution coming from SPS contained in a given blend may be calculated making use of the diffraction curve of the "pure" SPS sample. In this way, the diffraction curve of the blend could be resolved into the components arising from SPS and PA-6. The scaling factor S may be found from the following consideration. As a result of immiscibility of the components, they form separated regions within the volume of the considered blend and they scatter X-rays independently of each other. For this reason, the total intensity (intensity integrated over the whole reciprocal space) scattered by the blend is equal to the sum of total intensities coming from particular components. So, the ratio of the total intensity arising from SPS contained in the blend to the total intensity scattered by the whole blend may be calculated taking into account the weight fraction of this component and the scattering factors of the atoms of which SPS and PA-6 are built.

At first, using the chemical formulae of SPS and PA-6, the theoretical integral intensities scattered by one mer of each polymer are calculated. To this aim, we calculate the squared scattering factor for one mer from the scattering factors of the atoms present in the considered molecule. The atomic factors are taken in the form of power series [18]. Integrating the scattering factors of PA-6 and SPS mers with the

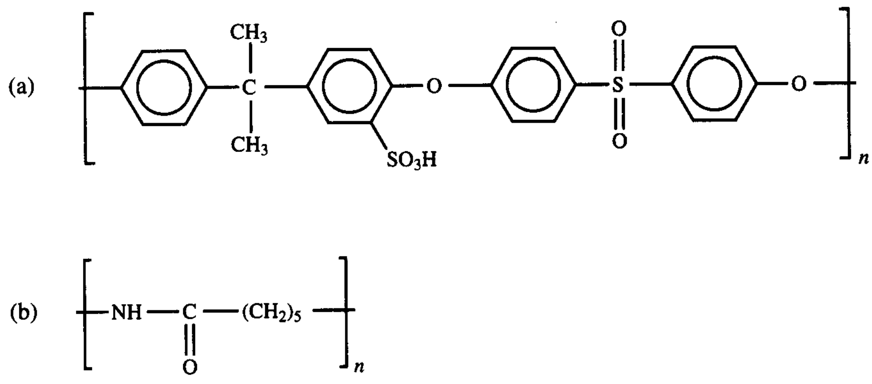

Fig. 3. Chemical composition of investigated polymers: (a) sulfonated polysulfone, (b) polyamide-6.

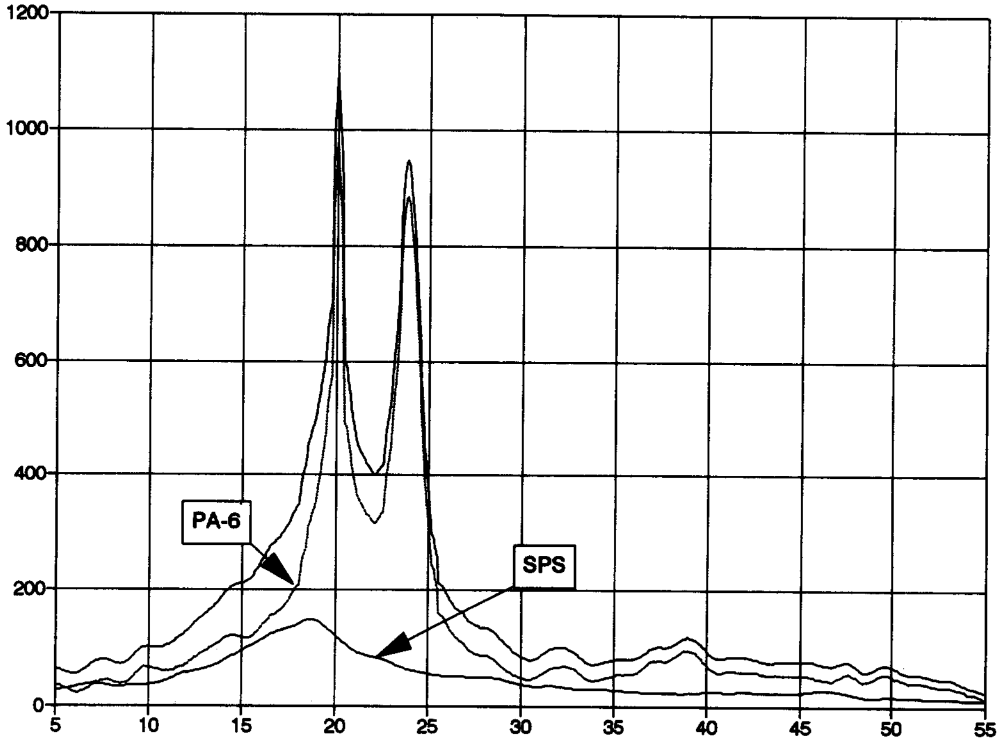

Fig. 4. Diffraction curve for the sample containing 20% SPS, resolved into the contributions arising from PA-6 and SPS.

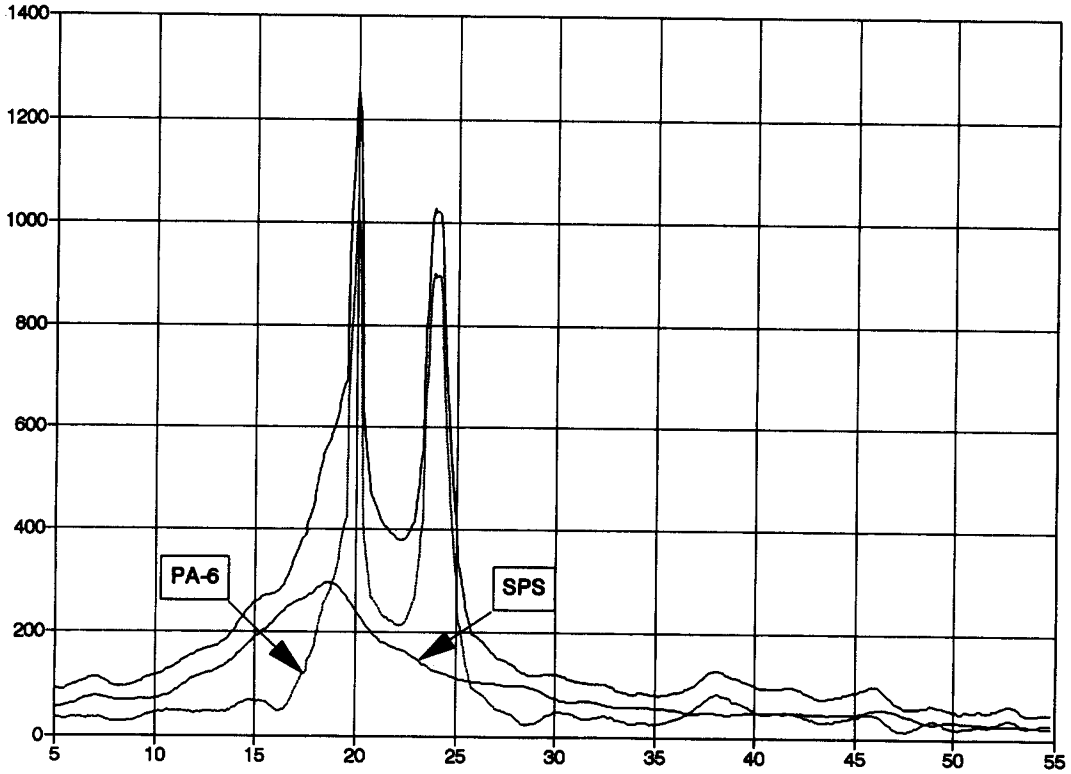

Fig. 5. Diffraction curve for the sample containing 40% SPS, resolved into the contributions arising from PA-6 and SPS.

same limits of integration as the limits of experimental registration of their X-ray diffraction curves we obtain the theoretical integral intensities related to one mer of each polymer.

Next, knowing the molecular masses of both polymers we find the theoretical intensities scattered by 1 g of PA-6 and SPS using the following equations:

$$i_{(\mathrm{PA})} = \frac{I_{(\mathrm{PA})} N_{\mathrm{A}}}{\mu_{(\mathrm{PA})}} \qquad i_{(\mathrm{SPS})} = \frac{I_{(\mathrm{SPS})} N_{\mathrm{A}}}{\mu_{(\mathrm{SPS})}}, \tag{1}$$

where $I_{(\mathrm{PA})}$ and $I_{(\mathrm{SPS})}$ are theoretical integral intensities scattered by one mer of PA-6 and SPS, respectively; $\mu_{(\mathrm{PA})}$ and $\mu_{(\mathrm{SPS})}$ are molecular masses of the polymers; N_{A} is Avogadro's number. Then, taking the same mass proportions of SPS and PA-6 as in the considered blend, we calculate the ratio R of the theoretical integral intensity scattered by SPS contained in the blend to the total theoretical intensity scattered by the blend as a whole.

$$R = \frac{i_{(\mathrm{SPS})} w}{i_{(\mathrm{SPS})} w + i_{(\mathrm{PA})}(1 - w)}, \tag{2}$$

where w is the weight fraction of SPS in the blend. Multiplying the integral experimental intensity scattered by the blend by the ratio R we obtain the integral experimental intensity arising from SPS contained in the blend $i_{\mathrm{m(SPS)}}$.

Finally, making use of the diffraction pattern of the "pure" SPS sample, we calculate the experimental integral intensity scattered by this sample, $i_{\mathrm{o(SPS)}}$. The ratio S is calculated according to:

$$S = \frac{i_{\mathrm{m(SPS)}}}{i_{\mathrm{o(SPS)}}}. \tag{3}$$

The diffraction curve related to SPS contained in the considered blend (SPS contribution) is determined by means of multiplication of the intensity values for the "pure" SPS sample at each particular angle by the scaling factor S. The diffraction curve obtained in this way is subtracted from the diffraction curve of the blend giving the curve related to PA-6 contained in it. In this work, all the calculations described above were made using a prepared computer program. Results are shown in Figs 4 and 5.

In order to calculate the degree of crystallinity of the polyamide contained in the blend, as well as the crystallinity of the blend, the diffraction curves of PA-6 obtained with the method described above must be resolved into crystalline peaks and amorphous part. The procedure of Hindeleh and Johnson [11] may be used. In this procedure a theoretical function composed of "peak" functions and a "background" function is constructed and fitted to the experimental curve by the least squares method. The degree of crystallinity is calculated as the ratio of the integral intensity under the resolved crystalline peaks to the total integral intensity under

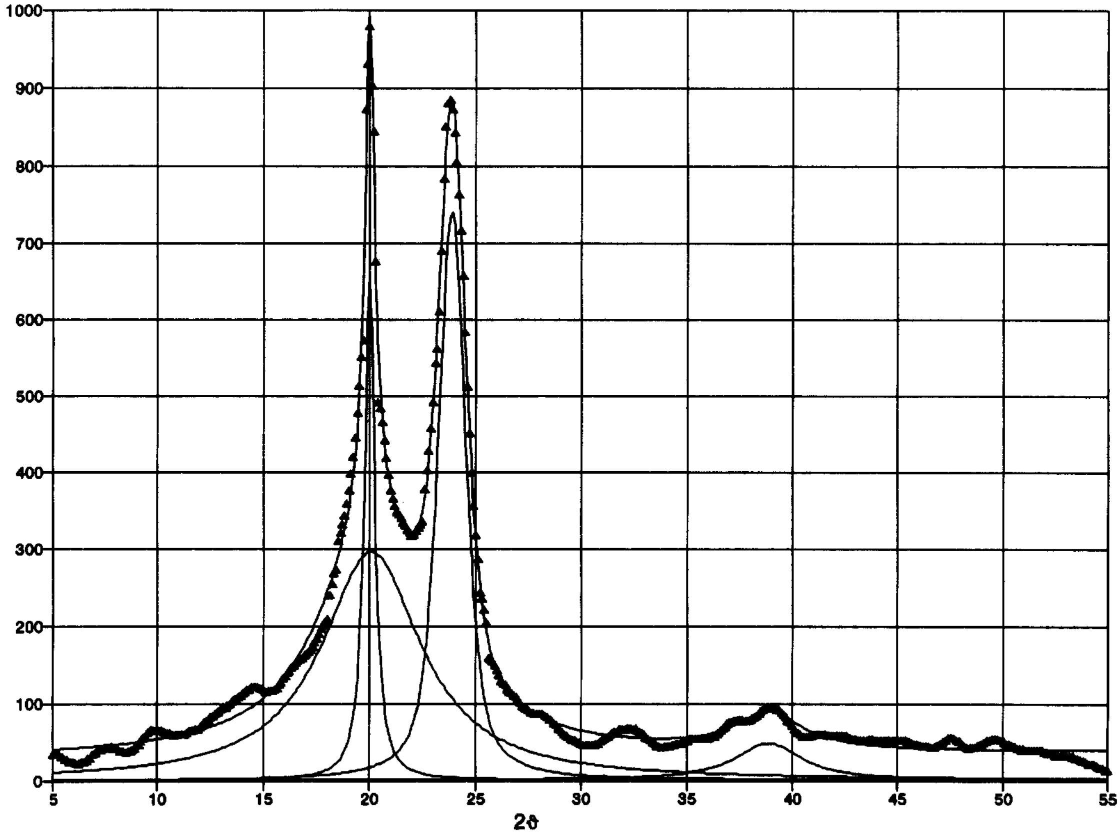

Fig. 6. Diffraction curve for PA-6 contained in the PA80/SPS20 blend (triangles) resolved into crystalline peaks and amorphous maxima.

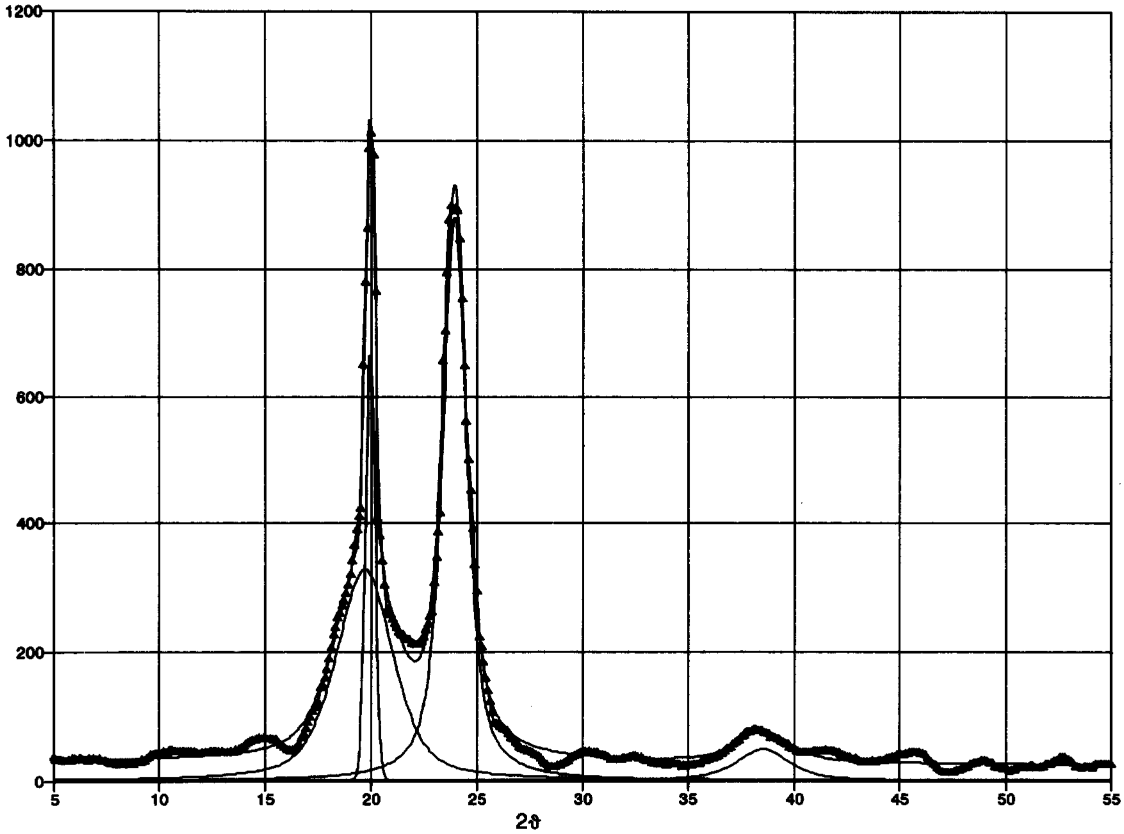

Fig. 7. Diffraction curve for PA-6 contained in the PA60/SPS40 blend (triangles) resolved into crystalline peaks and amorphous maxima.

the unresolved diffraction curve. The calculations are performed between two arbitrarily chosen angles [19]. This procedure has been applied to cellulosic materials [22], as well as to polyamide-6 and PET [19]. However, the values of crystallinity found by Hindeleh and Johnson for some polymers were very high. The values found for annealed polyamide-6 and PET samples were close to 100 and 85%, respectively [19]. The values were considerably larger than those reported by Ruland [9] and others [23, 24].

The procedure of Hindeleh and Johnson has been analysed in detail in Refs [25, 26]. It was shown that such high crystallinity values were directly connected with the type of function used for the amorphous background approximation: a polynomial of the third order. Investigations of PE, PP, PET and PA-6 have shown that for those polymers the amorphous part of the diffraction curve cannot be approximated by a polynomial of the third order. Such a polynomial gave a good fit in the works of Hindeleh and Johnson only because of a very narrow range of registration of diffraction curves, they were taken merely from 10° to 34°. When we examine the curves of most polymers in a sufficiently large range, we see that the amorphous background cannot be approximated by such a simple function. For instance, the amorphous background in the diffraction curves of the polymers mentioned above comprises two broad maxima. The first is located at about 20° and the second at about 40°. For this reason, it was suggested that the "background" function should be chosen individually for each investigated polymer. It was

Table 1. Angular positions of crystalline peaks (P_1 and P_2) and amorphous maxima (A_1 and A_2) obtained by resolution of the diffraction curves of PA-6 derived from the diffraction curves of the blends. Samples are denoted according to the weight fractions of components

Sample	P_1 (°) (200)	P_2 (°) (002) (202)	A_1 (°)	A_2 (°)
PA-6	19.98	23.78	20.66	39.71
PA90/SPS10	19.88	23.75	19.76	41.46
PA80/SPS20	19.99	23.88	20.08	38.88
PA70/SPS30	19.92	23.90	19.28	40.38
PA60/SPS40	19.95	23.95	19.69	38.53
PA50/SPS50	19.84	23.87	20.24	40.16
Average	19.93 ±0.06	23.86 ±0.06	19.95 ±0.44	39.85 ±0.97

Table 2. Widths at half heights of the crystalline peaks and amorphous maxima presented in Table 1

	P_1 (°)	P_2 (°)	A_1 (°)	A_2 (°)
PA-6	0.93	1.48	6.25	5.98
PA90/SPS10	0.84	1.42	7.68	8.86
PA80/SPS20	0.59	1.40	5.72	3.88
PA70/SPS30	1.02	1.34	11.54	9.12
PA60/SPS40	0.53	1.32	3.20	2.96
PA50/SPS50	0.79	1.24	7.65	6.50

Table 3. Crystallinity values of the blends determined by the X-ray diffraction method. X_{PA6} is the crystallinity of polyamide contained in a blend, X is the total crystallinity of the blend

	X_{PA} (%)	X (%)
PA-6	38.1	38.1
PA90/SPS10	44.0	39.6
PA80/SPS20	43.9	35.1
PA70/SPS30	55.5	38.9
PA60/SPS40	56.6	34.0
PA50/SPS50	41.1	20.6

Table 4. Crystallinity values of the blends determined by the DSC method. X'_{PA6} is the crystallinity of polyamide contained in a blend, X' is the total crystallinity of the blend

Sample	X'_{PA6} (%)	X' (%)
PA-6	36.9	36.9
PA90/SPS10	33.9	30.5
PA80/SPS20	40.9	32.7
PA70/SPS30	49.4	34.6
PA60/SPS40	50.3	30.2
PA50/SPS50	46.4	23.2

shown that reliable results were obtained when the approximating function was the composition of a third order polynomial and one or two functions related to the broad amorphous maxima. The latter functions were constructed as linear combinations of Gauss and Cauchy functions. The crystallinity values for PE, PP, PET and PA-6 obtained in this way were close to those obtained using Ruland's method for the same samples [25, 26].

In this work, we approximated the amorphous background in the same way: the "background" function was composed of a third order polynomial and two functions related to amorphous maxima. The fitting of the theoretical function to the experimental one, followed by its resolution, was performed using a computer program prepared to this aim. The fitting was realized by minimization of the sum of squares of differences between the experimental and theoretical curves making use of the Rosenbrock method [27]. Figures 6 and 7 present the intensity contributions arising from PA-6 derived from the diffraction curves of the blends.

The contributions are resolved into the crystalline peaks and amorphous background following the method described above.

RESULTS AND DISCUSSION

The angular positions of crystalline peaks and amorphous maxima obtained as a result of resolution of the diffraction curves of the blends are collected in Table 1. P_1 and P_2 are two crystalline peaks characteristic of the monoclinic α phase of PA-6. They are related to lattice planes (200) and (002) + (202), respectively. A metastable γ phase was absent in investigated samples (no peaks were

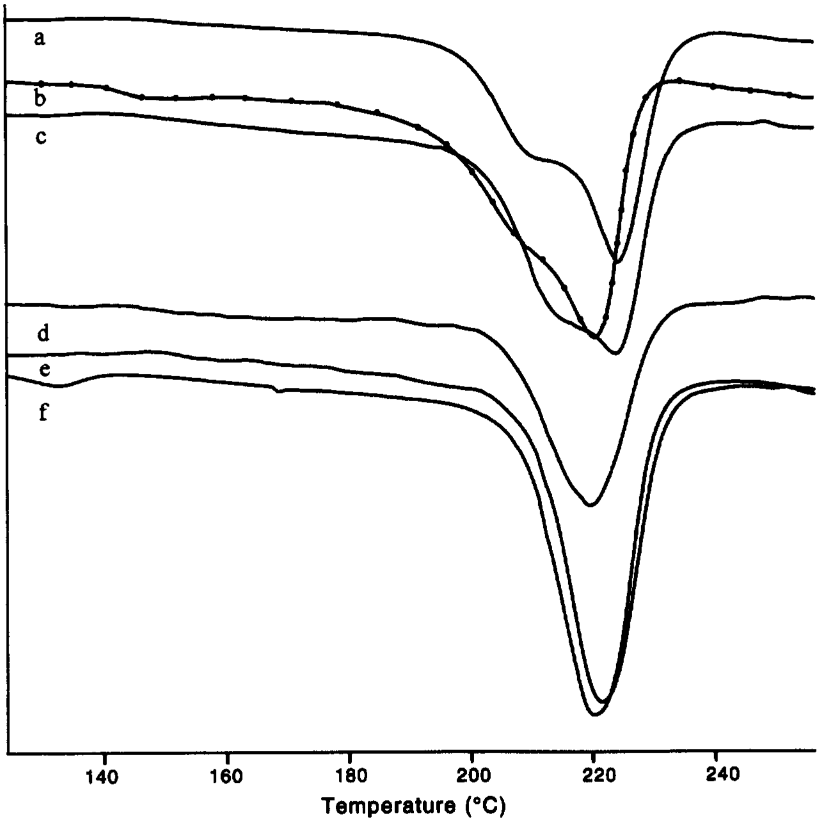

Fig. 8. DSC thermograms for PA-6 and investigated blends used for crystallinity determination. (a) PA-6, (f) PA50/SPS 50.

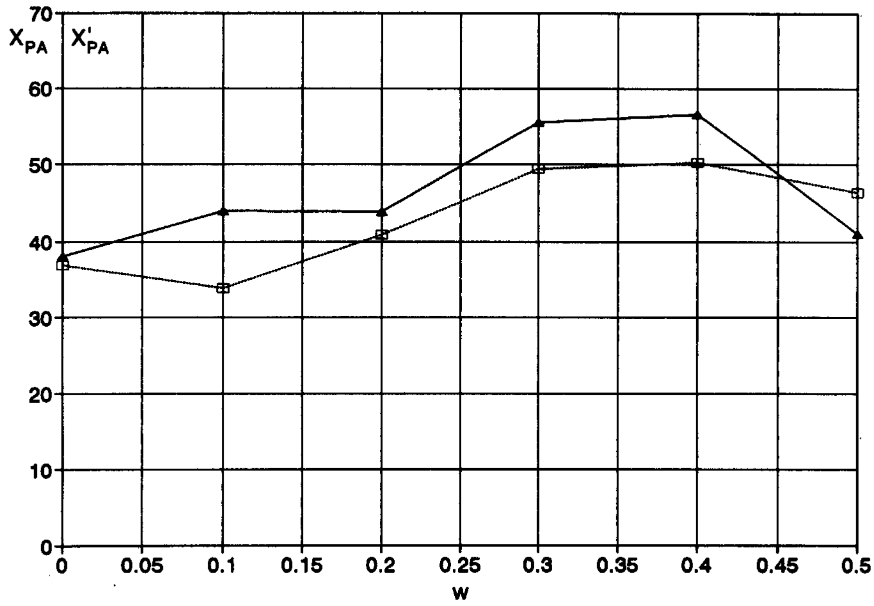

Fig. 9. Crystallinity of polyamide contained in PA/SPS blends as a function of the weight fraction (w) of SPS. Triangles are X-ray diffraction crystallinity, squares are DSC crystallinity.

observed). In the last row, the average values for all the samples are given, together with their standard deviations. One can see no changes in the angular positions of the peaks. Observed deviations are of the order of experimental error. It means that the parameters of the unit cell of PA-6 mixed with SPS remain the same as in the "pure" PA-6 sample. A_1 and A_2 in Table 1 are the amorphous maxima shown in Figs 6 and 7. Their angular positions vary over a wider range. However, the maxima are very broad themselves and observed variations are quite random. The widths at half height of crystalline peaks and amorphous maxima are given in Table 2.

As can be seen, the width of the crystalline peak denoted as P_2 decreases continuously. It suggests, that according to the Scherrer equation, the size of PA-6

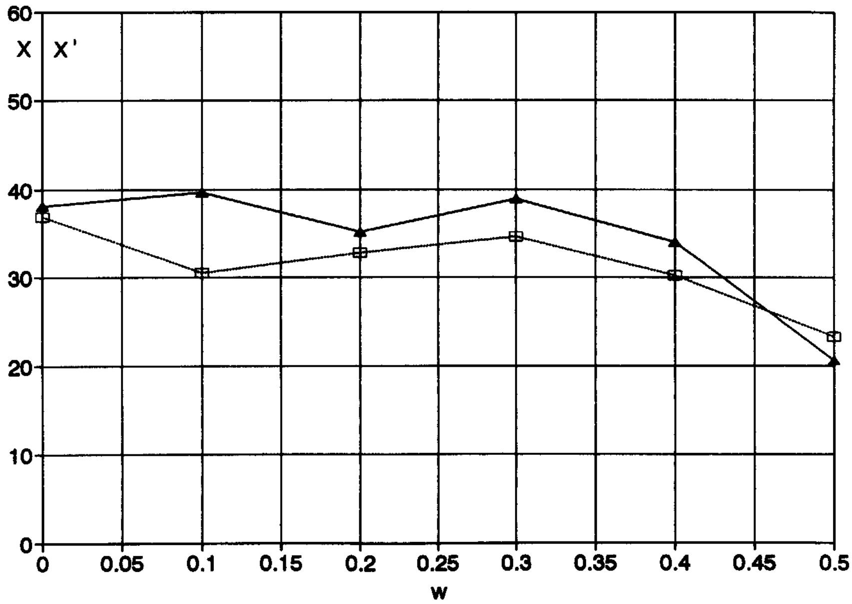

Fig. 10. Total crystallinity of PA/SPS blends as a function of the weight fraction (w) of SPS. Triangles are X-ray diffraction crystallinity, squares are DSC crystallinity.

crystallites increases slightly with increase in SPS weight fraction.

$$L_{hkl} = \frac{K\lambda}{\beta \cdot \cos\theta}, \tag{4}$$

where L_{hkl} is the mean dimension of the crystallites perpendicular to the planes (hkl), β is the width at half height of the peak, K is the Scherrer constant, θ is one-half the scattering angle. Particularly narrow crystalline peaks, P_1 and P_2, are observed for the sample containing 40% SPS. This fact indicates that the size of PA-6 crystallites in this sample is the largest.

In addition, the width of amorphous maxima for this sample is much less as compared with other samples. It may be interpreted in terms of better arrangement of polymer chains in the amorphous regions in this sample.

The crystallinity values found by X-ray diffraction are given in Table 3. The crystallinity of PA-6 contained in a blend (X_{PA6}) was calculated as the ratio of the area under the resolved crystalline peaks to the total area under the unresolved diffraction curve of PA-6, derived from the diffraction curve of the blend. The total crystallinity of the blend was calculated using the crystallinity of PA-6 and its weight fraction $(1 - w)$ in this blend:

$$X = X_{PA6}(1 - w), \tag{5}$$

w is the weight fraction of SPS. It can be seen that the presence of SPS has a distinct influence on the crystallinity of PA-6. The crystallinity of polyamide rises with increasing SPS concentration, reaching a maximum value for the sample containing 40% SPS. These results coincide with those presented in Table 2, which show the increase in the size of crystallites.

The DSC thermograms of investigated samples are given in Fig. 8. It is easy to see that the melting peaks of the samples PA-6, PA90/SPS10 and PA80/SPS20 are much wider compared with the others. The narrowest melting peak is observed for the sample containing 40% SPS. It may confirm the result of X-ray investigations, according to which the crystallites in this sample have the largest dimensions. The results of DSC investigations of crystallinity are given in Table 4. The DSC crystallinities X' and X'_{PA6} were calculated according to the following formulae:

$$X' = \frac{\Delta H_m}{\Delta H_m^\circ} \qquad X'_{PA6} = \frac{X'}{1 - w}, \tag{6}$$

where ΔH_m is the enthalpy of melting of a blend, ΔH_m° is the enthalpy of melting of a crystalline standard of PA-6 ($\Delta H_m^\circ = 160$ J/g, [28])

In Figs 9 and 10, the crystallinity values obtained by both methods are presented versus the weight fraction of SPS in a blend. As can be seen, both methods show the same trends in the variations of crystallinity as a function of SPS weight fraction. In both cases, the crystallinity reaches a maximum value for the sample containing 40% SPS. DSC crystallinities are slightly less than WAXS ones. However, these differences result from the specificity of the considered methods and they are always observed for semicrystalline polymers.

Of course, it is difficult to explain the observed changes in the molecular structure of PA-6 contained in the investigated blends solely using the data collected in this paper. Additional investigations should be performed to do this. However, this was not the aim of this work, the work was done in order to verify the new X-ray procedure for polymer blends crystallinity determination. It seems that the consistency of the results obtained by DSC and X-ray methods confirms its suitability.

The proposed method can also be used for block copolymers in which the components form separated phases. Using this method we can calculate not only the total crystallinity of the semicrystalline component of a blend or a block copolymer, but also the weight fractions of different crystalline phases in the case of polymorphic polymers can be estimated.

REFERENCES

1. Wakelin, J. H., Virgin, H. S. and Crystal, E., *J. Appl. Phys.*, 1959, **30**, 1654.
2. Statton, W. O., *J. Appl. Polym. Sci.*, 1963, **7**, 803.
3. Bosley, D. E., *J. Appl. Polym. Sci.*, 1964, **8**, 1521.
4. Challa, G., Hermans, P. H. and Weidinger, A., *Makromolek. Chem.*, 1961, **50**, 98.
5. Challa, G., Hermans, P. H. and Weidinger, A., *Makromolek. Chem.*, 1962, **56**, 169.
6. Fraser, R. D. B. and Suzuki, E., *Analyt. Chem.*, 1966, **38**, 1771.
7. Hermans, P. H. and Weidinger, A., *Text. Res. J.*, 1961, **31**, 558.
8. Ruland, W., *Acta Cryst.*, 1961, **14**, 1180.
9. Ruland, W., *Polymer*, 1964, **5**, 89.
10. Vonk, C. G., *J. Appl. Cryst.*, 1973, **6**, 148.
11. Hindeleh, A. M. and Johnson, D., *J. Phys.*, 1971, **4**, 259.
12. Coven, A. W., *Phys. Rev.*, 1932, **41**, 422.
13. Jouncey, G. E. M. and Pennell, F., *Phys. Rev.*, 1932, **43**, 585.
14. Jouncey, G. E. M. and Pennell, F., *Phys. Rev.*, 1933, **44**, 128.
15. Rabiej, S., *Eur. Polym. J.*, 1993, **29**, 625.
16. Brousse, C., Chapurlat, R. and Quentin, J. P., *Desalination*, 1976, **18**, 137.
17. Noshay, A. and Robeson, L. M., *J. Appl. Polym. Sci.*, 1976, **20**, 1885.
18. Ibers, J. I. and Hamilton, W. C. (eds) *International Tables for X-Ray Crystallography*. Kynoch Press, Birmingham, 1974.
19. Hindeleh, A. M. and Johnson, D., *Polymer*, 1978, **19**, 27.
20. Hindeleh, A. M. and Johnson, D., *Polymer*, 1972, **13**, 27.
21. Hindeleh, A. M. and Johnson, D., *Polymer*, 1972, **13**, 423.
22. Hindeleh, A. M. and Johnson, D., *Polymer*, 1924, **15**, 697.
23. Dumbleton, J. H., Buchanan, D. R. and Bowles, B. B., *J. Appl. Polym. Sci.*, 1968, **12**, 2067.
24. Włochowicz, A. and Jeziorny, A., *J. Polym. Sci. (A-2)*, 1972, **10**, 1407.
25. Rabiej, S., *Eur. Polym. J.*, 1991, **27**, 947.
26. Rabiej, S. and Włochowicz, A., *J. Appl. Polym. Sci.*, 1922, **46**, 1205.
27. Rosenbrock, H. H. and Storey, C., *Computational Techniques for Chemical Engineers*, Pergamon Press, London, 1966.
28. Rybnikar, P., *Collect. Czech. Chem. Commun.*, 1959, **24**, 2869.