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D. K. Mishra[a]; D. Parida[a]; S. S. Nayak[a]; S. Lenka[a]; P. L. Nayak[a]
[a] Laboratory of Polymers and Fibres, Department of Chemistry, Ravenshaw College, Cuttack, India

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POLYMERS FROM RENEWABLE RESOURCES. X. SEMI-INTERPENETRATING POLYMER NETWORKS BASED ON CASTOR OIL POLYURETHANE AND CARDANOL-FURFURAL RESIN: SCANNING ELECTRON MICROSCOPY AND XRD STUDIES

D.K. Mishra, D. Parida, S.S. Nayak, S.Lenka and P.L. Nayak.

Laboratory of Polymers and Fibres, Department of Chemistry, Ravenshaw College, Cuttack : 753 003, India.

ABSTRACT

A number of semi-interpenetrating polymer networks (Semi-IPNs) were synthesized by reacting the polyurethane prepared from castor oil and diisocyanates and the resin prepared from cardanol and furfural. The physico-chemical properties of the semi-IPNs have been investigated. The scanning electron microscopy of some of the semi-IPNs have been studied and the morphology has been examined. The samples were subjected to wide angle X-ray diffraction analysis. The degree of crystallinity (X_{cr}) were computed on the basis of crystal defect concept developed by Roland and Vonk.

INTRODUCTION

The research work involving interpenetrating polymer networks (IPNs) using naturally occuring triglyceride oils which was initiated by Sperling and Coworkers (1-5) at Leigh University has taken momentum in recent years. Over the years a large number of papers have been published in this area using biomonomers as the base materials. These oils are generally synthesized by the nature with multiple chemical functionality. The oils which have attracted attention for preparation of IPNs and semi-IPNs are castor, vernonia and lesquerella palmeri etc. Out of these oils, castor oil has received attention in recent years because of its availability in large commercial scale. Orissa is one of the states in India crowned with various forest products of oil bearing wild plants such as castor, tung, vernonia, linseed, crambe, lunaria, cashewnut, hipatage benghalensis, wrightia tinctoria, w.tomentosa and apocynaceace. These plants are abundantly grown in the forest of Orissa and the oils of some

of these plants contain trigleceride of recenoleic acid. This laboratory has taken up a program for the synthesis and characterization of IPNs and semi-IPNs from the oils available in the forests of Orissa. In the first step we have reported the characterization of some IPNs from castor oil and cashewnut shell liquid, a by—product of cashew industries (6-7). This communication presents the scanning electron microscopy and XRD study of some semi-IPNs prepared from castor oil polyurethane and cardanol-furfural based resins.

EXPERIMENTAL

Synthesis of Polyurethane (Polymer-I) : Castor oil (9.32gm, 0.01 mol) was allowed to react with toluene 2,4-diisocyanate (TDI) (4.18 gm, 0.024 mole) to maintain the NCO/OH ratio at 1.6. The reaction was carried out at 45°C with continuous stirring for 2 hours. The prepolymer was isolated as a viscous liquid. Other polyurethanes with different NCO/OH ratios were prepaired following the same procedure and also differing with diisocyanate.

Synthesis of Resin (Polymer-II) : A mixture of cardanol (4 m.mole) and furfural (40 m.mole) was refluxed at 110°C for about 8-10 hr in presence of NaOH (4N) with periodical shaking. At the end of reaction, the contents extracted with ice cold water, filtered and washed repeatedly with hot water to remove the unreacted materials. The product was dried in vacuum.

Synthesis of semi-IPNs: These components polymer- I and II were taken in various ratios (shown in Table-1) in benzene. Then 5cc of 1% EGDM (ethylene glycol dimethacrylate) was added to it and stirred well on electric stirrer. The stirring was continued till the reactions are intimately mixed. The entire process was carried out at ambient temperature. These two polymers continue simultaneously polymerization forming semi-interpenetrating polymer networks. The physico-chemical properties of the semi-IPNs are represented in Table-1 & 2.

Scanning electron micrographs were obtained from a phillips EM-400 equipped with scanning (transmission) electron microscope system PW6585. The film was cryogenically fractured in liquid nitrogen and was mounted vertically on a SEM stub by silver adhesive paste. The specimen was coated with gold using an EPS/carl zeiss vacuum system at about 10 torr.

Wide angle X-ray diffraction data were obtained using CuK_{α} radiation which was monochromatized by curved quartz crystal after transmission through the specimen. Intensity distribution was recorded using symmetrical reflection technique in a phillips diffractomer (PW1140). CuK_{α} (1.54A)

TABLE-1

Feed composition and physicochemical data of semi-IPNs

Sl. No.	Sample Code	Resin Code	COPU (NCO/OH)	COPU/ Resin	Decomposition temperature(°C)	Colour
1.	Semi-IPN-1	CARD+FU	1.6	25:75	> 360	Black
2.	Semi-IPN-2	CARD+FU	1.8	35:65	> 360	Black
3.	Semi-IPN-3	CARD+FU	1.8	45:55	> 360	Black
4.	Semi-IPN-4	CARD+FU	2	45:55	> 360	Black
5.	Semi-IPN-5	CARD+FU	1.6	25:75	> 360	Black
6.	Semi-IPN-6	CARD+FU	1.8	35:65	> 360	Black
7.	Semi-IPN-7	CARD+FU	1.8	45:55	> 360	Black
8.	Semi-IPN-8	CARD+FU	2	45:55	> 360	Black

(1-4)⟶ COPU— Castor oil polyurethane from DPMDI (diphenyl methane diisocyanate), CARD—— Cardanol, FU —— Furfural, (5-8)⟶ COPU — Castor oil polyurethane from TDI (toluene 2,4-diisocyanate).

TABLE-2

Percentage of weight loss on treatment with different chemical reagents

Chemical Reagents	Semi-IPN-1	Semi-IPN-2	Semi-IPN-3	Semi-IPN-4	Semi-IPN-5	Semi-IPN-6
25% H_2SO_4	1.0	1.0	1.1	1.0	1.1	1.1
25% HCl	1.7	0.3	0.7	1.5	1.5	1.3
40% NaCl	0.7	0.2	0.1	0.8	0.9	2.4
5% NaOH	1.8	9.2	12.0	10.3	12.4	1.7
5% HNO_3	1.8	0.5	0.6	1.6	1.6	2.3
10% NH_4OH	0	0	0	0	0.8	0
Distilled water	0.7	0.7	0.6	0.7	0.5	0.4

radiation at 30KV, 10MA with balanced filter of Ni-Al was used. Intensity measurement were taken using G.M counter employing fixed count step scanning Platinium powder was used as instrument standard.

XRD STUDIES

X-ray diffraction pattern of many polymers consisting both sharp and diffused ring reveals their two phase morphology. The high mechanical strength of these polymers are attributed to the presence of crystalline domains in the composite two phase microstructure. The determination of crystalline content of a given samples accurately, has been the subject matter of great interest for the last few decades in order to get a first hand knowledge about the performance of a polymer materials. Hermons (8) and Karst and Flaschner (9) developed quantitative methods for determination of the degree of crystallin (X_{cr}). These two methods define crystalline domains as those which contribute maxima in its X-ray diffraction curve and arrived at a crystalline proportion. By comparison of the intensity of maxima considered to be contributed by the crystalline part of the substance and the intensity of the background scattering supposed to be due to amorphous regions. Ruland (10) developed a method for the determination of (X_{cr}) by introducing crystal defect concept which was subsequently simplified and computered by Vonk(11). Hindleh (12) developed a peak resolution technique to find out X_{cr} values. The present study is basing on the determination X_{cr} of semi-IPNs prepared from castor oil based polyurethanes and cardanol-furfural based resins by Ruland-Vonk crystal defect method. Crystalline size can be determined by Scherrer's formula (13).

Ruland-Vonk method : Ruland (10) proposed the following equation based on the crystal defect concept.

$$X_{cr} = \frac{1}{R} \times K = \frac{\int_{S_o}^{S_p} I_{cr}(s)\, s^2 ds}{\int_{S_o}^{S_p} I(s) s^2 ds} \times \frac{\int_{S_o}^{S_p} \bar{f}^2 (s^2)\, ds}{\int_{S_o}^{S_p} \bar{f^2}(s^2) D.ds} \quad \ldots\ldots (1)$$

The term '$\frac{1}{R}$' refers to conventional 'X_{cr}' and 'K' is a crystal defect constant, 'I_{cr}' is the part of the intensity in the crystalline lattice vector S = 2 Sinθ/λ (for Bragg's angle (2θ) and wave length λ). 'I' is the total coherent scattering at point'S', $\bar{f}^2$ is the mean scattering factor

$$\bar{f}^2 = \frac{\sum N_i f_i^2}{\sum N_i}$$

where 'f_i' is the atomic scattering factor of an atom of the type 'i' and 'N_i' is the number of atoms of the type 'i', 'D' is the disorder function which taken into account the loss of intensity concentrated at the reciprocal lattice point due to deviations of the atoms from their ideal positions. These deviation may be due to thermal vibration of the first or second kind

$$D = 2 \exp(-as^2)/1 + \exp(-as^2) \quad \ldots\ldots (2)$$

where 'a' is the overal distortion factor due to temperature and lattice distortions. One of the problems in the evaluation of X_{cr} by this method is the large amount of calculation involved particularly in selecting the interval until X_{cr} remains constant while varying K (and hence D). Again knowledge of the exact chemical structure of the compound and unit cell parameters are necessary. Vonk simplified and computerised the Ruland's method. According to this method a plot of R_{sp} versus S_p will oscillate about a straight line defined by

$$R_{sp} = 1/X_{cr} + (K/2X_{cr})sp^2 \quad \ldots\ldots (3)$$

where 's_p' is the upper integration limit. X_{cr} is estimated from the intercept and 'K' from the slope. Thus we could generate a set of different 'R_{sp}' values and their corresponding 'S_p' values for getting a plot of R_{sp} Vs s_p^2. In this computation we have taken the help of the LOTUS 123 software in a PCAT. Table -3 shows the representative data and calculation results of semi-IPN-5. A series of R_{sp} values for different upper limit (s_p) have been found out. A plot of R_{sp} Vs s_p^2 was obtained from various R_{sp} values and their corresponding s_p^2 values. As expected, it will give an oscillating curve through which a straight line could be drawn. The intercept and the slope could be determined by least square method using regression analysis in the LOTUS 123 software. The intercept as described in equation (1) gave the values of ($1/X_{cr}$) and the reciprocal of this value gave X_{cr}.

SCANNING ELECTRON MICROSCOPY (SEM) OF SEMI-IPNs

The morphology of the semi-IPNs derived from castor oil based polyurethanes and cardanol-furfural based resins have been studied by scanning electron microscope (SEM) method. Fig.1(a) & (b) shows the SEM micrographs of the semi-IPN-2 prepared from castor oil-DPMDI polyurethane (NCO/OH - 1.8) and cardanol-furfural resin (35:65) with 2500 to 5500 magnification respectively. A heterogeneous surface was observed. Fig.2(a) & (b) shows the SEM micrographs of the semi-IPN-3 prepared from castor oil-DPMDI polyurethane (NCO/OH - 1.8) and cardanol-furfural (45:55) with 1500 to 2500 magnification respectively. By comparing both the figures, it is observed that the heterogeneity gradually

TABLE - 3

Computation of R_{s_p} values for different S_p^2 values and the determination of X_{cr} for Semi-IPN-5.

2Θ	I	S_p	$I_{s_p^2}$	S_p^2	A_{IW}	A_{IUB}	A_{IAB} $(A_{IW}-A_{IUB})$	A_{IW}	A_{IAB}	R_{s_p}
10	0.3	0.1131	0.7996	0.0127	0.0099	0.0083	0.0016	0.0099	0.0016	6.1888
11	0.3	0.1243	0.9671	0.0154	0.0119	0.0114	0.0005	0.0218	0.0021	10.3466
12	0.3	0.1356	1.1502	0.0184	0.0155	0.0144	0.0011	0.0374	0.0032	11.6447
13	0.35	0.1469	1.6189	0.0215	0.0231	0.0175	0.0056	0.0606	0.0088	6.8502
14	0.4	0.1581	2.5017	0.0250	0.0321	0.0205	0.0116	0.0928	0.0204	4.5365
15	0.45	0.1694	3.2285	0.0286	0.0432	0.0236	0.0196	0.1361	0.0401	3.3909
16	0.6	0.1806	4.4860	0.0326	0.0586	0.0266	0.0320	0.1947	0.0721	2.6987
17	0.65	0.1918	5.9801	0.0368	0.0796	0.0296	0.0499	0.2744	0.1221	2.2461
18	0.85	0.2030	8.2442	0.0412	0.1037	0.0326	0.0711	0.3781	0.1933	1.9561
19	1.45	0.2142	9.6241	0.0458	0.1178	0.0355	0.0822	0.4960	0.2756	1.7998
20	1.3	0.2253	10.193	0.0507	0.1302	0.0385	0.0917	0.6263	0.3673	1.7050
21	1.3	0.2365	9.7864	0.0559	0.1382	0.0414	0.0967	0.7646	0.4641	1.6474
22	1.21	0.2476	9.2654	0.0613	0.1331	0.0444	0.0887	0.8978	0.5529	1.6237
23	0.9	0.2587	8.7166	0.0669	0.1255	0.0473	0.0782	1.0233	0.6311	1.6214
24	0.85	0.2698	8.3220	0.0728	0.1150	0.0501	0.0648	1.1383	0.6959	1.6356
25	0.7	0.2809	7.8636	0.0789	0.1015	0.0530	0.0485	1.2399	0.7444	1.6655
26	0.6	0.2919	6.3237	0.0852	0.0912	0.0558	0.0353	1.3311	0.7798	1.7070
27	0.5	0.3029	6.8321	0.0917	0.0848	0.0587	0.0261	1.4160	0.8059	1.7569
28	0.45	0.3139	6.3937	0.0985	0.0840	0.0615	0.0225	1.5000	0.8285	1.8105
29	0.4	0.3249	6.9198	0.1055	0.0897	0.0642	0.0254	1.5897	0.8539	1.8616
30	0.35	0.3359	5.8626	0.1128	0.0955	0.0670	0.0285	1.6853	0.8824	1.9098

X_{cr} = 0.677229

KEY WORDS :-

S_p = upper limit of s, $I_{s_p^2}$ = the intensity value in the Y coordinate corresponding to 'sp', A_{IW} = individual whole area (for varying lower and upper limits) e.g area of trapezium BCEF, A_{IUB} = individual area under the base line (for varying lower and upper limit e.g area of trapezium PQEC), A_{IAB} = individual area above the base line, A_{IW} = summation of individual (whole area between fixed initial s_o and varying s_p values e.g. area under the curve upto AF), A_{IAB} = summmation of individual areas above the base line (area between fixed initial s_o and varying s_p above the base line such as area above the line AQ).

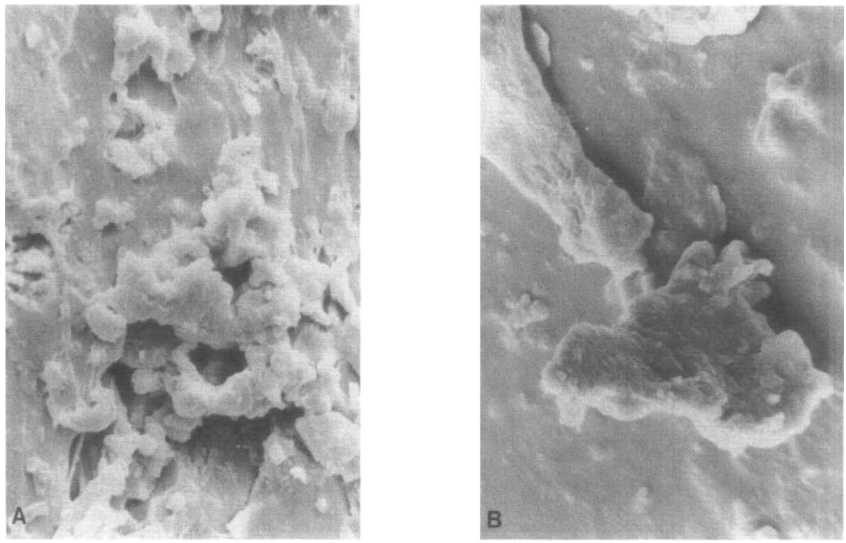

Fig. 1 (a) SEM Micrograph of Semi-IPN-2 with magnification 2500
(b) SEM Micrograph of Semi-IPN-2 with magnification 5500

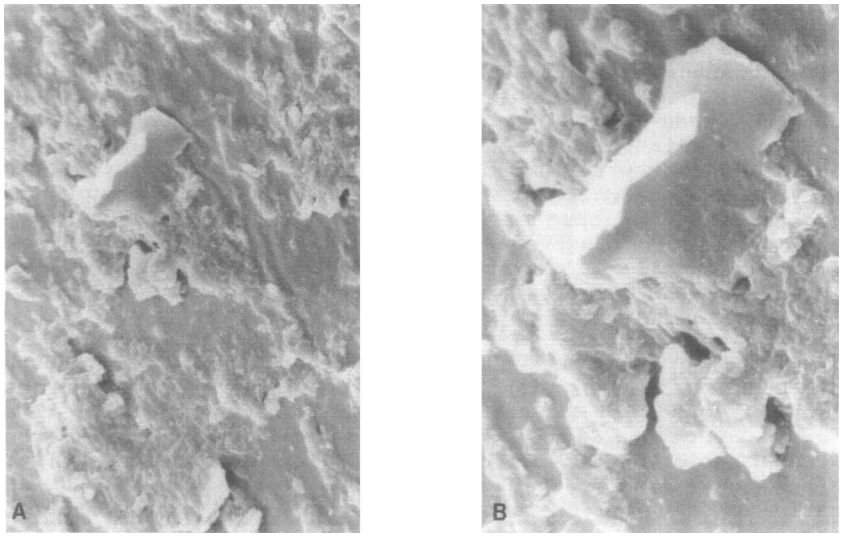

Fig. 2 (a) SEM Micrograph of Semi-IPN-3 with magnification 1500
(b) SEM Micrograph of Semi-IPN-3 with magnification 2500

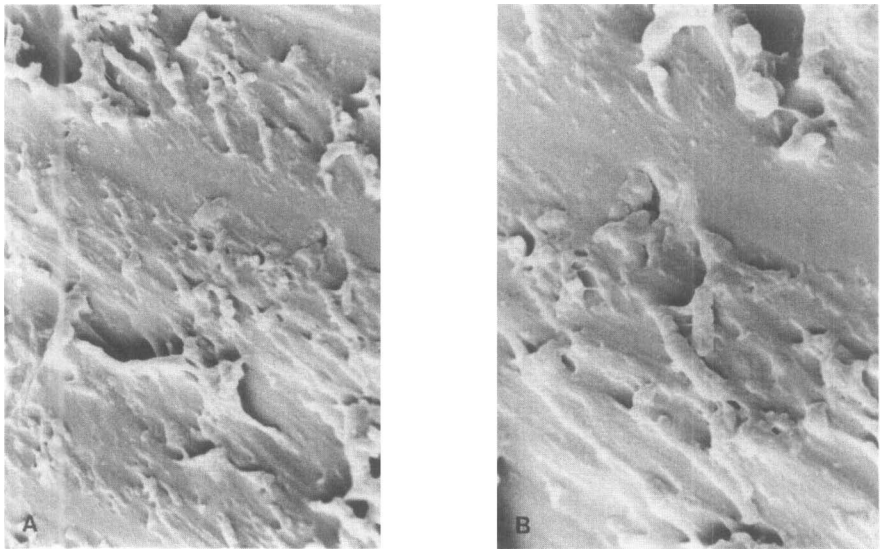

Fig. 3 (a) SEM micrograph of Semi-IPN-6 with magnification 1500.
(b) SEM micrograph of Semi-IPN-6 with magnification 3000.

decreases and the morphology gradually changes from discontinuous to continuous with increaging the resin content from 55% to 65%. Similarly varying the COPU-resin content constant when NCO/OH ratio of the polyurethane changes from 1.6 to 2 again the heterogenity becomes more prominent. This indicates that with increasing the resin content, the system becomes homogeneous as is evident from the nature of crystallinity in case of XRD study. Similarly observations have also been observed in case of the semi-IPN-6 prepared from castor oil-TDI polyurethane (NCO/OH - 1.8) and cardanol-furfural resin (35:65) with 1500 to 3000 magnification which is shown in the fig.3(a) & (b).

It is observed that the semi-IPN-4 prepared from castor oil-DPMDI (NCO/OH-2) with the resin copolymer (45:55) has the highest degree of crystallinity (X_{cr}) i.e. 0.73772. The degree of crystallinity value decreases to 0.567738 as the NCO/OH ratio of the polyurethane decreases from 2 to 1.6. Hence in this case the crystallinity depends on the NCO/OH ratio of the polyurethane rather than COPU resin ratio. Similar observation has also been observed in case of the polyurethane prepared from TDI. The order of crystallinity of different samples under investigation are furnished in Table- 4 . From the observation, it can be ascertained that

TABLE-4

Degree of Crystallinity (X_{cr}) of Polymer Samples

Sl.No.	Sample No.	X_{cr}
1.	Semi-IPN-1	0.567738
2.	Semi-IPN-3	0.639362
3.	Semi-IPN-4	0.737720
4.	Semi-IPN-5	0.677229
5.	Semi-IPN-7	0.681324
6.	Semi-IPN-8	0.849149

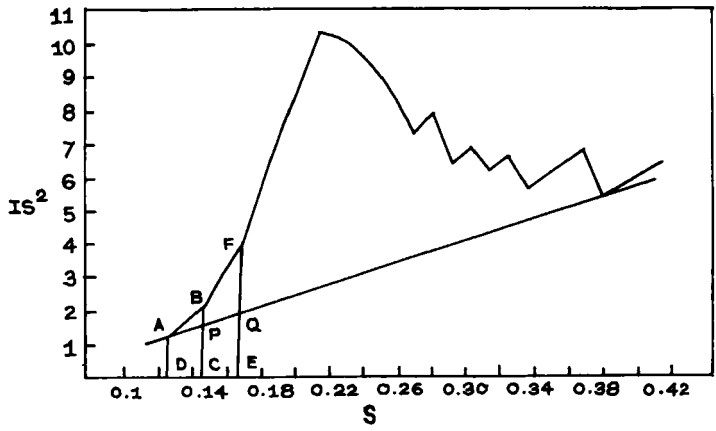

Fig. 4 Intensity distribution plot of semi-IPN-5

most probably the resins one of comparatible with the polyurethanes and a two phase system exists.

RESULT AND DISCUSSION

In the present investigation Ruland and Vonk method has been employed for calculating the degree of crystallinity (X_{cr}) values. The detailed method of computing X_{cr} for the semi-IPN- 5 is furnished in Table-3. In fig.(4) the XRD intensity distribution plot for the semi-IPN- 5 which plots Is^2 Vs S is furnished.

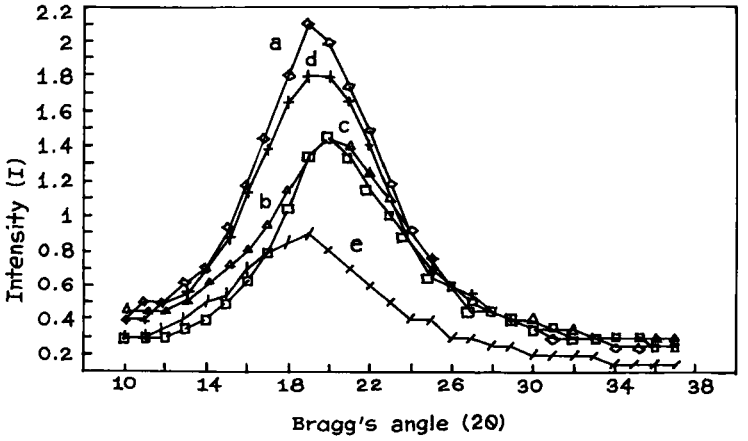

Fig.5 : Intensity (I) Vs Bragg's angle (2θ), (a) semi-IPN-8 (◇), (b) semi-IPN-7 (△), (c) semi-IPN-5 (□), (d) semi-IPN-4 (+), (e) semi-IPN-1 (/).

This plot has been obtained from the plot of intensity (I) Vs Bragg's angle (2θ) is shown in fig.(5). The plot indicate the presence of two sets of reflection planes corresponding to the (2θ) values of 14° and 28°. Since our aim is to draw a plot of Rsp Vs sp different upper limit (sp) values had to be chosen. This is more clearly observed in fig.(4). Let'So' is the lower limit and 'sp' is the first upper limit. The area bounded by the curve upto 'Sp' can be found out by calculating the area of the trapezium ABCD. The area below the background line between So to Sp is the area of the trapezium APCD. The area above the base line which is predominantly due to the crystaline domain obtained by substracting the area of the trapezium ABCD.

The ratio of the areas of triangle ABP and trapezium ABCD is $1/R_{sp}$ and hence the reciprocal of this value is R_{sp} and this is restricted to the limits So to $S'p$. Now a new upper limit $S'p$ whose value is higher than 'Sp' is taken. The area below the curve So to $S'p$ is found out as follows. First the area of the trapezium BCEF and PQEC are calculated between limits Sp to $S'p$ as before. These areas added to the previous area of trapezium ABCD and APCD respectively to find out the total area under the curve and below the base line between the limits So to $S'p$. The total area above the background line between So to $S'p$ is obtained by substracting the total area area below the line from the total area under the curve

between the limits So to S_p^1. In this manner the higher limits that is Sp values were increased and the total areas between So to Sp is obtained by summing up technique. The R_{sp} value at each limit could be calculated by taking the ratio of the areas under the whole curve and above the base line between these limits.

$$R_{sp} = \frac{\int_{s_o}^{s_p} I(s)s^2 ds}{\int_{s_o}^{s_p} I_{cr}(s)s^2 ds}$$

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