Polyisoprene modified polystyrene

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Polyisoprenes have been used to prepare modified polystyrenes in an attempt to improve impact strength. It has been determined that polyisoprene reinforces polystyrene by the formation of complex rubber phase particles, similar to those in commercial polybutadiene reinforced polystyrenes. These particles, however, are subject to breakdown by melt shearing, resulting in a significant drop in impact strength and an increase in tensile strength. This particle destruction is due to the fact that polyisoprene does not crosslink during the polymerization process. It is significant that before shearing these uncrosslinked rubber particles satisfactorily toughen polystyrene.

INTRODUCTION

Rubber modified polystyrenes are large volume commodity polymers with significantly improved impact resistance over that of polystyrene[1]. These polymers are prepared by dissolving about 5% of a butadiene rubber in styrene, followed by an early phase polymerization to about 20% conversion with shearing agitation to establish stable rubber droplets through phase inversion[2]. Subsequent polymerization to completion is carried out in mass or in suspension. During the latter stage of polymerization, rubber phase crosslinking which assures the permanence of rubber phase morphology[3,8] is achieved.

The purpose of this work is to establish some possible reasons for the apparent absence of commercial polyisoprene (PI) modified polystyrenes. While PI appears to be suitable for the modification of polystyrene, some critical factor apparently discourages its use. Accordingly, polyisoprene modified polystyrenes have been prepared and their properties have been examined by various techniques to gain an understanding of their behaviour.

EXPERIMENTAL

Materials

The following rubbers were used: natural rubber crumb (SMR, 5L TP 0203), Shell polyisoprene 305 (Code 90312), Goodrich–Gulf polyisoprene SN600 (903-09-F3), Firestone Diene HD-55 and Diene CF-35. Natural rubber was compounded on cold 3 x 8 in. rolls before use.

Polymerization procedure

Rubbers were dissolved in a 1 l stratified, stirred reactor. A typical recipe comprised 10% rubber, 89% styrene and 1% mineral oil. Partial polymers were obtained by thermal polymerization at 120°C and 60 r.p.m. to about 30% solids. Polymerization was completed (at 130° to 180°C) without further agitation. The polymers were devolatilized at about 200°C for 2 h.

Di-tert-butyl peroxide (DTBP) (0.08%) was added in styrene to some partial polymer by slowly stirring. The uniform mixture was finished as described above.

Ground polymer was moulded into ASTM test bars for impact and tensile testing. It was also compounded on heated 3 x 8 in. rolls in the presence of 0.5% Ionol.

Methods used for gel determination and dynamic mechanical testing have been reported earlier[4]. Dynamic shear modulus (G') and logarithmic decrement of damping (δ) are plotted as a function of temperature.

RESULTS AND DISCUSSION

Gel determinations shown in *Table 1* indicate that PI modified polystyrenes contain essentially no insoluble fraction when measured in toluene, while in methyl ethyl ketone (MEK) the gel content varies between 11.3 and 13.6%. These data indicate that very little crosslinking, if any, has occurred during the synthesis. The addition of 0.08% DTBP in the finishing stage does not increase the toluene gel. With the use of MEK, a selective solvent, the gel data indicate that some grafting of PS onto PI has taken place. It is also seen that in polystyrene, reinforced with polybutadiene (PBD), gel content is also high in non-selective toluene, showing that the rubber phase is crosslinked. The reason for the lower gel content in MEK is not readily apparent, although these results have been reproduced repeatedly with other PBD rubber modified polystyrenes. It has been reported that in dimethylformamide, the gel content is even lower in relationship to the value for the toluene determination[9]. Apparently, as the solvent becomes a poorer one for PBD, more PS may be extracted because of the collapsed and fragile state of the PBD membranes.

Polyisoprene modified polystyrenes were all prepared by the same procedure. Accordingly, the volatile contents were in the range of 1.3 to 1.6% resulting in Vicat heat distortion

Table 1 Gel content in polyisoprene (10%) modified polystyrene

Rubber	Gel (%) Toluene	Gel (%) MEK
Natural rubber	1.5	11.3
Solprene 305	1.1	13.6
SN 600	1.2	12.3
Diene HD-55* (Control)	18.6	16.7

* 6% in PS; after three extractions in toluene, gel – 16.6%

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Table 2 Effect of melt shearing on tensile and impact strengths

Polyisoprene (10%)	Melt flow rate (g/10 min)	Tensile (p.s.i.)		Notched Izod (ft lbs/in)	
		Moulded directly	Sheared[1]	Moulded directly	Sheared
Natural rubber	7.2	2800	3800	2.7	0.2
Natural rubber +0.08% DTBP	20.2	2230	2610	0.2	0.2
Solprene 305	3.9	1860	3830	2.5	0.2
Solprene +0.08% DTBP	12.7	2030	2990	0.9	0.3
SN 600	5.5	1600	3560	1.9	0.2
SN 600 +0.08% DTBP	12.8	1820	2380	0.2	0.3

[1] Melt sheared on 3 X 8 in. compounding rolls for 10 min

values of 96° to 102°C. Upon shearing on compounding rolls, Vicat values were slightly enhanced (to 103°C), presumably due to an additional loss of volatile material. It may be presumed then that the significant changes in the impact and tensile strengths (*Table 2*) are predominantly due to some change of the rubber particle structure. The change in rubber particle morphology due to melt shearing is shown in *Figures 1* and *2*. In some non-sheared polymers, photomicrographs show some very large (to 40 μm), but typically complex, particles with PS occlusions.

It was further noted that with the 0.08% DTBP in the finishing stage, in addition to no significant change in the gel content measured in toluene, the rubber damping peak was not affected (*Figures 3* and *4*), nor were the volatile content in the final polymer or the Vicat heat distortion. Melt flow rate was increased significantly and impact strength was reduced (*Table 2*).

It may be concluded from these data that the change in the rubber phase in this case may be of secondary importance, while the reduction of PS molecular weight due to DTBP has been significant, causing the increase in melt flow rate, and the reduction of impact strength.

Further, it may be of interest to consider the expected change in the grafting of rubber during the high temperature finishing with additional initiator. It has been proposed that short and more numerous grafts may shift the rubber damping peak to a higher temperature (ref 1, p. 75).

In our experiments (*Figures 3* and *4*), no noticeable increase of the temperature of the rubber damping peak was noted due to the use of free radical initiator in the final finishing stage.

Dynamic mechanical property characterizations are shown in *Figures 5–7* for PI (SN600) modified polystyrenes. It is seen that significant PI peaks at about –55°C occur with polymers containing 5–15% PI, when measured on specimens directly as polymerized. Upon mechanical shearing of the melt, severe reductions of the rubber peaks take place with corresponding increases in the dynamic shear moduli. The temperature of the rubber phase damping peak appears to be affected little, if at all. Since the rubber content is not varied by shearing, a significant change in the rubber particle morphology must cause the reduction in the rubber peak (ref 5, ref 1 pp. 112, 113 and 123–125). It also is seen that impact strength reduction is associated with the reduction of the rubber loss peak, normally resulting from reduced rubber content[12,4].

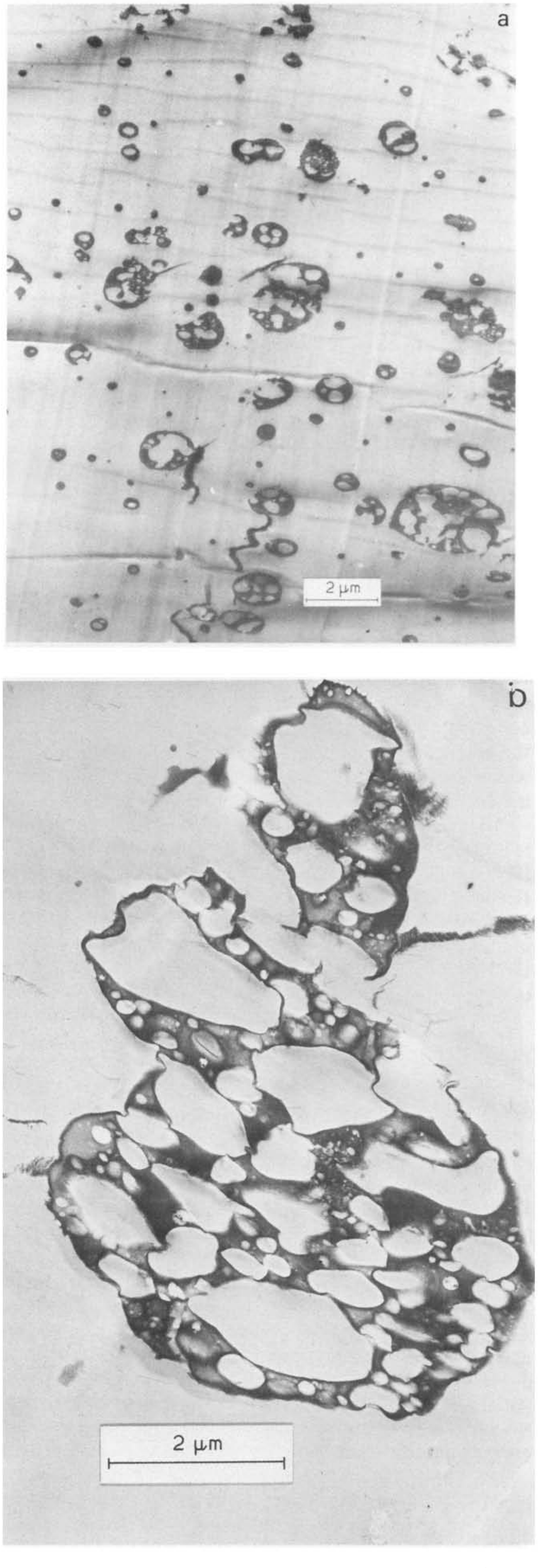

Figure 1 Polyisoprene (5% SN 600) modified polystyrene. (a) typical particles; (b) one of the numerous large particles

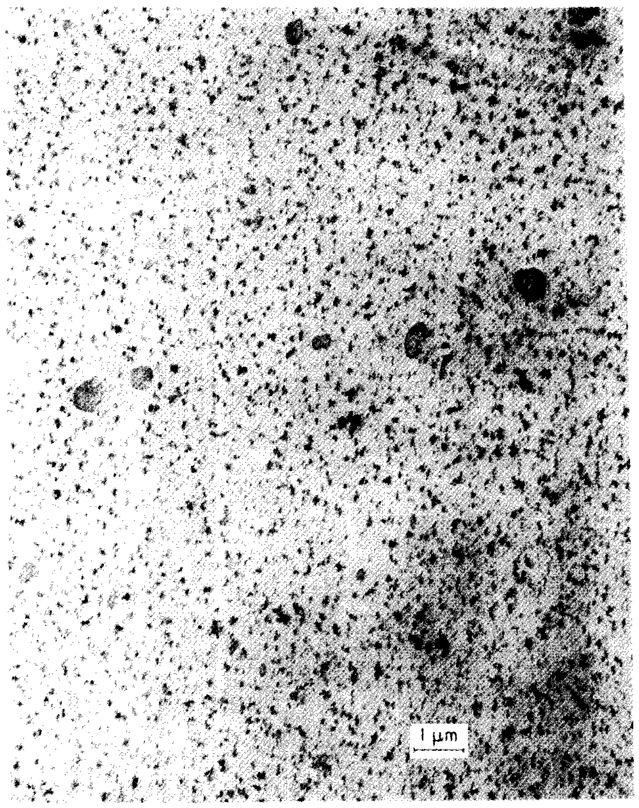

Figure 2 Polyisoprene particles after mechanical shearing

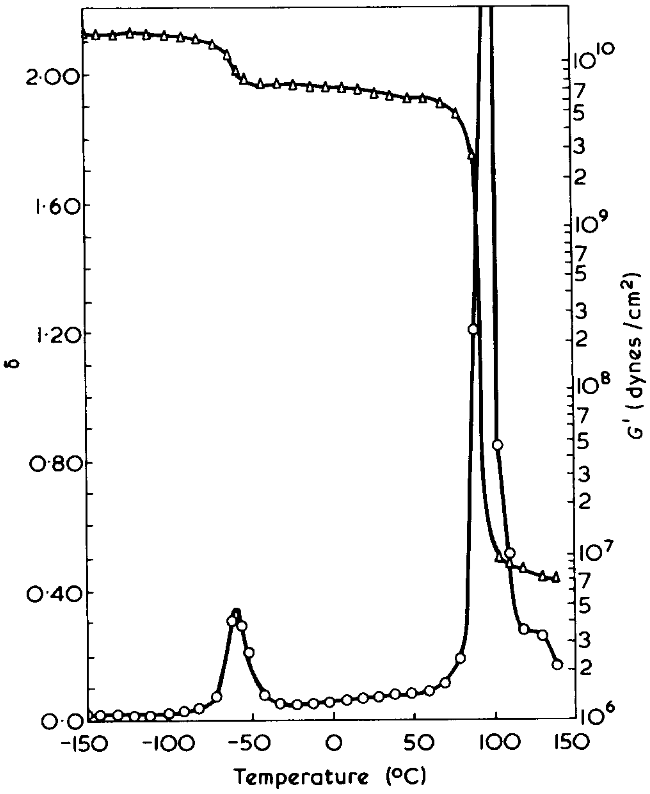

Figure 3 Dynamic mechanical characterization of natural rubber modified polystyrene (10% rubber)

The cause for the reduction of the rubber phase appears to be related to the lack of sufficient crosslinking of PI. Data in *Table 1* shows the solubility of the PI phase in toluene, indicating its lack of crosslinking. The relative lack of PI thermal crosslinking in comparison to polybutadiene is further shown in heating solid rubber samples over 200°C. Diene CF-35 forms in excess of 90% gel at 220°C in less than 1 h, while at 230°C, 94% is obtained in 30 min. The introduction of a free radical source to PBD further reduces the

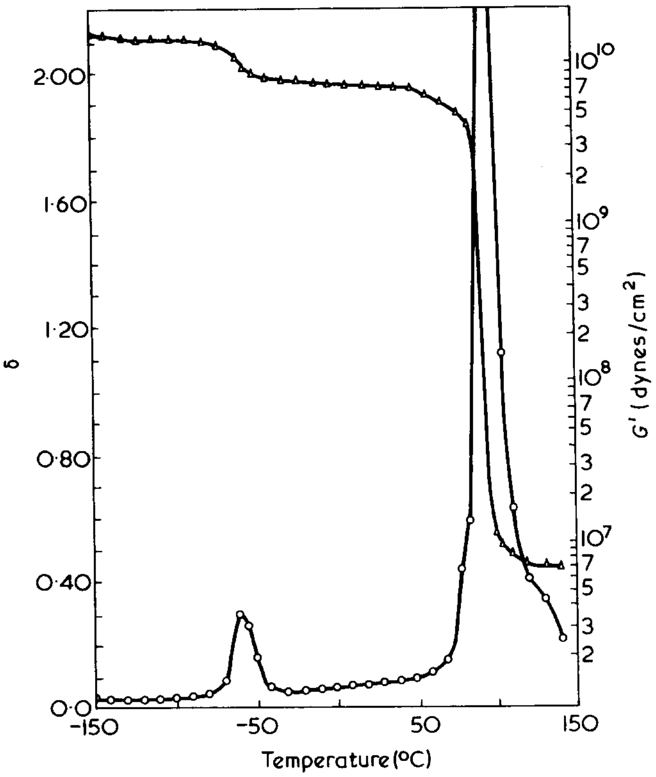

Figure 4 Dynamic mechanical characterization of natural rubber modified polystyrenes (10% rubber, 0.08% DTBP in the finishing stage)

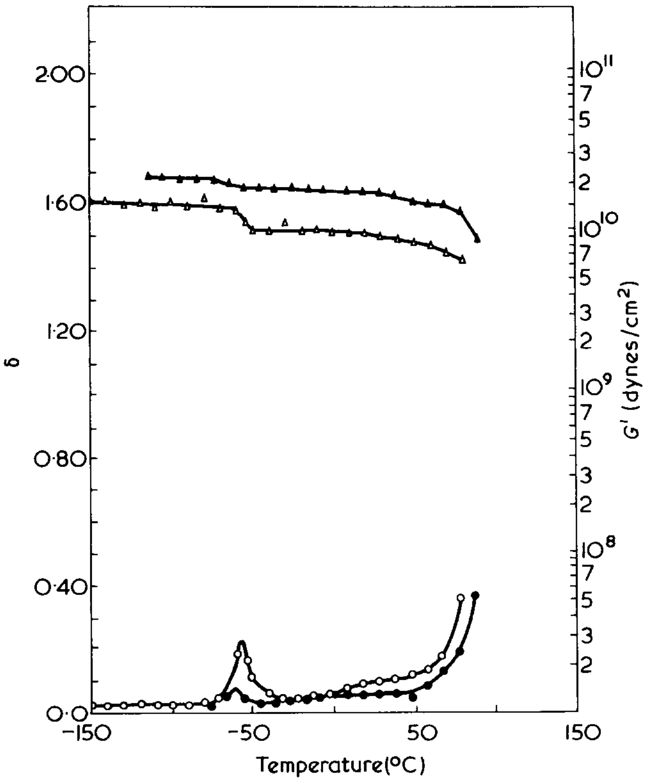

Figure 5 Dynamic mechanical characterization of polyisoprene (SN 600) modified polystyrene (5% rubber). △, ○, As polymerized 1-1 N. I; ▲,●, melt sheared 0.2 N.I.

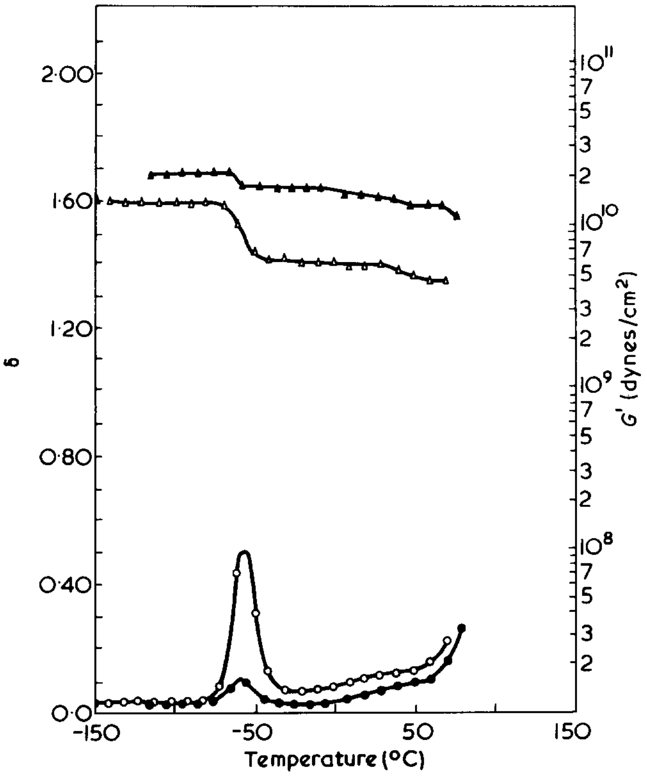

Figure 6 Dynamic mechanical characterization of polyisoprene (SN 600) modified polystyrene (10% rubber). △, ○, As polymerized 1.9 N.I; ▲,●, melt sheared 0.2 N.I.

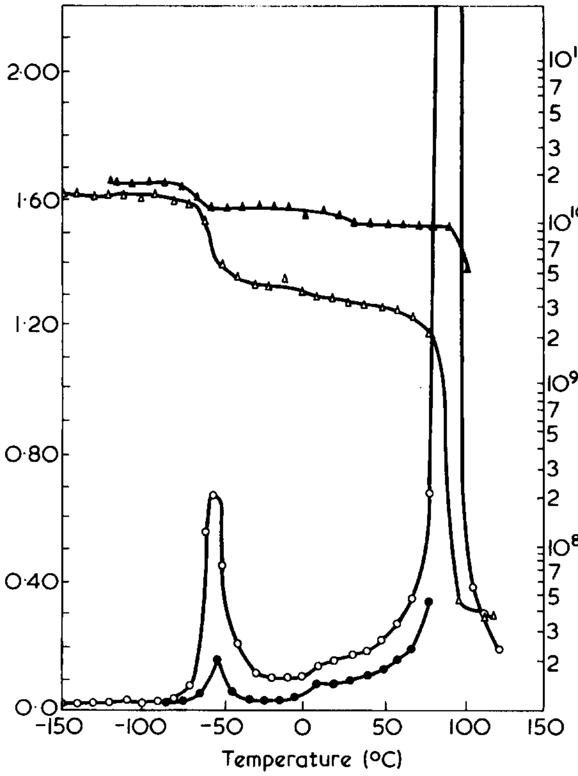

Figure 7 Dynamic mechanical characterization of polyisoprene (SN 600) modified polystyrene (15% rubber). △, ○, As polymerized 3.1 N.I; ▲, ●, melt sheared 1.2 N.I.

time and temperature for substantially complete gel formation. PI, on the other hand, can be heated to over 300°C for 1 h without crosslinking. The substantial difference in the crosslinking mechanism[6,10] of the two rubbers apparently accounts for this significant difference.

The difference between the thermal behaviour of the two rubbers is further shown by the thermogravimetric analysis data. PBD is shown to exhibit the high degradation temperature of 447°C, due to the development of a crosslinked network during the test[7]. PI degrades at the significantly lower temperature of 364°C, more typical of the similar hydrocarbon polymer, polypropylene.

It appears then that the lack of particle integrity of the complex PI–PS particles is due to the inadequate level of crosslinking in PI, giving rise to the breakdown of rubber particles by melt shearing. This breakdown causes a reduction in toughness and an increase in tensile strength. Commercial high impact polystyrenes do not show any significant change in mechanical properties or rubber particle integrity due to melt shearing on compounding rolls, extruders or in injection moulding machines[8].

Finally, it may be of interest to consider the fact that significant impact improvement was obtained in a rubber modified PS with an uncrosslinked rubber phase. There are numerous papers indicating the importance of rubber crosslinking for PS toughening[1,3,5]. Additionally, Schmitt[11] presents a convincing argument for the need of a crosslinked rubber phase in order for it to be capable of supporting triaxial tension.

It appears possible to propose, however, that in the case of complex rubber particles for toughening, presumably grafting is important in providing sufficient matrix–particle adhesion for the mechanical coupling necessary to prevent crazes developing into cracks, while the principal purpose of crosslinking is to maintain the integrity of the rubber particles. For a better understanding of PS toughening, it may be of considerable interest to study the relative importance of variable crosslinking of the rubber phase, independent of the practical consideration of particle integrity.

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REFERENCES

1 Bucknall, C. B. 'Toughened Plastics', Applied Science Publishers, London, 1977
2 Molau, G. E. and Keskkula, H. *J. Polym. Sci. (A-1)* 1966, **4**, 1595
3 Stein, D. J., Fahrbach, G. and Adler, H. *Adv. Chem. Ser.* 1975, **142**, 148
4 Keskkula, H., Turley, S. G. and Boyer, R. F. *J. Appl. Polym. Sci.* 1971, **15**, 351
5 Wagner, E. R. and Robeson, L. M. *Rubber Chem. Technol.* 1970, **43**, 1129
6 van der Hoff, B. M. E. *Ind. Eng. Chem. Prod. Res. Dev.* 1960, **2**, 273
7 McCreedy, K. M. and Keskkula, H. *J. Appl. Polym. Sci.* to be published
8 Keskkula, H. *Appl. Polym. Symp.* 1970, **15**, 51
9 Thomas, C. M. *Br. Plast.* 1963, **36**, 645
10 van der Hoff, B. M. E. *Appl. Polym. Symp.* 1968, **7**, 21
11 Schmitt, J. A. *J. Polym. Sci. (C)* 1970, **30**, 437
12 Buchdahl, R. and Nielsen, L. E. *J. Appl. Phys.* 1950, **21**, 482