Tensile strength of joints bonded with ABA poly(styrene-b-isoprene) films

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INTRODUCTION

We have investigated the adhesive properties of non-compounded ABA poly(styrene-b-isoprene) block copolymers (SIS) used as heat activated films in simple overlap joints. Glass is used as the substrate. The break resistance of such joints is studied as a function of the molecular characteristics of the SIS copolymers[1]. Results concerning tensile shear strength have been published, only for well defined molecular characteristics (molecular weight $\sim 30\,000$ and 30% by weight polyisoprene content), SIS copolymers have good adhesive properties. We have ascribed this behaviour to a particular morphology of these copolymers[2].

As the values found depend on the test used[3], we have also investigated the tensile strength of such joints, again as a function of the total molecular weight (M_{tot}) and the elastomer content (%I).

In this note, we report results obtained for about 40 SIS copolymers, of varying M_{tot} (30.10^3–200.10^3) and %I (4–86%). All copolymers were prepared in our laboratory except one, Cariflex ® TR 1107, an industrial SIS copolymer manufactured by Shell.

EXPERIMENTAL

Synthesis and characterization of materials

SIS copolymers were prepared by the now classical three-step anionic polymerization, in benzene at 50°C, using n-butyl lithium as initiator[4]. Molecular characteristics were determined by gel permeation chromatography (g.p.c., Waters, in THF) and by ultra-violet spectroscopy (Cary, 1501) and appear in *Table 1*. SIS copolymer films were obtained by compression moulding for 2 min at 180°C to 0.1 mm thickness, and rapid cooling.

Joint formation

Glass plates were degreased before use. A simple lap joint was formed: according ASTM D 1344–72, two glass plates were disposed so as to form a cross and the film, cut to size, was inserted between the glass plates. Overlap area $= 6.25\ \text{cm}^2$. A special device allowed exact positioning of the different parts of the joint, and the whole was heated at 135°C for 2 h. The temperature was then decreased slowly to room temperature.

Joint breaking

The average tensile resistance at break, $\bar{\sigma}$, (Pa) of all joints was measured on a Zwick testing machine (mod Z 13), with a cross-head separation speed of 2 mm/min. For each copolymer at least five joints were tested. The standard deviation, s (Pa) and the confidence limit at 95% (IC_{95} in Pa) were determined[5] and are listed in *Table 1*.

RESULTS AND DISCUSSION

In *Table 1* the average tensile strength at break, $\bar{\sigma}$, for the different SIS copolymers studied in this work is shown. The experimental values were rather dispersed, so that we noted for each the standard deviation s, and the confidence limit at 95%, IC_{95}. The average overall dispersion was found to be around 18%. Though fairly high, such an

Table 1 Molecular characteristics and average tensile strength at break for various SIS copolymers

SIS sample	$10^{-3} M_{tot}$ (g/mole)	% PI	$10^{-5}\ \bar{\sigma}$ (Pa)	$10^{-5}\ s$ (Pa)	$10^{-5}\ IC_{95}$ (Pa)
200	200	25.4	1.1	0.3	1.5– 0.7
207	142	8.5	1.6	0.1	1.8– 1.4
222	49.5	47.5	13.7	2.6	16.8–10.6
242	110	82.0	11.5	2.0	14.0– 9.0
246	108	57.4	5.6	1.1	7.0– 4.2
250	48	44.0	3.0	0.8	3.9– 2.0
252	93	26.9	2.2	0.5	2.8– 1.6
253	85	34.1	1.9	0.3	2.4– 1.5
267	53	70.3	20.8	3.2	24.3–17.3
296	48	54.2	14.0	2.8	17.5–10.5
302	35	28.6	3.5	0.7	4.3– 2.6
309	123	26.9	1.8	0.2	2.0– 1.5
312	89	67.0	10.9	2.8	14.6– 7.2
313	51	33.3	4.6	1.4	6.5– 2.7
314	85	59.0	8.9	1.1	10.3– 7.5
315	140	50.0	2.5	0.3	2.9– 2.1
316	78	22.9	1.0	0.3	1.4– 0.8
320	45	37.8	5.2	0.9	6.5– 3.9
323	65	38.5	2.2	0.3	2.5– 1.9
336	63	49.6	3.1	0.6	3.9– 2.3
342	52	64.8	22.1	3.2	26.1–18.1
346	31	29.9	2.6	0.5	3.2– 2.0
357	210	58.0	2.5	0.3	2.9– 2.1
372	52	23.5	3.2	1.3	5.5– 0.9
374	55	12.7	2.7	0.4	3.3– 2.1
376	115	23.7	1.0	0.2	1.3– 0.8
378	86	11.4	0.7	0.4	1.1– 0.2
399	110	3.8	0.5	0.1	0.7– 0.3
511	51	67.4	19.8	1.7	21.9–17.7
514	45.5	29.7	4.0	0.5	4.5– 3.5
520	220	86.5	9.6	1.9	12.0– 7.2
521	98.5	71.9	18.0	2.3	27.7–14.3
522	96	45.8	5.7	1.6	7.9– 3.5
574	59.5	29.9	2.5	0.6	3.3– 1.7
580	32.5	20.0	3.7	0.9	4.8– 2.6
583	31.5	40.1	8.6	0.3	9.0– 8.2
594	160	73.9	19.4	2.5	22.5–16.3
596	105	74.3	21.0	1.5	22.9–19.3
609	69	73.3	24.6	4.5	29.9–19.3
TR1107	125	86.1	7.8	1.6	9.8– 5.8

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error is usual in the evaluation of the mechanical properties of polymers. The values of $\bar{\sigma}$ are generally low, the highest being around 2 MPa. They are reported in *Figure 1* as a function of the %I of the various copolymers. According to their M_{tot}, the SIS copolymers have been divided arbitrarily into four groups. It appears that for the same elastomer content, the highest $\bar{\sigma}$ values belong to the copolymers with lowest M_{tot}. In each series, $\bar{\sigma}$ increases with the polyisoprene %. But above 75–80 %I, we have tested too few samples to be able to assess clearly any direction of variation for $\bar{\sigma}$, however, it appears that it decreases. Note that a continuous increase of tensile strength with %I is not likely, as it would mean that pure homopolyisoprene has the highest $\bar{\sigma}$ value, which is incorrect.

An adhesive rupture was observed for all but two of our joints. Thus the measured value gives an indication of the strength of the adhesive bond formed between the SIS copolymer film and the glass plates. It is commonly accepted[6] that only bonding forces are involved in tensile tests. So, at first sight, our results seem to reflect the variation of adhesion onto glass of the different SIS, hence corroborating classical ideas[7] concerning the rheological response of polymers. Our results state that adhesion is improved: (i) when the molecular weight of a polymer decreases, as the creation of van der Waals-type bonds is easier thanks to a lower viscosity in the molten state; (ii) with raising polyisoprene content, as the elastomer imparts the adhesive properties.

It appears that this interpretation fits well at least up to a 75–80%I content; but it fails to explain the experimental behaviour observed for the joints as a whole. And as such, cohesion has to be taken into account as it imparts the mechanical properties to an adhesive.

For triblock copolymers, cohesion arises mainly from their structure involving two distinct phases[8]. For the low M_{tot}, phase separation is not achieved and such SIS copolymers resemble in some way random copolymers known to have weak cohesion without vulcanization[9,10]. The same has been found for SIS copolymers with high elastomer content[11]. Although adhesion increases with %I, the joint breaks at lower tensile stresses. A weak cohesion accounts also for the observed cohesive break at about 2 MPa for SIS 267 and SIS 511: both copolymers having at the same time, low molecular weight and high elastomer content.

Finally, whereas the tensile test is usually described as an evaluation of only the adhesive bonding between the film and the substrate, the diphasic morphology of SIS block copolymers also introduces cohesional aspects. And between 60% and 75–80% polyisoprene content (*Figure 1*), where the rigid polystyrene domains act fully as reinforcing fillers[11], we have observed the best tensile resistance for the SIS copolymer films used. We may therefore assume that the observed decrease in $\bar{\sigma}$, despite little experimental data, is not coincidental, but corresponds well to a change in the rheological behaviour of the SIS copolymer films.

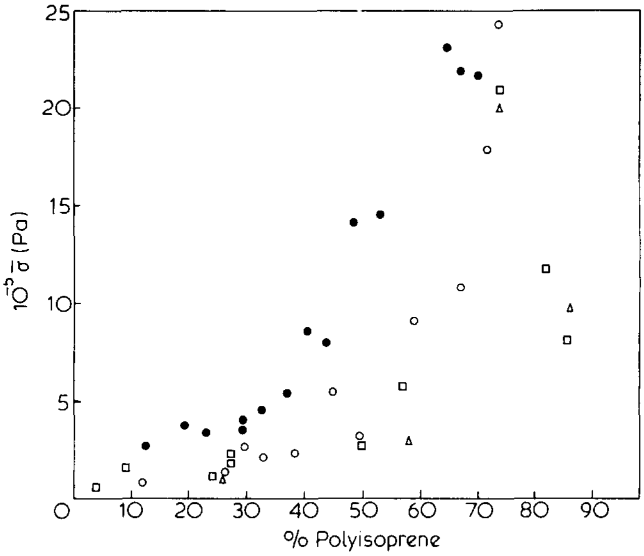

Figure 1 Mean tensile strength at break, $\bar{\sigma}$, *versus* polyisoprene content, for glass/glass joints. (●), 35–55 000; (○), 60–100 000; (□), 100–150 000; (△), >150 000

CONCLUSION

The results are not inconsistent with the fact that in diphasic systems such as in SIS copolymers, the tensile strength at break of the joints does not depend only on the adhesive forces created between adhesive and substrate. The cohesion of such copolymers, through their morphology, i.e. their molecular characteristics, plays an important role also. The simultaneous variation of both parameters yields high tensile strength near 75–80% polyisoprene content.

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