

Adhesive properties of ABA poly(styrene-*b*-isoprene) block copolymers

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ABA poly(styrene-*b*-isoprene) block copolymers with various molecular weight and elastomeric content were used as heat activated adhesives. The shear strength of glass to glass joints was tested. The influence of activation temperature and ageing on shear strength was also examined. Good adhesive and cohesive behaviour was found for copolymers with low total molecular weight and identical block lengths. These results were explained by the fact that phase separation does not easily occur in such copolymers.

INTRODUCTION

Block copolymers have so far not frequently been used industrially, because their synthesis, at least on a large scale, is not easy, though other reasons may exist also. The obligatory step-wise preparation often gives terminations by impurities, therefore yielding mixtures of homopolymers and copolymers which decrease mechanical and other properties¹. Up to now, anionic synthesis² has proved to be the most suitable way to obtain pure block copolymers. The low polydispersity in molecular weight which results contributes to improved properties. Nevertheless, only a few monomers are polymerizable in this way because synthesis has to proceed in a given order depending on the polarizability of the monomers involved³. This shortcoming is particularly troublesome in the preparation of copolymers with more than two blocks, the only type presenting acceptable mechanical properties⁴.

Despite the difficulties in synthesis, the use of block copolymers should be considered when different end-use properties are sought in a polymeric material. Each block, according to its chemical nature and chain length, contributes individually to give a distinct property. The use of block copolymers also overcomes the problem of mutual incompatibility inherent to polymers. This incompatibility leads to separation in simple polymer blends, but in block copolymers such separation is limited to phase formation on a microscopic scale because of the chemical bonds existing between blocks. The resulting structure gives new properties to block copolymers⁵.

So far, the only copolymers prepared industrially by anionic synthesis are of the ABA poly(styrene-*b*-diene) type. At room temperature, they behave like vulcanized elastomers, but above the glass transition temperature of the polystyrene blocks may be processed like any other plastic material. The commercial polymers are usually about 1.2×10^5 in molecular weight, with diene content near 80%. Butadiene generally constitutes the elastomer block although sometimes isoprene is used. Copolymers are usually blended with oils, resins, mineral fillers, etc. depending on their end-use.

Our laboratory has been examining for some time the

properties of ABA poly(styrene-*b*-isoprene) copolymers (SIS), in relation with their structure⁶.

Non-compounded SIS, whether cast or compression moulded, give very clear and transparent films. This led us to investigate their use as adhesives in glass to glass bonding, the isoprene block imparting the adhesive, and the styrene blocks the mechanical properties.

In this paper, we examine the shear strength of simple lap glass joints, where SIS films of various molecular weights and isoprene content are used as the adhesive media. Joints are realized by heat activation. We also study the influence of activation temperature and ageing on the shear strength of such joints.

EXPERIMENTAL

Synthesis of SIS copolymers

Styrene, isoprene and solvent were purified for anionic use. A three-step anionic synthesis was used, with *n*-butyl lithium as initiator and benzene as solvent, at 50°C⁷. After completion of each step, a sample was taken for analysis. The final product was isolated by precipitation in methanol or by freeze-drying, and dried at 50°C under vacuum.

Analysis by g.p.c. (Waters Associates, in THF) and u.v. spectroscopy (Cary 1501) gives the block lengths and isoprene content. Molecular characteristics of SIS used in this work are given in *Figure 1*. \bar{M}_{tot} stands for total molecular weight. All the SIS show by g.p.c. a sharp single peak with no shoulders.

Joint formation

SIS films were obtained by compression moulding for 2 min at 180°C, to 0.1 mm thickness, and rapid cooling. Glass plates were degreased before use (dimensions: 50 × 25 × 6 mm). A simple lap joint (overlap area 6.25 cm²) was formed by inserting the SIS film, cut to size, between two glass plates.

A special device allowed exact positioning of the different parts of the joint. A spring, set to 1 kg/cm², pressed on the centre of the overlap area, and the whole was heated for 2 h.

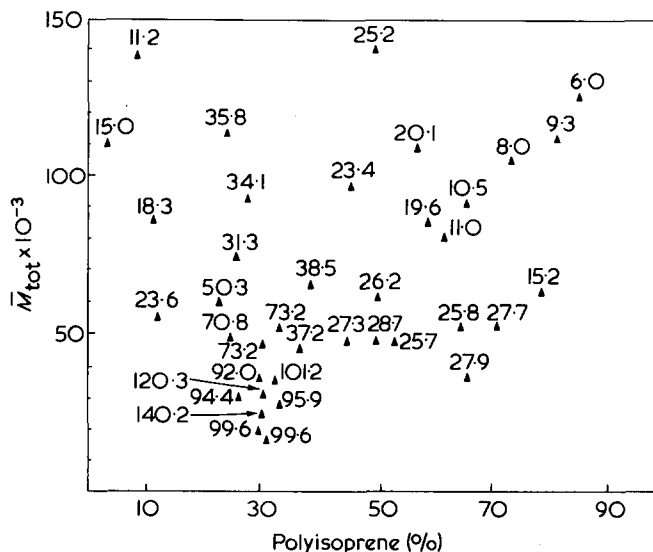


Figure 1 Total molecular weight (\bar{M}_{tot}) versus isoprene content (% I). Numbers indicate average tensile shear strength at break for joints formed with the SIS corresponding to (\bar{M}_{tot} , % I)

If not otherwise indicated, activation temperature was 135°C . After 2 h, the temperature was decreased slowly to room temperature.

Breaking the joint

The shear resistance of all joints was measured one week after joint formation, on a Zwick testing machine, model Z 13 with a crosshead separation speed of 2 mm/min. For each copolymer, at least five joints were tested. \bar{F} is the average value of the tensile shear strength at break in kg/cm^2 .

RESULTS AND DISCUSSION

Two types of breaks are observed. Up to 50% isoprene content, the SIS film is destroyed. This cohesive failure is characterized by the fact that a part of the film remains glued to the substrates, thereby denoting that the adhesion to glass is superior to the cohesion of the SIS film. Over 50% isoprene content, the film can, in most cases, be peeled off the glass substrates without any trace of polymer remaining on them. This denotes an adhesive failure. Around 50%, both breaks occur together.

Shear resistance

Shear resistance of joints has been measured for over 40 SIS copolymers. In Figure 1, a point (\bar{M}_{tot} , % I) characterizes a copolymer, its number gives \bar{F} . In Figure 2, \bar{F} is plotted against isoprene content and the resulting curve shows a marked peak.

Both Figures indicate that high shear resistance ($\sim 100 \text{ kg}/\text{cm}^2$) is obtained for copolymers with \bar{M}_{tot} between 20 000 and 50 000, having an isoprene content near 30%. Outside of this zone, resistance is weak ($\sim 30 \text{ kg}/\text{cm}^2$) and molecular weight does not seem to play a role.

In Table 1 are listed the molecular characteristics of SIS having the highest shear resistance.

According to several authors^{5,8}, domain formation is more difficult for copolymers where the different blocks are all at once small in size. Moreover, some phase blending⁸ occurs if their solubility parameters are not very different. Amongst

the SIS investigated, only those with the best adhesive properties meet exactly the above conditions and these considerations help to explain our results: in these copolymers, domain formation does not occur easily and then results in very small diene nodules well dispersed within the polystyrene matrix.

Films obtained from such copolymers show therefore a rather continuous polyisoprene distribution, favouring multiple contact and thus good adhesion to substrate. As stress distribution is uniform over the bonded area, shear resistance is improved similarly.

Equal block lengths give a diene content of 33.3% corresponding within experimental error to the observed position of the maximum in Figure 2.

Activation temperature

Figure 3 gives plots of \bar{F} against activation temperature for different SIS. Curves have their maximum values shifted towards higher temperatures as isoprene content decreases. Joints assembled at these temperatures show cohesive break, whatever the isoprene content.

Higher temperatures favour better adhesion because of

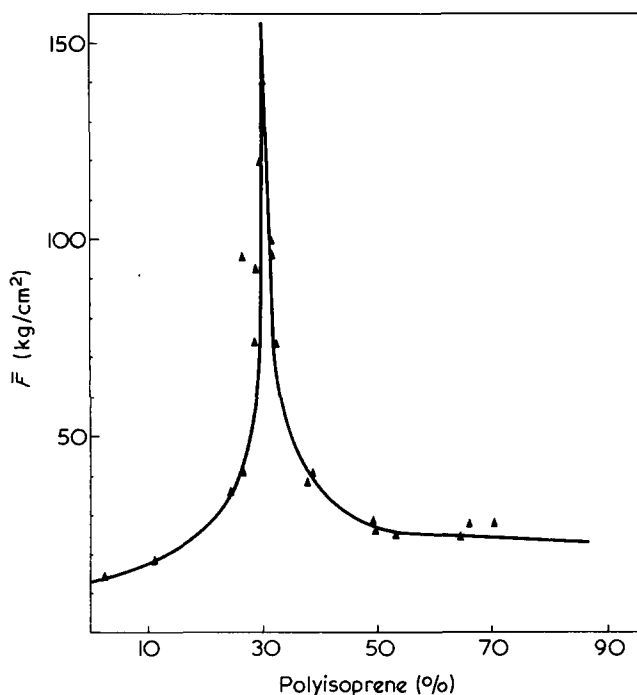


Figure 2 Average tensile shear strength at break (\bar{F}) versus isoprene content (% I)

Table 1 Molecular characteristics of some SIS block copolymers, and corresponding tensile shear strength

Sample	$\bar{M}_n \text{ SIS} \times 10^{-3}$	$\bar{M}_{tot} \times 10^{-3}$	Polyisoprene (%)	$\bar{F} \text{ (kg/cm}^2\text{)}$
351	8.5/7.5/8.5	24.5	30.5	140.2
346	11/9/11	31	29	120.3
321	12/11.5/12	35.5	32.5	101.2
349	6.8/6/6.8	19.5	31	99.6
348	5.5/5/5.5	16	31.5	99.6
330	9/9/9	27	33.5	95.9
344	11/8/11	30	26.5	94.4
302	12.5/10/12.5	35	28.5	92.0

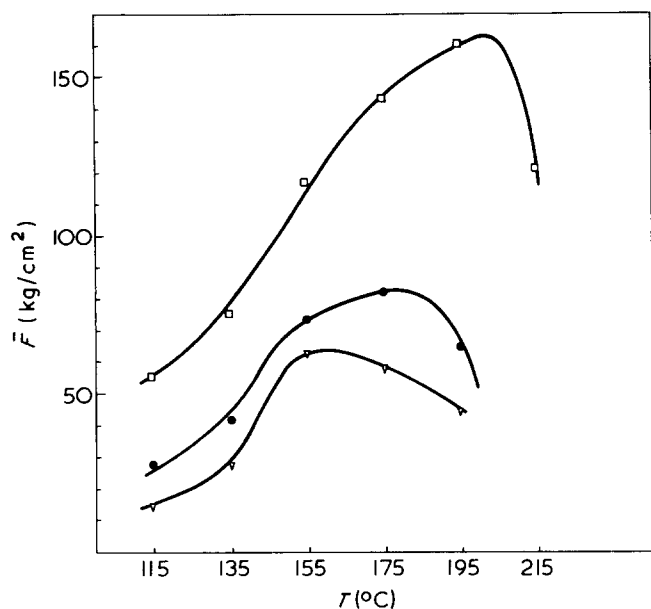


Figure 3 Average tensile shear strength at break versus activation temperature for SIS with different polyisoprene content: □, 30%; ●, 48%; ▽, 65%

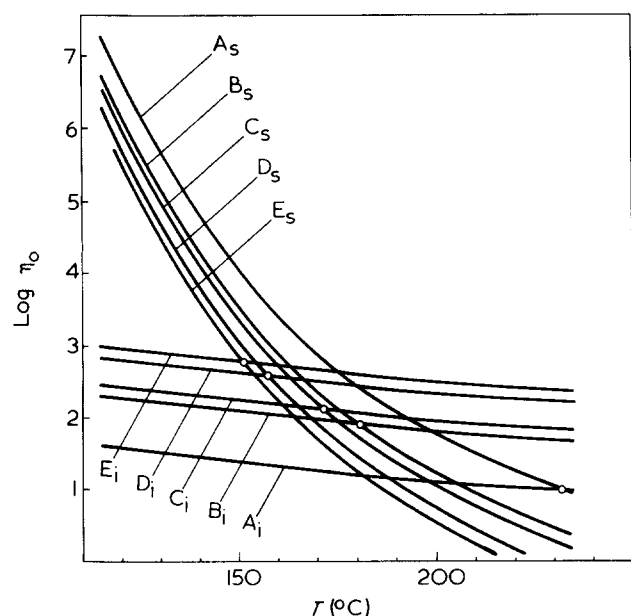


Figure 4 Logarithm of viscosity at zero shear rate versus temperature for SIS with an isoprene content of: A, 30%; B, 48%; C, 54%; D, 65%; E, 70%. s and i refer to polystyrene and polyisoprene blocks, respectively

the lower viscosity of the films. But the existence of a maximum cannot be explained only by viscosity unless SIS is heat degraded. G.p.c. and other appropriate tests have not shown any degradation. The observed optimum temperatures may result from a better chain mobility of the copolymers. One contributing factor may be an identical viscosity of the different blocks in the melt state which makes flow easier. In order to verify this point, we evaluated the viscosities of the individual blocks at zero shear rate (η_0) according to calculations made by several authors^{9,10}.

In Figure 4, two curves correspond to a given SIS: the S curve denotes the polystyrene block, while the I stands for

Table 2 Ageing: tensile shear strength of a joint

Time	\bar{F} (kg/cm ²)
1 week	120.3
2 weeks	118.2
1 month	120.5
2 months	121.9
3 months	105.1
6 months	87.2
1 year	48.5

the polyisoprene block. Their point of intersection is the temperature at which both blocks have the same viscosity. This occurs rather exactly at the temperature at which \bar{F} is optimal thereby indicating good agreement with our test results.

Ageing

We investigated the behaviour of our joints over a long time period. Table 2 shows the evaluation of joints prepared with copolymer SIS 346. Until measuring, test joints were kept at constant temperature and humidity, but not in the dark.

During the first two months, shear resistance stayed at its initial value but then a rather fast decrease was observed. After one year, only 40% of the initial resistance remained.

As films did not show any degradation, decrease may result from separation effects, although, as pointed out earlier, solubility parameters are not very different. Such a slow and limited separation effect induces stresses which weaken the glass to copolymer bond and therefore shear resistance.

CONCLUSION

The high transparency of non-compounded SIS films, associated with a variable elasticity when isoprene content is changed, led us to investigate their adhesive properties for glass joints.

Initially, our experimental results were in contradiction with what was expected. Reasoning in terms of the generally accepted ideas concerning phase separation and structure in block copolymers, we were unable to explain the fact that SIS proved to be a better adhesive when there was only a small amount of what is, in fact, the adhesive agent. This is an example of the need to take into account borderline cases like critical block size in explaining the extent of phase separation and the resulting end properties.

Our results show that SIS gives satisfactory adhesion and cohesion for glass/glass joints. However, when isoprene content is around 30% and molecular weight roughly 25 000, some block copolymers which do not easily phase separate show exceptionally good tensile strength. In other cases, tensile strength can be increased when activation is realized at an appropriate temperature, no matter what the isoprene content.

Over a one-year period, no chemical degradation is observed, but the tensile shear strength decreases to less than half of its initial value. This loss in shear resistance can be attributed to a slow change in the film structure inducing joint-weakening stresses.

Recently, we have investigated the structure of SIS films by optical and electronic microscopy, and the results confirm our findings about the relationship between domain formation and adhesive behaviour of block copolymers. This study will appear in a later paper.

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