JOURNAL OF MATERIALS SCIENCE 21 (1986) 1769–1774

Rubber-crumb modified polystyrene

Part 1 *Tensile properties*

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Peroxide crosslinked polybutadiene and styrene butadiene rubber powders were converted to semi-interpenetrating networks by swelling in styrene monomer and subsequent homopolymerization. Two initiator types were selected, one causing bonding between polystyrene and the rubber (benzoyl peroxide), the other allowing independent polymerization (azobisisobutyronitrile). The polystyrene modified powders were then incorporated into a polystyrene matrix and tensile properties of the resulting composite determined. Improvements in performance over untreated crumb-modified composites were observed, with increased breaking strains due to crazing. Little difference could be distinguished in composites derived from different initiator usage, indicating that polystyrene interpenetration in the rubber, rather than grafting, is the predominant factor.

1. Introduction

Attempts to recycle rubber have followed several paths, including reincorporation of powder or crumb into unvulcanized rubber compounds [1–4], and into asphalt for roadmaking [5, 6]. In the former case, we have shown the role of interfacial adhesion and crumb modulus upon tensile properties and tear strength [7, 8]. Ultimately, however, there appears to be little scope for dramatic improvement in overall properties, and thus the main advantage in recycling in elastomers lies with reducing expense in non-critical applications.

By comparison, it has been well established that appropriate addition of small amounts of rubber can toughen normally brittle thermoplastics [9, 10], and a wide range of "impact-modified" plastics including those based on polystyrene, epoxy resins, polyvinyl chloride and acrylate polymers. In most cases the rubber can be resolved as a separate phase which may incorporate inclusions of the thermoplastic. In general, less than 10 wt % rubber is accommodated in this way (although the volume distribution may be widespread), but associated increases in breaking strain, ε_b, and fracture toughness, G_c, can be dramatic.

Some potential exists for bringing about improvements in thermoplastic properties when blended with recycled, crosslinked rubber crumb, although there has been little published to date.

Tuchman and Rosen [11] blended untreated crumb from the cryogenic grinding of tyres with polystyrene. They showed that impact strength increased with increasing crumb particle size, this being attributed to greater crack deviation. They also found that grafting even a small amount of plastic to the surface of the crumb led to greater impact strength. A method has been patented [12] for producing high-impact thermoplastics by polymerizing monomers in the presence of the swollen crumb. Plastics thus produced have higher impact strengths than those of Tuchman and Rosen [11] and show a linear relationship between impact strength and crumb loading.

Our preliminary investigations [13] used similar techniques to those described in the patent [12]. It was shown that whilst some toughening of polystyrene (PS) can be achieved using recycled rubber crumb, increasing rubber-to-plastic interfacial adhesion and reducing crumb particle size is beneficial. These studies were restricted to crumb modified solely by benzoyl peroxide (BP), which is known to form chemical bonds between the rubber and polystyrene [14]. Volume fraction of the rubber phase (ϕ_r) and adhesion between untreated crumb and thermoplastic matrix were also unquantified although the latter was assumed to be low.

In this study we describe the effect of rubber-phase volume fraction, initiator type and rubber-phase polystyrene content on tensile properties of crumb-modified polystyrene. Fracture morphologies of polystyrene containing both ungrafted and grafted crumbs, using two quite different types of initiators, are also given.

2. Experimental procedures

2.1. Crumb preparation

Rubber compounds were prepared and tested according to conventional ASTM procedures. Full details of formulation and mechanical properties are given in Table I. Peroxide-cured pads were ground in a high-speed miniature mill at −125° C, for BR, and −100° C for SBR compounds. The resulting crumb was passed through a 1 mm screen. We estimate mean diameters to be approximately 300 μm.

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TABLE I Fillers used in PS composites

	BR50	SBR50	SBR25
BR	100		
SBR		100	100
Carbon black	50	50	25
Dicumyl peroxide, DICUP 40C	0.5	0.5	0.5
100% modulus, E_{100} (MPa)	1.10 ± 0.05	1.67 ± 0.03	1.17 ± 0.14
Stress at break, σ_b (MPa)	7.75 ± 0.89	9.90 ± 0.28	7.88 ± 0.83
Strain at break, ε_b (%)	349 ± 18	386 ± 27	360 ± 20
Strain energy density at break U_b (MJ m^{-3})	10.45 ± 1.36	16.18 ± 2.25	10.83 ± 2.14
Tear energy, τ (kJ m^{-2})	5.80 ± 0.70	51.6 ± 8.0	14.2 ± 6.5

2.2. Crumb modification

Approximately 20 g rubber crumb was swollen in dried, inhibitor-free styrene containing 1×10^{-3} mol initiator/100 g. The initiators selected were benzoyl peroxide (BP), to achieve chemical bonding between PS product and rubber crumb, and azobisisobutyronitrile (AIBN) which independently polymerizes styrene. After 24 h, the container was flushed with nitrogen and sealed, and the mixture was heated to 80° C for 48 h to effect polymerization. The product generally took the form of an aggregate of loosely to moderately adhering particles. After drying for 24 h at 60° C under vacuum, conversion and % PS in the product was determined from the weight of the recovered material. Typically PS content varied from 30 to 75%, which was lower than the equilibrium swelling ratio ($\approx$80% styrene at 30° C). Yields were generally 98 to 100% when AIBN was used, and 70 to 80% for BP.

2.3. Composite preparation and testing

Composites, containing either untreated or modified crumb were prepared by blending in a Haake internal mixer. The procedure was to melt "Lustrex HH101A-300" polystyrene granules at 150° C, and add the crumb while the melt is being mixed using cam rotors operating at 30 r.p.m. The density of the modified crumb was calculated from the density of the rubber and that of PS. This enabled the addition of a set volume fraction of modified crumb to the polystyrene. After 4 min the mixture was transferred to a compression mould in which 2 mm thick sheets were prepared. The mould was allowed to cool slowly whilst under pressure, resulting in essentially warp-free product. Conditions were 30 min at 150° C and 3.5 MPa. From each 2 mm thick sheet, four dumb-bells conforming to ASTM D638 (Type I) were carefully shaped to avoid edge flaws.

Stress at break (σ_b) was determined in an Instron 1115 Universal machine with a grip separation rate of 20 mm min^{-1}. Strain at break (ε_b) was measured using a strain gauge extensometer.

2.4. Peel tests

Peel specimens were fabricated from the three rubber compounds with cloth backing, and polystyrene sheet. These were compressed together under the same conditions as employed for moulding of the composites. Sandwiches were separated by peeling at an angle of 180° using a crosshead speed of 5 mm min^{-1}. Adhesive energy, G_a, was calculated from the peel force, F, and tear width, W, using Equation 1 [15].

$$G_a = \frac{2F}{W} \qquad (1)$$

2.5. Microscopic examination

Microscopic examination was carried out using uncoated samples in an ISI-100A scanning electron microscope (SEM) equipped with a "Robinson" backscatter detector. Fracture surfaces of the samples were stained by immersion in a 0.5% aqueous solution of OsO_4. This was found to give good contrast between rubber and polystyrene, the rubber appearing as the light phase in the micrograph.

3. Results and discussion

3.1. Influence of crumb to PS adhesion and crumb modulus

Composites containing untreated crumb behaved in a similar manner to those studied previously [13]. σ_b, ε_b and U_b all fell as crumb volume fraction, ϕ_r, increased from 0 to 0.25. Figs 1 and 2 reveal ε_b and σ_b of composites containing crumbs BR50, SBR50 and SBR25 at various ϕ_rs. There is little difference between the properties of composites containing crumbs SBR25 and SBR50 even though they have differing moduli. This arises because small changes in crumb modulus become negligible when compared to the modulus of PS which is three orders of magnitude greater.

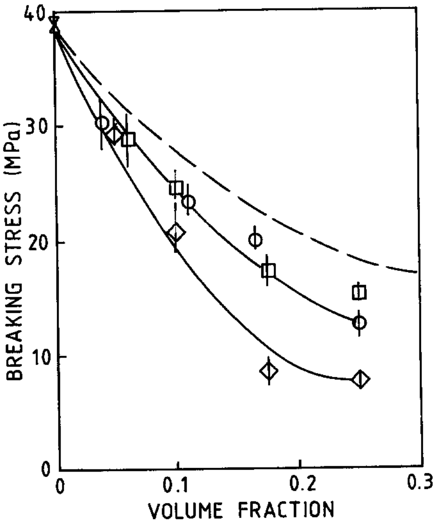

Figure 1 Breaking stress as a function of crumb volume fraction. (◇) BR50, (□) SBR50, (○) SBR25.

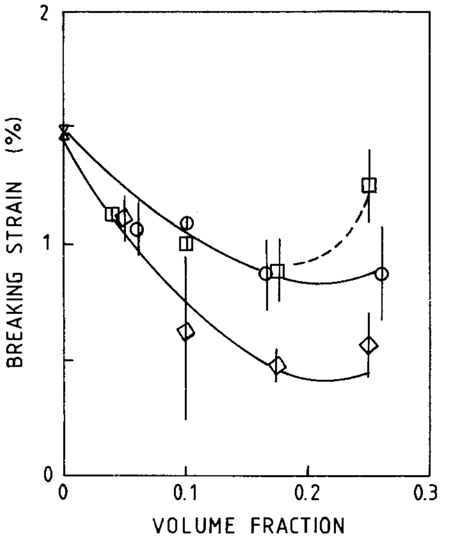

Figure 2 Breaking strain as a function of crumb volume fraction. (◇) BR50, (□) SBR50, (○) SBR25.

Composites containing BR50 crumb have significantly lower σ_b and ε_b. Both SBR compounds adhere to the PS matrix and G_a was determined, from peel tests, to be approximately 0.37 kJ m^{-2}. However BR50 showed no measurable adhesion to the PS, which may explain why composites containing this crumb have lower σ_b and ε_b. The low G_a means the crumb acts as a void leading to failure at lower σ_b and ε_b.

The broken line in Fig. 1 is σ_b predicted using a minimum load-bearing area model (Equation 2) [16].

$$\sigma_b = \sigma_M(1 - 1.21\phi_r^{2/3}) \qquad (2)$$

where $\sigma_M = \sigma_b$ for unfilled matrix.

All experimental values fall below this line indicating the crumb particles act as stress concentrators, causing failure of the matrix at stresses below its normal σ_b.

Observation of the fracture surface reveals that interfacial failure predominates, even for the composites containing SBR50 and SBR25. Fig. 3 shows the fracture surface of the composite, containing 25% SBR50, which has been stained with OsO_4. As well as interfacial failure there is evidence of crazing in the matrix. Regions of the matrix appear to have been stained as well as the rubber (Fig. 4). These regions have a porous appearance suggesting plastic deformation of the matrix has occurred. The stained zone emanates from a cavity from which a crumb particle has been pulled out. This is also a region of high stress concentration so it is probable that the whitened appearance results from OsO_4 staining of crazes and microcracks.

Figure 4 Fracture surface of composite containing 25% SBR50. ×220.

In some cases, usually at low ϕ_r, "mackerel" markings are apparent at the point of initiation. In Fig. 5 a large dewetted particle (marked P) is evident near the origin of the "mackerel" pattern suggesting it was the fracture precursor.

These results indicate that the large weakly adhering crumb particles act as fracture precursors in the PS matrix. Although the particles are capable of initiating crazes they also act as sites for crack nucleation due to their low adhesion to the matrix. This results in failure at low values of σ_b and ε_b.

3.2. Grafting PS to the crumb

Initial grafting reactions were carried out using BP as the initiator as this is reported to give chemical bonding between the PS and rubber [14]. The σ_b and ε_b of composites containing crumb treated in this manner are given in Figs. 6 and 7, respectively. Also shown are results for composites containing crumb treated with styrene, using AIBN as the initiator.

Fig. 6 shows σ_b increases with increasing rubber

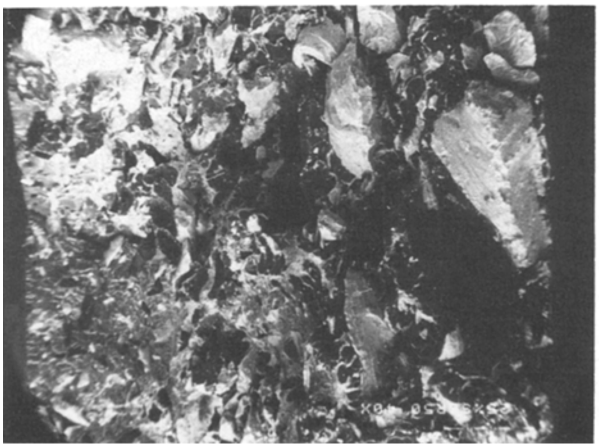

Figure 3 Fracture surface of composite containing 25% SBR50. ×27.

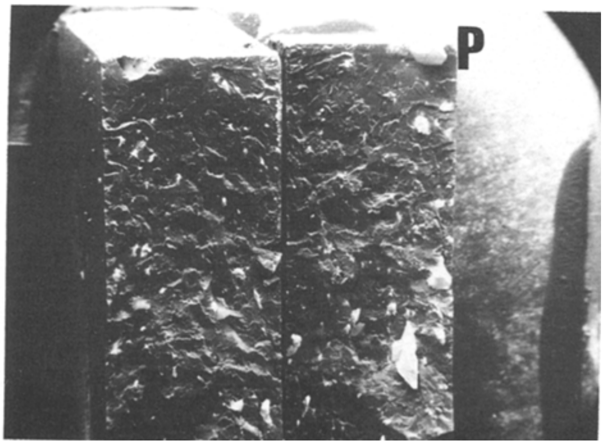

Figure 5 Fracture surface of composite containing 5% SBR50. ×10.5.

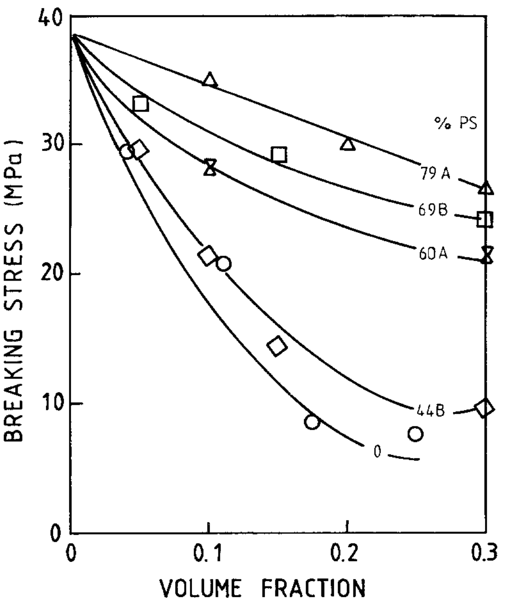

Figure 6 Breaking stress as a function of rubber-phase volume fraction for composites containing PS modified BR50.

phase PS content. However, at the 44% level there is very little improvement in σ_b. Similar trends for composite ε_b are shown in Fig. 7, although at 60% PS with AIBN initiator (crumb BR50/60A), ε_b at $\sigma_r = 0.30$ is unexpectedly high. Again little improvement in ε_b is observed at PS levels of 44% and BP initiator (crumb BR50/44B).

Examination of the fracture surfaces reveals that filler rupture occurred in all composites except those containing BR50/44B. Composites containing BR50/44B appear to undergo interfacial failure as is shown in Fig. 8. However, the pitted appearance of the crumb and the presence of stained rubber in the cavities indicate there was some improvement in interfacial adhesion. It is also thought that crosslinking of the rubber by the BP may also contribute to the low σ_b and ε_b.

Composites containing crumbs BR50/60A (60% rubber phase PS and AIBN initiator) and BR50/79A had improved σ_b and ε_b compared with composites containing untreated crumb, BR50/44B or BR50/69B. AIBN was used as an initiator so that no chemical bonding between the PS and rubber would occur [14]. Further crosslinking of the crumb is also avoided. The high σ_b and ε_b of these composites indicate that interpenetration of the crumb by the PS is sufficient to improve interfacial adhesion.

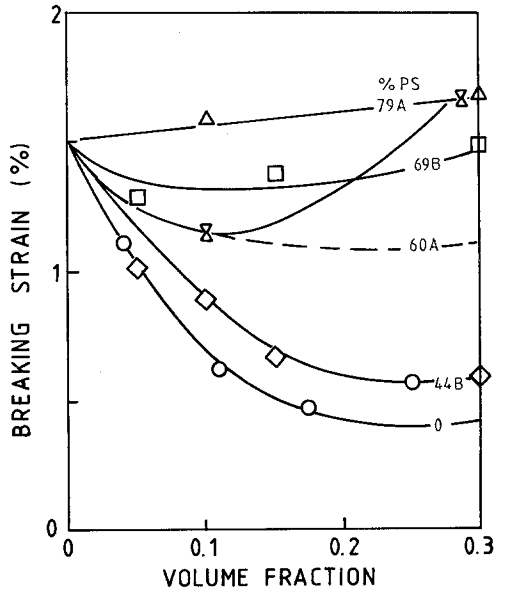

Figure 7 Breaking strain as a function of rubber-phase volume fraction for composites containing PS modified BR50.

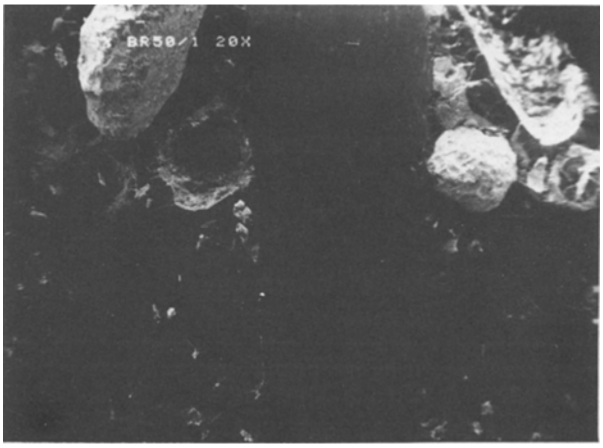

Figure 8 Fracture surface of composite containing modified crumb BR50/44B. × 13.5.

A clear indication of the effect of initiator type is given in Table II which presents the tensile properties of compounds containing crumb with equal rubber-phase PS content but prepared with different initiators. With AIBN the composite has higher σ_b, ε_b and U_b compared to BP. Fracture surfaces revealed internal filler rupture in the composite containing SBR50/37A (Fig. 9) whilst in that containing SBR50/37B interfacial failure predominated. The results suggest crosslinking of the SBR50/37B crumb may lead to increased modulus and reduced extensibility of the rubber phase, promoting interfacial failure. This leads to fracture at lower values of σ_b and ε_b.

3.3. The effect of rubber-phase PS content

The influence of crumb PS content on the mechanical properties of composites is illustrated in Figs 10 and 11 which show σ_b and ε_b of composites containing SBR50 crumb. AIBN was used as the initiator in all cases and ϕ_r held constant at 0.30.

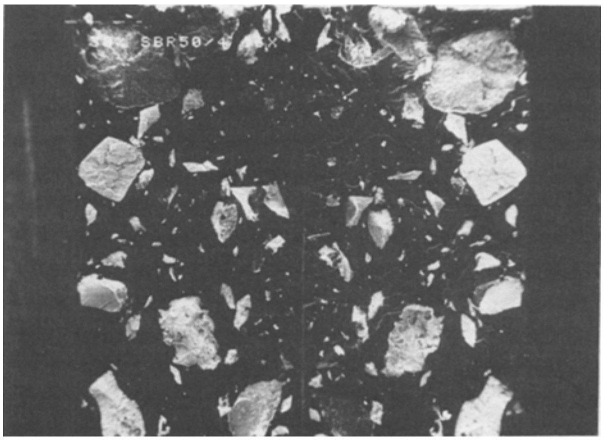

Figure 9 Fracture surface of composite containing modified crumb SBR50/37A. × 10.5.

TABLE II Tensile properties of PS composite at $\phi_r = 0.30$

Code	% PS in crumb	ϕ_r	σ_b (MPa)	ε_b (%)	E^* (MPa)	U_b (kJ m^{-3})
PS	–	–	38.83 ± 3.11	1.48 ± 0.19	2780 ± 113	297 ± 63
SBR50	0	0.25	15.23 ± 0.64	1.25 ± 0.16	1546 ± 170	108 ± 15
SBR50/37B	37	0.30	19.87 ± 1.12	1.25 ± 0.32	2068 ± 189	156 ± 54
SBR50/37A	37	0.30	23.05 ± 0.64	1.71 ± 0.23	1967 ± 16	249 ± 54

*E = modulus at 0.4% strain.

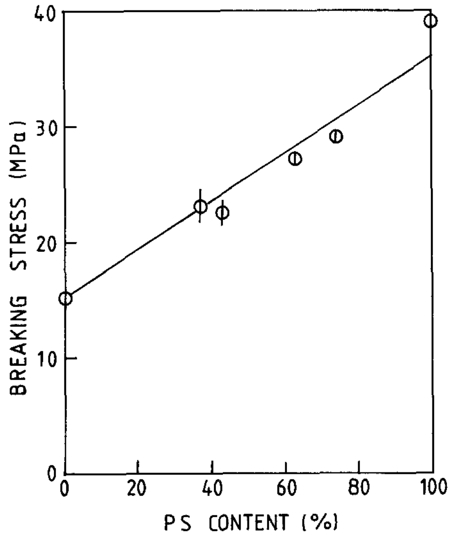

Figure 10 Breaking stress, of composites with $\phi_r = 0.30$ as a function of rubber-phase PS content.

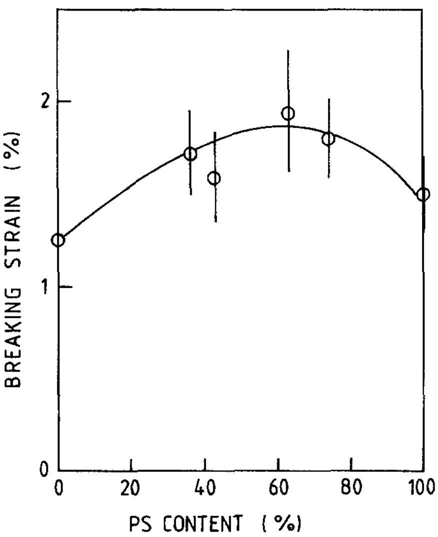

Figure 11 Breaking strain, of composites with $\phi_r = 0.30$ as a function of rubber-phase PS content.

Composite σ_b shows an almost linear increase with increasing crumb PS content reflecting increases in modulus due to the reduced rubber content (on a weight basis). Composite ε_b increases from a minimum (below matrix ε_b) to a maximum of about 2% at a crumb PS content of approximately 65%. The initial increase in ε_b is attributable to the increased crumb-to-PS adhesion and crumb strength which allows it to bridge crazes and cracks, leading to increased composite ε_b. As crumb PS content increases, the stress concentration around the particle will decrease and so crazing in the matrix becomes limited. The shape of the $\varepsilon_b - \phi_r$ curve results from competition between these two trends.

4. Conclusions

When crumbs were converted into semi-IPNs using either initiator, improvements in interfacial adhesion with PS matrix were observed. This was found not only when BP initiator was used, where chemical bonding between incorporated PS and crosslinked rubber is expected, but also for the AIBN, where such bonding is absent. This indicates that the main factor is interpenetration.

With benzoyl peroxide, concommitant increased crosslinking of the rubber is expected, and this was reflected in harder semi-IPN particles than was the case for the AIBN modification. This, together with binding of the PS to rubber, can have an adverse effect on σ_b and ε_b for composites prepared with benzoyl peroxide.

Although incorporation of PS into crumb leads to improved composite σ_b and ε_b, σ_b falls continually with increasing ϕ_r, reflecting the reduction in composite modulus. Composite ε_b, however, may increase to a value greater than that of the matrix. This is due to crazing of the PS matrix, effectively the only mode available under the conditions employed. Indeed increased craze incidence was observed. Increased toughness is a consequence of both increased crazing, together with a contribution from crumb rupture.

These materials may be considered as a two-phase dispersion within a complementary primary/embedding phase. As composites they fall structurally within two limiting cases, one being PS itself, as particulate size diminishes to zero, and the other being the semi-IPN, with no resolvable PS homopolymer. Scope exists for further structural characterization of these composites, although a molecular interpretation of network structure would be quite difficult to formulate. Important fracture toughness data exist for polystyrene alone, but not for the semi-IPN material, nor the composites. However, the latter aspects are currently under investigation.

References

1. M. D. BURGOYNE and G. R. LEAKER, Paper 20, American Chemical Society, Rubber Division Fall Meeting (October 1975) New Orleans, Louisiana, USA (ACS Rubber Division Library, University of Akron, Ohio).
2. D. J. ZOLIN, N. B. FRABLE and J. F. GENTILCORE, Paper 52, American Chemical Society Rubber Division, Fall Meeting (October 1977) Cleveland, Ohio, USA (ACS Rubber Division Library, University of Akron, Ohio).
3. L. E. PETERSON, J. T. MORIARTY and W. C. BRYANT, *ibid.*, Paper 53.
4. R. P. BURFORD and M. PITTOLO, *Rubber Chem. Technol.* **55** (1982) 1233.
5. J. W. H. OLIVER, "Modification of Paving Asphalt by Digestion with Scrap Rubber", Internal Report, Australian

Road Research Board (1980).

6. C. H. McDONALD, paper presented at the Cryogenic Recycling and Processing Institute, University of Wisconsin (May 1980).
7. R. P. BURFORD and M. PITTOLO, *J. Mater. Sci.* **19** (1984) 3059.
8. M. PITTOLO and R. P. BURFORD, *ibid.* **19** (1984) 3330.
9. C. B. BUCKNALL, "Toughened Plastics" (Applied Science, London, 1977).
10. S. NEWMAN, in "Polymer Blends", Vol. 2, edited by D. R. Paul and S. Newman (Academic, New York, 1978) Ch. 13.
11. D. TUCHMAN and S. R. ROSEN, Paper 55, American Chemical Society Rubber Division, Fall Meeting (October 1977) Cleveland, Ohio, USA (ACS Rubber Division Library, University of Akron, Ohio).
12. Air Products Ltd, British Patent Application 2 022 105, 12 December (1979).
13. M. PITTOLO and R. P. BURFORD, *Rubber Chem. Technol.* **58** (1985) 97.
14. G. C. CAMERON and M. Y. QURESHI, *J. Polym. Sci. Polym. Chem. Ed.* **18** (1980) 3149.
15. A. N. GENT, *Rubber Chem. Technol.* **55** (1982) 525.
16. O. ISHAI and L. J. COHEN, *J. Compos. Mater.* **2** (1968) 302.

Received 29 March
and accepted 11 July 1985