

Graft Copolymers of cis-1, 4-Polyisoprenes with Poly(methyl methacrylate)

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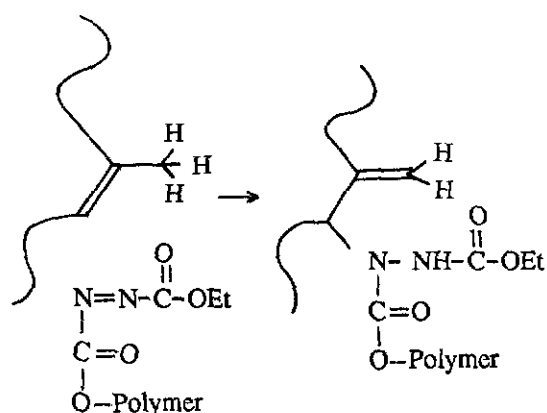
Graft copolymers of natural and synthetic cis-1, 4-polyisoprene with poly(methyl methacrylate) have been prepared by reaction of the polyisoprenes with azodicarboxylate-functional poly(methyl methacrylate). The reactivity of the functional polymer is compared with that previously observed for reactions of similarly functional polystyrene. Within an appropriate composition range, the unvulcanised graft copolymers have elastomeric properties. The dependance of these properties on material and sample preparation conditions is discussed.

Both graft and block copolymers of natural rubber (NR) with poly(methyl methacrylate) (PMMA) have been known for many years. Block copolymers can be prepared by mechanical breakdown of NR in the presence of methyl methacrylate monomer¹ but although the technique has considerable versatility in some respects², control of the block structure and the block molecular weight is poor. Graft copolymers have been prepared by free radical polymerisation of methacrylate monomer in NR solution³ or in NR latex^{4, 5}. The technological product prepared from NR latex (Heveaplus-MG) is discussed by Pendle⁵. Heveaplus-MG contains little PMMA homopolymer when prepared by the method of Sekhar⁶ but it does contain ungrafted NR. The latter material can be removed by extraction⁷.

NR-g-PMMA obtained by these free-radical processes characteristically has PMMA chains of high molecular weight⁸, and consequently has a small average number of graft sites per backbone chain. Such a structure is believed to be inappropriate for the evolution of a strong elastic network by micro-phase separation in the unvulcanised copolymer⁹ and it is the case that Heveaplus-MG does not behave as a thermoplastic elastomer.

Graft copolymers of NR or synthetic polyisoprene (IR) can be prepared in which the

length of the graft chains and the average number of graft chains per backbone are controlled¹⁰⁻¹³. The process uses molecular cyclo-addition reactions ('ene' reactions) of azodicarboxylate functional groups in which one of the ester alkyl groups of the azodicarboxylate is a polymeric species (*Scheme 1*). The reaction as represented in *Scheme 1* is one of three regiochemical alternatives, of which the other two give rise to double-bond migration within the polymer chain. The process has been applied to the preparation of graft copolymers of polyisoprenes with methacrylates having higher ester alkyl groups¹³. We now use the same



Scheme 1

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procedure to prepare NR-g-PMMA and IR-g-PMMA copolymers with relatively short graft chains and higher grafting frequencies than are obtainable from the free-radical grafting techniques. Features of the preparation of these materials and of their properties relative to other graft copolymers of similar molecular architecture will be discussed.

EXPERIMENTAL

Infra-red spectra were recorded on a Perkin-Elmer 157 spectrometer, ^1H NMR spectra were recorded on a Perkin-Elmer R32 spectrometer. Vapour-phase osmometry (VPO) was performed on a Coran Wescan 232A molecular weight apparatus at 50°C using toluene as solvent and benzil as calibration standard. Gel permeation chromatography (GPC) used Laboratory Data Control equipment. Five Micrel columns of nominal pore size 10 , 1×10^2 , 1×10^3 , 1×10^4 and 1×10^5 nm were run in series with an ultra-violet (UV) detector. The chromatograms were run at 25°C using tetrahydrofuran as solvent and molecular weights were calculated from a calibration prepared using PMMA standards supplied by Polymer Laboratories.

Polyisoprenes were Cariflex IR305 (Shell Chemical Co.; 92% *cis*-1, 4-, 4.5% *trans*-1, 4- and 3.5% 3, 4- and 1,2-) and NR (commercial SMR 5L). Hydroxyl-terminated PMMA was prepared by free-radical polymerisation of methyl methacrylate in the presence of 2-mercaptoethanol as chain transfer agent. The procedure was described earlier¹³ for the preparation of hydroxyl functional poly(alkyl methacrylates) with higher alkyl ester chain lengths. Values of 0.62 for the transfer constant¹⁴ and 3.6×10^5 for the PMMA molecular weight in the absence of transfer were used in the Mayo equation¹⁵ as a basis for trial runs carried out to $>50\%$ conversion. Reaction was carried out at 60°C with equal weights of benzene and monomer and with azobis(2-methyl-propionitrile) (AIBN) as initiator (0.01% weight/weight on monomer). Molecular weights of the products indicated that under these conditions, the effective

transfer constant varied with the ratio of transfer agent to monomer and with the monomer conversion. The preparative conditions for the main batch of polymer were: monomer 611 g, benzene 611 g, 2-mercaptoethanol 15.2 g, AIBN 0.61 g, 22 h at 60°C . Polymer was recovered by precipitation into a five-fold excess of a mixture of methanol and petroleum spirit (boiling point $40^\circ\text{C} - 60^\circ\text{C}$) (4:1) and dried in vacuo. Monomer conversion was 68%.

Hydroxyl polymer (200 g, nominally 0.03 mole hydroxyl group) was further dried by azeotropic distillation of toluene¹¹ before esterification with a four-fold molar excess of 2-carbethoxyazo-carbonyl chloride (CEAC). CEAC reagent solution was prepared immediately before use by drop-wise addition of bromine (20.7 g, 0.130 mole) to a solution of 2-carbethoxyhydrazinecarbonyl chloride¹⁶ (20.8 g, 0.151 mole) and pyridine (60 g, 0.74 mole) in dried dichloromethane (300 ml), the reaction being maintained below 5°C with an ice bath. The reagent solution was added to the dried solution of the polymer in toluene and the mixture heated under gentle reflux overnight. Azodicarboxylate functional polymer was recovered by precipitation into aqueous methanol (1:3) and dried in vacuo. The azodicarboxylate functionality of the polymer was confirmed by the presence of a UV absorption maximum at 409 nm (10% weight/volume solution in dichloromethane) and by an infra-red shoulder at 1780 cm^{-1} which was clearly visible on the side of the ester carbonyl of the polymer backbone. An extinction coefficient of 34 was used to calculate the azodicarboxylate concentration from the UV absorbance.

Graft copolymers with polyisoprenes were prepared either by reaction in toluene solution (3% weight/volume) for seven days at 60°C or by direct mixing of the polyisoprene and the functional polymer in a Hamden-Shawbury Torque Rheometer¹². Grafting efficiency (GE) was determined by GPC analysis in tetrahydrofuran solution using a separately determined response factor for PMMA to estimate the amount of material present in the elution peak for ungrafted polymer,

which immediately followed the main peak of the chromatogram¹⁷. GE was expressed as the percentage by weight of the total prepolymer that became bound to the backbone in the course of the reaction. The values are therefore influenced by the presence of any non-functional material in the polymer sample.

RESULTS AND DISCUSSION

Earlier work with poly(isoprene-*g*-styrene) copolymers prepared by the azodicarboxylate coupling process has identified a graft chain molecular weight range of 5×10^3 to 10×10^3 as being appropriate for conferring elastomeric strength to the copolymers. This range can be seen⁹ as representing a compromise between a sufficiently high average number of graft sites per backbone chain and a sufficiently high molecular weight to ensure that the glass transition temperature for the graft chains does not drop too far towards ambient temperature. Reactive prepolymer preparation for the present work concentrated on obtaining material with $\bar{M}_n$ in the region of 6×10^3 , on the assumption that similar criteria would apply to PMMA graft copolymers. Use of free-radical polymerisation with chain transfer necessarily introduced a substantial broadening of the molecular weight distribution of the PMMA prepolymers relative to the narrow distribution materials used in the work with poly(styrene) (PS).

Characterisation of the hydroxyl and azodicarboxylate functional PMMA prepolymers is summarised in Table 1. There is some discrepancy between the $\bar{M}_n$ values

from VPO and GPC analyses which results in an ambiguity in the calculated values for the effective transfer constant in the polymerisation reaction and the percentage azo functionality of the azo polymer. The source of the discrepancy was not identified but the results for extent of grafting to IR (see below) suggest that the functionality based on GPC molecular weight is the more reliable figure and that the prepolymer contained some 10% to 15% of non-functional material.

The azo functional PMMA reacts with IR in the presence of a common solvent. Analytical demonstration that the reaction occurs is less straight-forward than for previous work with functional PS, where the UV absorption characteristics of the aromatic ring were used to selectively identify PS in the GPC peaks of the reaction product¹¹. In the absence of a selective absorption for PMMA, it was necessary to identify the decrease in absolute area of the longer retention peak corresponding to PMMA prepolymer and to isolate material from the shorter retention peak (graft product) for identification of methacrylate and isoprene components by ¹H NMR.

Work with azo functional PS¹¹ established rate constants for reaction with IR in cyclohexane and toluene solutions at 60°C. Cyclohexane gives the higher reaction rate but was not suitable for the present work because it is a non-solvent for PMMA. The rate constant for reaction in toluene (pseudo-first-order kinetics) gives an expectation of >97% reaction of the azo functionality in seven days (168 h). When the same experimental conditions were applied to reaction of the azo functional PMMA, the GE at seven days was 76% and 71% in duplicate experiments. However, the reactions were incomplete. Evaporation of the solvent and heating the total polymer residue at 150°C for 10 min increased GE to 88% and 87% respectively. The reaction of the PMMA in solution was therefore slower than the corresponding PS reaction. Using the single-point values for GE at seven days and assuming pseudo-first-order reaction conditions, the second-order rate constant for the PMMA-IR reaction is estimated to be

TABLE 1. CHARACTERISATION OF HYDROXYL AND AZODICARBOXYLATE FUNCTIONAL POLYMERS

Item	Analyses	
	VPO	GPC
$\bar{M}_n$ (Hydroxyl polymer)	6 400	5 300
$\bar{M}_w/\bar{M}_n$	—	1.47
Effective transfer constant	0.48	0.58
Azo end groups (%)	103	85

0.7×10^{-5} litre $\text{mol}^{-1} \text{s}^{-1}$ (c.f. 2.47 litre $\text{mole}^{-1} \text{s}^{-1}$ for azo functional PS under the same conditions).

Figure 1 and Table 2 summarise information on the formation of graft copolymer from azo

functional PMMA and IR by direct mixing in the Hamden-Shawbury Torque Rheometer. Data for a similar reaction with functional PS is included for comparison. The maximum in the curve for the PS reaction between 4 min and 8 min is associated with the major part of the

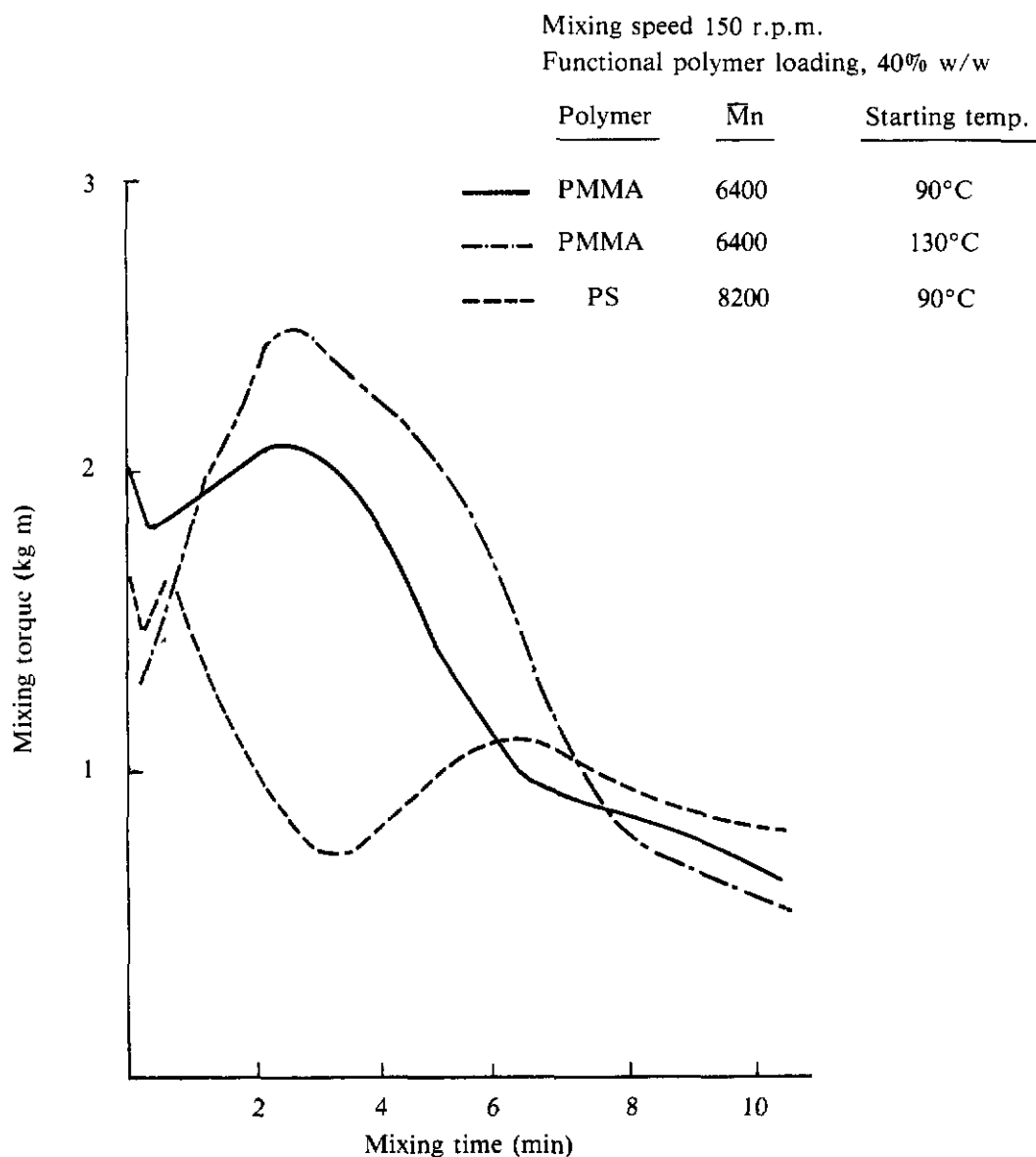


Figure 1. Mixing torque versus time for azodicarboxylate functional polymers with Cariflex IR305 polyisoprene.

TABLE 2. GRAFTING OF FUNCTIONAL POLYMER TO CARIFLEX IR305 POLYISOPRENE BY DIRECT MIXING

Polymer	$\overline{M}_n^a$	Initial temp. (°C)	Final temp. (°C)	GE (%)	
				Mix	Solution
PS	8 200	90	143	75	76
PMMA	5 300	90	128	64	86
PMMA	5 300	130	174	82	86

^aGPC estimate of molecular weight

grafting process¹² and the GE at 10 min mixing time is essentially the same as the estimated polymer functionality. Under the same mixing conditions, azo functional PMMA gives a torque maximum at an earlier mixing time but the GE at 10 min mixing is substantially less than the highest values obtained in the solution experiments. The final mix temperature is also lower than for the PS reaction. Increasing the initial mix temperature to 130°C for the PMMA reaction results in an expected decrease in the initial mixing torque but gives a sharper rise in torque and a higher maximum torque. The GE after 10 min is now within a few percent of the maximum value for the solution reactions and the mix temperature is higher than for the other reactions.

Although the torque traces give the impression that the PMMA reaction is faster than the PS reaction at the same initial mix temperature, the grafting efficiencies suggest that this is not the case. The results are more consistent with the viscosity of the PMMA reaction mixture being more sensitive to the number of graft chains that have become attached to the backbone compared with the PS system. Such behaviour is consistent with the greater thermodynamic incompatibility of the polyisoprene-PMMA polymer pair compared with that of the polyisoprene-PS pair as expressed in the difference in solubility parameter for each of the pairs (Table 3). The mixing process is not isothermal. There is an autocatalytic effect of a rise in temperature causing increasingly rapid reaction of the functional polymer. This thermal imbalance is likely to be strongly sensitive to the mix viscosity and thus to the magnitude of the

TABLE 3. SOLUBILITY PARAMETERS^a

Polymer	Solubility parameter, σ
<i>cis</i> -polyisoprene	8.10
PS	9.05
PMMA	9.24

^aCalculated from group molar attraction constants of Hoy by the procedure documented by Krause¹⁸.

solubility parameter difference of the reacting polymer pair. Further evidence that the increased incompatibility between the graft and backbone chains is important in the polyisoprene-PMMA system comes from the sharp decrease in viscosity after the torque maximum. The decrease is not accompanied by a decrease in the amount of grafted PMMA (Table 4). It is the result of mechanical

TABLE 4. VARIATION OF GRAFTING EFFICIENCY WITH MIXING TIME FOR THE REACTION OF FUNCTIONAL PMMA WITH IR BY DIRECT MIXING^a

Mixing time (min)	GE (%)
5	77
7	84
10	82
12	83
15	84

^aInitial cavity temperature 130°C

breakdown of the backbone chains, the severity of which is enhanced relative to the PS system because of the higher energy required to move PMMA chains through the IR matrix.

The pattern of behaviour shown in *Figure 1* is repeated in mixes having different levels of PMMA prepolymer and, with minor variations, in mixes where NR is the polyisoprene. Grafting efficiencies decrease slightly with increasing PMMA levels for the IR reactions (*Table 5*). This is thought to be a

TABLE 5. VARIATION OF GE WITH PMMA LOADING FOR DIRECT MIXING REACTIONS OF FUNCTIONAL PMMA WITH IR AND NR

PMMA loading (% w/w)	GE(%) ^a	
	IR	NR
25	78	—
30	76	36
35	72	38
40	71	42
45	67	—
50	65	48

^aInitial cavity temperature 130°C, mixing time 10 min

consequence of a side-reaction between the azodicarboxylate functional groups and the thioether link that is present as a consequence of incorporation of the radical transfer agent¹³. The situation is different for reaction with NR. Grafting efficiency is lower at all PMMA levels relative to the IR reactions, because of reaction of azodicarboxylate functional groups with non-rubber constituents¹¹, but the grafting efficiency increases with increasing PMMA level, *i.e.* as the ratio of functional groups to non-rubbers increases.

The tensile properties of IR-g-PMMA and NR-g-PMMA copolymers vary with PMMA content in a way similar to that previously reported¹² for analogous polyisoprene-g-PS copolymers. Low PMMA content gives low modulus materials with relatively high

elongations at break. Increasing PMMA content increases modulus, decreases elongation at break and eventually introduces plastic yield at low elongations. The tensile strength measured at any given composition is affected by the conditions of preparation of the test sample (*Figure 2*), compression moulding at 180°C resulting in significantly stronger samples compared with compression moulding at 140°C, with a further improvement occurring if the test samples are obtained as cast films from toluene solution.

The inferior strengths of the compression moulded samples are indicative of residual moulding stresses or flaws. Visual imperfections from poor mould flow were evident at 140°C and even at 180°C, the quality of the moulded sheets was not as good as that obtained for corresponding PS copolymers moulded at 150°C. The effects are another manifestation of the increased viscosity of polyisoprene-g-PMMA relative to polyisoprene-g-PS, arising from the difference in the solubility parameters.

Tensile strengths of the PMMA graft copolymers are at a maximum in the composition range 40% to 50% weight/weight PMMA (*Figure 3*, solution cast films). For NR-g-PMMA, the maximum strength is comparable to that obtained for the NR-g-PS copolymers, and is probably associated with extensive strain-induced crystallisation of the highly stereo-regular NR backbone. The strengths at lower PMMA contents are lower than for corresponding PS copolymers and the strengths for the IR-g-PMMA copolymers are appreciably lower than for IR-g-PS copolymers at all compositions. We believe that these differences are related to differences in relaxation behaviour under the testing and failure conditions but a more extensive study of physical properties would be required to be able to construct a full explanation of the behaviour.

CONCLUSION

NR-g-PMMA copolymers can display rubbery strength in the unvulcanised stated provided

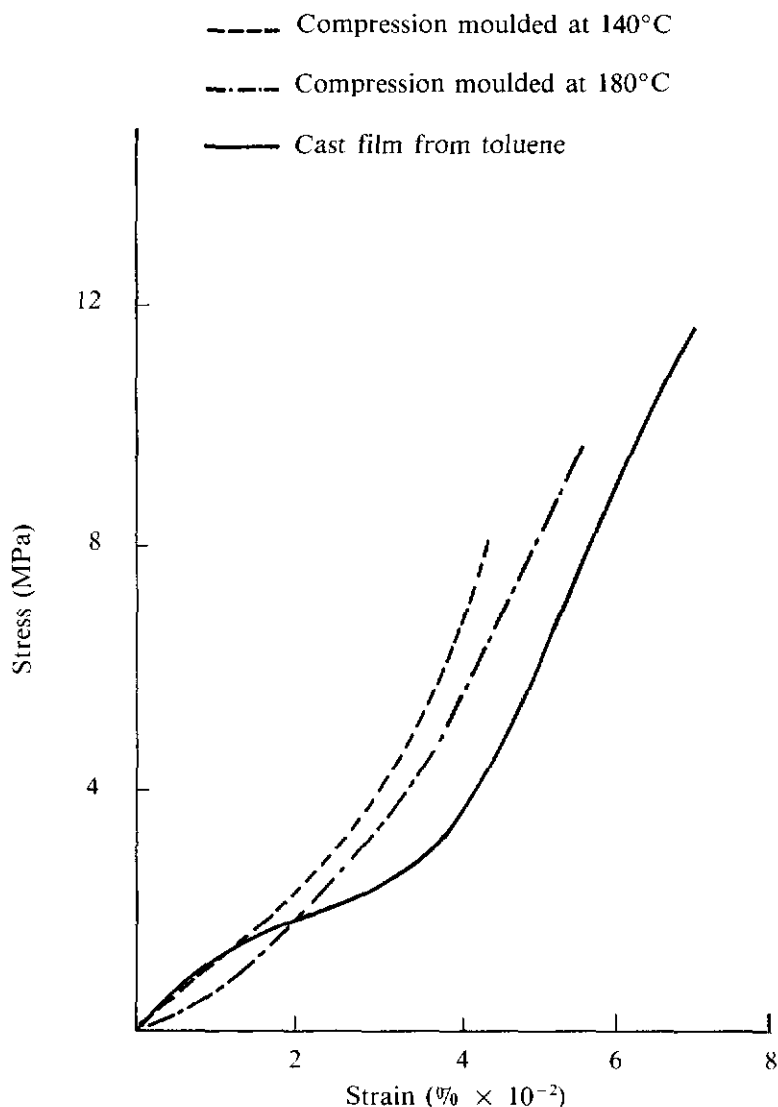


Figure 2. Stress-strain curves for NR-g-PMMA copolymer samples (30% w/w PMMA) from different sample preparation techniques.

sufficient attention is paid to the details of the molecular architecture. The greater thermodynamic incompatibility of the polyisoprene-PMMA polymer pair relative to the polyisoprene-PS polymer pair has a

pronounced effect on the ease of reaction of the functional polymer with the backbone, and is also apparent in the higher temperatures required to prepare compression moulded sheets of the PMMA graft copolymer.

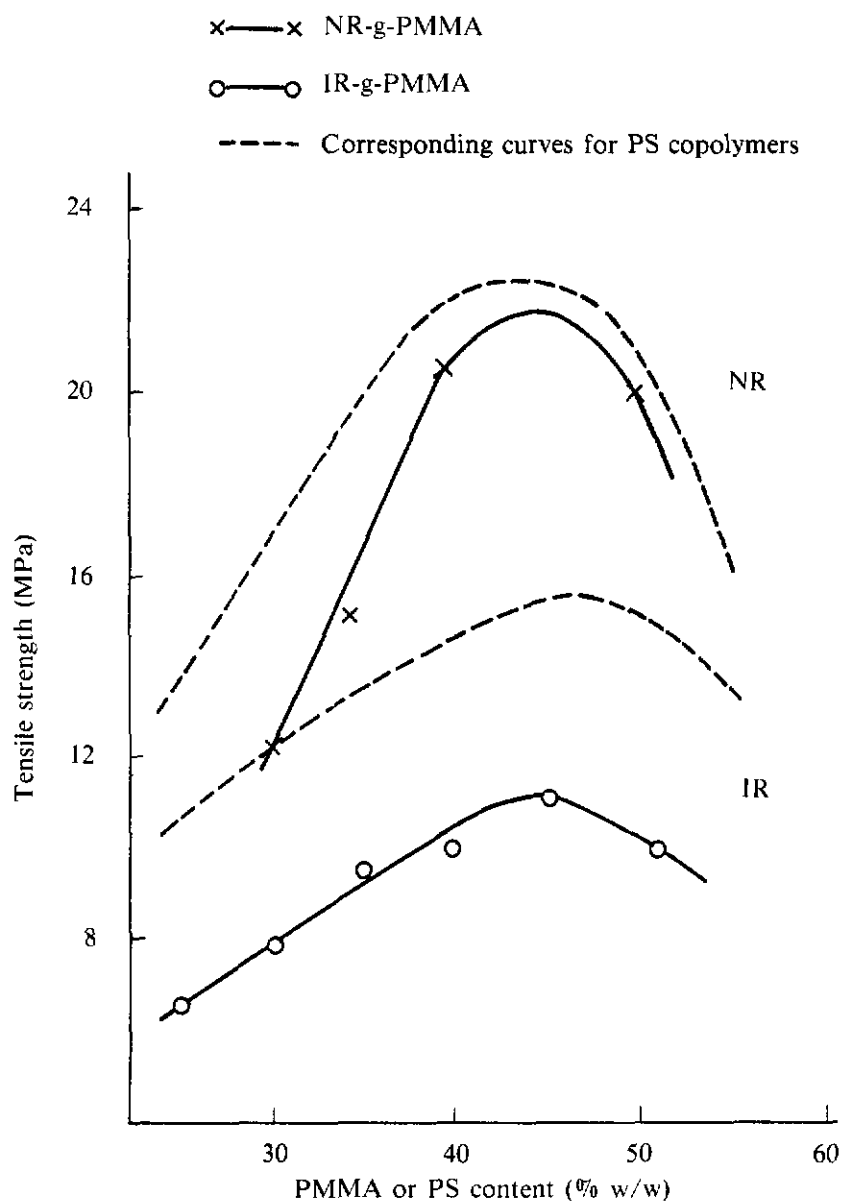


Figure 3. Tensile strength versus composition for polyisoprene-g-PMMA copolymers (cast films).

The behaviour of Heveaplus-MG in the unvulcanised state, where heavy mastication is necessary to achieve processability and the masticated material does not show useful strength, can be readily interpreted on the basis

of these new results and the known architecture of Heveaplus-MG.

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