Letters

Efficient grafting of polystyrene on to polydienes by dry mixing

In a recent Letter we described the preparation of polydiene-g-polystyrene graft copolymers by reaction of a monofunctional polystyrene prepolymer with polydiene elastomers in cyclohexane solution[1]. The reactive end-group on the polystyrene was the azodicarboxylate function ($-O{\cdot}CO{\cdot}N{=}N{\cdot}CO{\cdot}OR$ where R is a short chain alkyl group) which is capable of undergoing a cycloaddition ('ene' reaction) with the double bond system of the polydiene backbone. For a polydiene backbone of high chemical purity the efficiency of graft formation is very high.

We have now shown that the same grafting reaction occurs when the polydiene and the functional polystyrene are mixed mechanically in the absence of a common solvent.

The necessary conditions for high grafting efficiency in the direct mixing process are that the temperature should exceed the glass transition temperature of the polystyrene and that the severity of mixing should be high during a major part of the grafting process. This severity must be comparable to that employed for the dispersion of carbon black in elastomers. Indeed, the process should lend itself to operation in the kind of internal mixer used industrially for this purpose.

For experimental work, the mixing is conveniently carried out in a Hampden-Shawbury Torque Rheometer* which consists of two contra-rotating paddles within a heated 'figure-of-eight' cavity. The drive to the paddles is fitted with a torque transducer which provides a continuous record of mixing torque. A thermocouple in the cavity wall provides a measure of the mixing temperature. The batch weight is 28 to 32g, depending on polymer density.

Table 1 summarizes results for reaction of an azodicarboxylate-terminated polystyrene of $\bar{M}_n$ 8 900 with synthetic polyisoprene (IR) and natural rubber (NR) backbones under dry mixing conditions. The preparation and characterization of the functional polystyrene has already been described[1]. The mixing conditions for both IR and NR backbones are 10 min at maximum mixing speed (150 r.p.m.). The initial temperature setting of the machine is 90°C and in the course of the mixing cycle the temperature rises to 135–155°C depending on the backbone polymer and mix composition. The efficiency of grafting (i.e. the percentage of the total polystyrene which becomes bound to the polydiene backbone) can be determined by g.p.c. analysis. The efficiency is comparable to that obtained for reaction in solution when a chemically clean polyisoprene (IR) is used. Non-rubbers in NR interfere to some extent with the grafting process, as is shown by the lower grafting efficiency for the 40% polystyrene reaction compared with the corresponding IR reaction and by the further drop in efficiency as the polystyrene level is decreased.

The products from the reactions are translucent or even completely transparent. They are fully soluble in common solvents for polystyrene and polyisoprene and can be compression moulded at 150°C. The materials have tensile strengths ranging from a few MPa to more than 20 MPa depending on the proportion of polystyrene and on the nature of the backbone.

Table 1 Grafting of azodicarboxylate-terminated polystyrene on to polyisoprene backbones

Polystyrene		Backbone polymer	Grafting efficiency (%)	Tensile strength (MPa)
$\bar{M}_n$	Content (wt %)			
8900[a]	40	IR[b]	74	11.6
	20	IR	76	4.2
	40	NR[c]	45	21.1
	20	NR	26	4.9
8200[d]	40	IR	–	<0.5
8200[e]	40	IR	–	<0.5

[a] 77% of the polymer chains terminated with azodicarboxylate groups; [b] Synthetic polyisoprene, Cariflex IR305; [c] Natural rubber, SMR 5L; [d] Polystyrene with no reactive end-group. High shear mixing conditions; [e] 72% of the polymer chains terminated with azodicarboxylate groups. Mixing at 50°C on a two-roll mill followed by static heating at 150°C for 15 min

When polystyrene of molecular weight comparable to that of the azodicarboxylate-terminated polymer but with no reactive end-group is mixed with IR under the same conditions the product is opaque and has very low tensile strength (*Table 1*). It has the characteristics of a simple physical blend. When the azodicarboxylate-terminated polystyrene is blended into IR under mild mixing conditions and the blend is subsequently heated under static conditions (*Table 1*) no appreciable grafting occurs and the product resembles the weak opaque blend obtained by mixing non-reactive polystyrene. The reactive end-group and intensive mechanical mixing are both essential parts of the process.

Similar grafting processes occur when azodicarboxylate-terminated polystyrene is mixed under high shear conditions with styrene–butadiene rubber, nitrile rubber, polybutadiene and polychloroprene. The optimum mixing conditions depend on the nature of the backbone polymer but grafting efficiences in excess of 40–50% can be achieved.

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