

Similar results were obtained for the graft copolymers of polyethylene.

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The Graft Polymerization of Methyl Methacrylate to Natural Rubber

At the recent International High Polymer Conference (Nottingham, July 21-24, 1958) the problem of isolating ungrafted polymethyl methacrylate from a mixture with grafted polymethyl methacrylate-natural rubber and free natural rubber attracted some comment. Cooper, Vaughan, Miller, and Fielden¹ obtained free homopolymer by extracting the reaction product, either in the form of a cast film or as the coagulated and dried mixture, with hot acetone for a minimum period of 24 hr. Turner and Angier² and Kobryner and Bandaret³ pre-extracted ungelled natural rubber with cold gasoline and then isolated free homopolymer by extracting with hot acetone for three to five days. An accurate estimate of the proportions of ungrafted polymer is of great significance in determining the reaction kinetics of the γ -radiation-initiated graft copolymerization. It was decided therefore to compare several techniques for the isolation of uncombined homopolymer. Five graft polymer mixes containing 50 parts of polymethyl methacrylate per 100 parts of natural rubber were examined. Sample A was a tertiary butyl hydroperoxide-polyamine-initiated system whereas the others were prepared using γ -radiation initiation under conditions which gave fairly high homopolymer contents. The results for percentage free homopolymer from extraction with hot acetone data are given in Table I.

It can be seen that extraction for less than 48 hr. gives low results and that 24 hr. extraction removes only about 80% of the free polymer. The amount is dependent, as would be expected, on the size of the sample, and using 0.5 g. quantities of cast film 94% of the free polymer is removed after 24 hr. extraction. It follows, therefore, that the results for proportions of grafted polymer quoted in the earlier paper¹ are too high, but, since the total amounts of free homopolymer (10-20%) were small, the values are not seriously affected.

One or two experiments were also carried out where the latex was not coagulated. Benzene was added with shaking

to the graft polymer latex and then free rubber and graft copolymer precipitated by pouring into excess acetone. Suspended graft copolymer was removed by centrifuging the solution. The amount of polymethyl methacrylate isolated in this way was generally considerably higher (ca. 20%) than in corresponding extraction experiments. However, the purity of the free polymethyl methacrylate isolated, as judged by oxygen content, was low (ca. 98%) and it clearly contained some rubber. If this were present as short chains attached to polymethyl methacrylate, the estimate of free homopolymer by this technique would give much higher values.

TABLE I

Sample	Treatment	Sample size, g.	Extraction time, hr.	% homopolymer
A	Acetone extraction of solid rubber	2	16	54.0
			32	59.7
			72	59.7
B	Acetone extraction of cast film	2	20	38.0
			44	47.0
			68	48.4
			84	48.4
B	Acetone extraction of coagulated polymer	2	24	41.7
			48	46.5
			64	46.9
C	Acetone extraction of cast film	2	24	23.3
			48	26.8
		0.5	24	26.6
			48	28.3
			72	28.6
D	Acetone extraction of cast film	0.5	24	24.4
			72	31.7
E	Acetone extraction of cast film	2	24	31.1
			72	37.7

It is concluded that all soluble homopolymer is extracted by hot acetone in 48-72 hr., the time being dependent on the size of the sample. The methods, however, particularly the precipitation separation, require further examination since the solubility characteristics of graft copolymers rich in one component are not completely known.

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