Natural Rubber Latex as Initiator for Vinyl Polymerisation

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A process is described by which it is possible to use ammoniated hevea latex as initiator for the polymerisation of vinyl monomers.

VARIOUS METHODS HAVE BEEN PROPOSED in the literature for the polymerisation of vinyl monomers in latex. All these methods involve the addition of an initiator system consisting of a peroxide or hydroperoxide and an activator which is usually a reducing system or a polyamine $\binom{1-4}{2}$.

Natural rubber latex has been found to contain an 'amine' which, in the presence of hydroperoxide, will cause polymerisation of vinyl monomers. Thus, a part of the initiator system is already available in natural rubber latex.

Experiment 1

Latex from two sources, one from the R.R.I. Experiment Station and the other from the R.R.I. holding in Ulu Klang, were used for this experiment. Ten ml of methylmethacrylate containing 0.07 ml of cumene-hydroperoxide was mixed with 30 ml ammoniated field latex containing 0.5% on rubber of ammonium oleate. The maximum temperature attained in one hour and the dry yield on overnight standing were determined. Table 1 shows the efficiency of this naturally present 'amine' in latex, in causing polymerisation of methyl-methacrylate containing added cumene-hydroperoxide.

Table 1. Polymerisation Efficiency of Latex 'Amines'

Sample	Temperature rise °C	Monomer polymerised
Experiment Station bulk	6	85
Ulu Klang bulk	10	90

It has further been shown that peroxidation takes place in ammoniated latex on standing or agitation, in the presence of oxygen. At ambient temperatures such peroxidation resulted mostly in the production of active centres on the polyisoprene. These active centres had hydroperoxide properties and were capable of polymerising vinyl monomers in presence of a reducing system.

Experiment 2

To 50 ml of activated latex, 15 ml of methyl-methacrylate was added followed by 0.15 ml of 1% ferrous sulphate and 1.5 ml of tetra-ethylene-pentamine. The maximum temperature attained in one hour and the dry yield on overnight standing were then determined. Table 2 shows the efficiency of peroxidised latex in causing the polymerisation of methyl methacrylate in the presence of ferrous sulphate and tetra-ethylene-pentamine.

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Sample	Temperature rise °C	Monomer polymerised
Ordinary latex	0	nil
Activated latex (agitated in air for 96 hrs)	20	88%

TABLE 2. POLYMERISATION EFFICIENCY OF PEROXIDISED LATEX

It is thus possible to obtain the entire initiator system for polymerisation of vinyl monomers from natural rubber latex itself by combining the effect demonstrated in the first experiment with that of the second. This is clearly shown in the following experiment.

Experiment 3

A sample of agitated latex (25 ml) is mixed with ordinary field latex (25 ml) in the ratio of 1:1 and monomer (15 ml) containing 0.15 ml of ferrous-sulphate is added to it and the mixture left standing overnight. The resulting temperature rise and yield are given in Table 3. Polymerisation of vinyl monomers can thus be initiated by specially prepared natural rubber latices.

Table 3. Polymerisation Efficiency of Mixtures of Peroxidised Latex and Fresh Latex

Samples	Temperature rise °C	Monomer poymerised %	
Agitated latex + field latex Agitated latex Field latex	15 LIGHT 2	80 5 0	

It is well known that latices from different sources and clones vary considerably in their non-rubber content. This is particularly true in the case of the naturally present 'amine' in latex. The efficiency of polymerisation will therefore vary from latex to latex. This is clearly demonstrated in Table 4. Latices from different clones were mixed with methyl methacrylate containing cumene-hydroperoxide, as in the first experiment and the increase in temperature and yield on overnight standing measured.

Table 4. Polymerisation Efficiency of 'Amines' in Clonal Latex

Sample	Latex	Temperature rise °C	Monomer polymerised %
1	Pil B84	10	100
2	Pil D65	11	100
3	AVROS 50	6	86
4	PB 23	9	97
5	BD 5	13	92
6	AVROS 49	11	100
7	Tjir l	12	96
8	PB 86	13	98

In addition to this variability of the 'reduction activator' present in latex, the capacity of latices to undergo peroxidation in the presence of air is itself also variable. In other words, latices stored in presence of air will peroxidise to different extents. This is clearly shown in Table 5. Latex concentrates from different clones were stored for one month in presence of air. These latices were then mixed with methyl-methacrylate and tetra-ethylene-pentamine and the increase in temperature and yield on overnight standing measured as in Experiment 2.

Table 5. Polymerisation Efficiency of Peroxidised Clonal Latex Concentrates

Sample	Latex	Temperature rise °C	Monomer polymerised %
1	Pil B84	1.5	5
2	Pil D65	6.5	33
3	AVROS 50	4.5	26
4	PB 23	4.7	24
5	BD 5	7.6	35
6	AVROS 49	8.5	43
7	Tjir 1	0	0
8	PB 86	8	40

The implications of these observations on graft polymerisation and a detailed study of the reactions involved will be published elsewhere. However it is evident from the work reported in this paper that these observations can form a basis by which the active 'amine' contents and extent of peroxidation of latex can both be measured. Such measurements are important for the latex industry since amines influence vulcanisation behaviour and peroxidation leads to changes in the physico-chemical properties of the rubber hydrocarbon.

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