

A LINEAR GEL/POLYMER SYSTEM BASED ON RADIATION PREVULCANIZED NATURAL RUBBER LATEX

By

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INTRODUCTION

Stable cross linked natural rubber (NR) latices were developed initially by Schidrovitz in 1923 and its use as a processing aid was first patented by Philpott in 1958. This patent covers the production of superior processing (SP) rubbers by blending a NR latex containing prevulcanised rubber particles with excess vulcanising agents removed by centrifugation with an ordinary unvulcanised latex or raw latex and coagulating them together.

It is now well known that the processing properties of raw rubber could be improved by incorporating cross linked gel into the essentially linear polymer. These gel containing compounds extrude faster with lower and more uniform die swell greater die definition with a smoother surface and better shape retention. They also calender well giving smooth surfaces with lower shrinkage factor (Mooney, 1985; Makelvery, 1962; Middleman and Gavis, 1965; Gavis and Gill, 1956). Die swell is caused by the recovery of elastic deformations imposed by the restricted flow through a die cavity. The presence of gel polymer reduces the amount of material that is elastically deformed during flow since the gel particles being cross linked material undergoes relatively little deformation. This, again, will be determined by the extent of cross linking in the gel particles. In addition to the sol gel ratio in the compound the extent of cross linking in the gel fraction or the relative tightness of the gel could also influence the rheological properties. A convenient method to study this effect is to blend irradiated latex with raw latex.

This paper describes the rheological properties with special emphasis on extrusion characteristics, of superior processing rubber prepared by preblending radiation prevulcanized NR latex with raw latex.

MATERIALS AND METHODS

Preparation of linear gel/polymer systems

A commercial grade of LA centrifuged latex was diluted to 40% dry rubber content (DRC) and irradiated using a C_{60} source (gamma-rays). A dose of 3 megarads was given over a period of 5 hours. A sensitiser, CCl_4 was used at 3% on the latex, in order to bring about efficient cross linking at a reduced dose level.

The irradiated latex was diluted to 15% DRC and mixed with field latex adjusted to the same DRC. 2% Formic acid was used as the coagulant. After coagulation the rubber was milled into a crepe, and dried in a drying tower at 35°C.

Post extrusion Swelling of a Linear gel/polymer system based on Radiation Pre-vulcanised Latex (RPVL) was studied using the formulation given in Table 1. This was compared with a formulation without the gel component but with the incorporation of factice (similar quantity to gel fraction).

Table 1. Formulations for extrusion of gum compounds

	(1)	(2)
RSS 3	67.0	100.0
IPVR/NR blend (50 : 50)	66.0	—
Factice	—	33.0
ZnO	5.0	5.0
Stearic acid	2.0	2.0
Flectol H	1.5	1.5
MBTS	0.9	0.9
TMTD	0.2	0.2
Sulphur	2.5	2.5

Compounding procedure is given in Table 2. A laboratory intermix was used in the investigations. The rotor and chamber temperature in the intermix was 60°C.

Table 2. Compounding procedure using the laboratory intermix

Action	Time (Mins)
Add rubber	0
+Factice/(NR/IPVL) blend	3/4
Add ZnO, stearic acid	1 3/4
Flectrol H	
MBTS+TMTD	3 1/2
Dump	4
Sulphur was added on the two roll mill in 5 minutes	

	(1)	(2)
Compound Mooney (ML 1 + 4) — 100°C	26	18
Mooney scorch time at 120°C mins	18.0	16.0
Compound density, g/cc	0.903	0.926

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Extrusion Swell (ES) was calculated using the formula.

$$ES = \frac{D - D_0}{D_0} \times 100$$

Where D_0 is the die diameter and D is the diameter of the extrudate. Diameter of the extrudate was calculated using the formula,

$$D = 2R = 2 \sqrt{\frac{M}{G \Lambda}}$$

Where M is the wt per cm of the extrudate. and G is the compound density.

DISCUSSION OF RESULTS

General properties of linear gel/polymer systems

Due to their two-phase structure they would normally increase the stiffness and Mooney viscosity of the rubber mix and at the same time improve its flow behaviour under factory processing conditions as in extrusion. Unlike most processing aids SP rubber does not impair the excellent physical properties, such as tensile strength (TS) of NR vulcanizates.

Extrusion rates and the percentage swell were measured at 3 different screw speeds (20, 40 and 80 rpm). At all 3 speeds the rate of extrusion was faster with the linear gel/polymer system and as the screw speed was increased the difference in rate of extrusion was also magnified (Table 3).

Table 3. Extrusion results

	Compound (1)	Compound (2)
Extrusion rate cm/min		
at		
20 RPM	44.0	34.0
40 RPM	75.0	60.0
80 RPM	155.0	120.0
Weight of extrudate (as above) In gms/min		
20 RPM	84.0	84.0
40 RPM	146.2	155.1
80 RPM	288.0	310.2
Diameter of extrudate/in cm		
20 RPM	1.64	1.84
40 RPM	1.65	1.88
80 RPM	1.61	1.89
Extrudate swell		
20 RPM	41.3	58.6
40 RPM	42.2	62.0
80 RPM	38.8	62.9

The unfilled compound remains least affected by irradiation pre vulcanized rubber (IPVR) and the rate of vulcanization remains relatively unaltered compared to the control. The compound containing factice can be easily identified due to its lower Mooney viscosity.

The effect of SP rubber (as linear gel/polymer system based on RPVL) in filled compounds was determined using the formulation given in Table 4. The compounding procedure is given in Table 5. The extrusion characteristics and cure characteristics are given in Tables 5, 6 & 7.

Table 4. *IPVL/NR blends in extrusion*

Formulations with filler		
RSS 3	100.0	100.0
SP Rubber (as IPVL/NR blend)		
50 : 50	25.0	—
ZnO	5.0	5.0
Stearic acid	2.5	2.5
MBTS	1.0	1.0
TMTD	0.3	0.3
Sulphur	2.5	2.5
Flectol H	1.0	1.0
Clay	25.0	25.0
Whiting	25.0	25.0
Dutrex R	3.5	3.5
Paraffin wax	1.0	1.0

Table 5. *Compounding procedure*

Intermix rotor and chamber at 60°C

Action	Time (Mins)
Add rubber (+SP rubber)	0.0
Add ZnO + stearic acid	
Antioxidant + wax	1.0
Add whiting + clay + oil	1 3/4
Dump	4.0

Accelerator and sulphur were added on the two roll mill in 5 minutes.

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Table 6. Extrusion characteristics

	Compound with SP	Compound without SP
Compound density g/cc	1.110	1.113
Extrusion rate/cm/min		
20 RPM	53.0	44.0
40 RPM	95.0	77.0
80 RPM	181.0	157.0
Weight of compound extruded (as above) in gms per minute		
20 RPM	106.4	111.0
40 RPM	190.6	189.8
80 RPM	366.2	374.6

Table 7. Vulcanization characteristics.

	With SP	Without SP
Compound Mooney		
ML 1 + 4 at 100°C	33	29
Mooney scorch time mins at 120°C	21	22½
Monsanto rheometer at 150°C		
Minimum torque (N.m.)	7	11
Scorch time Ts ₂ (mins)	3.5	5
Maximum torque, (N. m.)	86	79
Time for 90% cure (mins)	6	8
Physical properties of vulcanizates (Vulcanization time, 20 mins at 140°C)		
Tensile strength MPa	24.9	21.5
EB%	625	610
Modulus at 300% MPa	4.7	5.0
Modulus at 100% MPa	2.05	1.96
Hardness, IRHD	53	50

The physical properties of vulcanizates before and after ageing at 100°C for 3 days is given in Table 8.

Table 8. Physical properties after ageing at 100°C for 3 days.

	With SP	Without SP
Tensile strength (MPa)	11.3	7.3
Modulus at 300% (MPa)	5.9	5.5
Modulus at 100% (MPa)	2.4	2.5
EB%	415	290
Change in hardness IRHD	+2	+3

Even in the filled compound there is a substantial reduction in die swell and also there is a substantial improvement in the extrusion rate, when SP rubber (linear gel/Polymer system) is incorporated in to the formulation. The percentage retention of physical properties after ageing at 100°C for 3 days is much better in formulations containing a linear gel polymer system based on RPVL.

CONCLUSION

A linear gel-polymer system based on RPVL remains substantially altered in structure from normal rubber and it is necessary to make a few compounding adjustments to secure optimum properties.

In gum vulcanizates the improvement in processability with the addition of cross linked polymer is much more evident than in filled vulcanizates. This is to be expected as the filler incorporation reduces the nervousness of the rubber and results in the suppression of the die swell during extrusion. The cross linked polymer in the gel-polymer system behaves as a highly structured filler capable of improving the processability of the system far in excess of the proportion of the gel-polymer system incorporated in the compound. The amount of deformation of an extrudate is determined also by the extent of cross linking in the gel fraction as the extent of deformation is controlled by the tightness of the gel and its ability to restrict elastic deformation during the motion within the extruder. By increasing the irradiation dose, the extent of cross linking within the latex particles can be increased up to an optimum value, and this system can be used to carry out a more complete investigation on shear stress/shear rate characteristics in polymers.

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