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DEPOLYMERIZED NATURAL RUBBER AS A PROCESSING AID

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ABSTRACT

The development of a commercially viable, light coloured, non toxic grade of depolymerized natural rubber by the Rubber Research Institute of Sri Lanka (proprietary) has led us to carry out research and development work on the potential industrial applications of depolymerized rubber, for example, as a speciality rubber in raw rubber blends to improve processability and certain physical properties due to its covulcanizable characteristics.

The effects of percentage of depolymerized rubber on the processability and vulcanization characteristics are discussed in this paper. The results show that the use of depolymerized rubber in controlled amount enhances the processability and lowers the power requirement without adversely affecting the properties of the compounds. Also, the results obtained with the vulcanized mixes demonstrate that the behaviour of depolymerized rubber is comparable to synthetic polyisoprenes and is an improvement over ordinary processing oils. Results show that the incorporation of certain percentages of depolymerized rubber in the formulations can significantly improve the abrasion resistance.

Clearly, if depolymerized natural rubber can surpass the existing processing aids in quality and price, then a much larger market is potentially available world wide.

Key words: depolymerization, low molecular weight, non extractable, non toxic, vulcanizable processing aid

INTRODUCTION

In processing of NR, the basic unit operations involved are the mastication and compounding steps.

The process of mastication, to soften the rubber by reducing the molecular weight is a labour intensive operation and requires powerful mixing equipment with high power consumption. With the rapid increase in energy and labour costs, especially in the developed countries the processing costs of natural rubber has increased dramatically. Hence, there has been an increasing demand from consumers, for natural rubber with lower mooney viscosity together with consistent breakdown characteristics.

Earlier research work and publications (Hardman & Lang, 1961; Tillekaratne *et al.*, 1977 and UNIDO report contract no 86/118, 1989) encourage the use of depolymerized rubber for commercial applications such as in ebonite manufacture and in the adhesive industry.

However, the toxicity of the chemicals such as nitrobenzene, hydroxyl amine hydrochloride *etc.*, high cost of the chemicals and the sophisticated reactors involved have discouraged the commercial production of the material.

Attempts have also been made (UNIDO report - contract no 86/118, 1989) to use depolymerized natural rubber as a viscosity modifier/processing aid for natural rubber. It has been shown that depolymerized natural rubber can reduce processing cost with the added advantage of an enhancement in the physical properties in addition to acting as a non - extractable, vulcanizable processing aid.

The development of a commercially viable, non toxic lighter colour depolymerized natural rubber by the Rubber Research Institute of Sri Lanka has led us to carry out research and development work on the potential and industrial applications of depolymerized rubber, for example, as a processing aid in raw rubber blends to improve processability and certain physical properties due to its covulcanizable and non extractable characteristics as discussed in this paper.

In Sri Lanka, research work on the potential commercial applications of depolymerized natural rubber is still at a very early stage. Previous studies on chemical modifications of high molecular weight natural rubber did not always have useful outcomes, usually for technological and economical reasons. However, these studies are also applicable to depolymerized natural rubber using an easier operating mode and the transformations can sometimes even be carried out by the producer.

Accordingly and as an initial step, efforts have been intensified to study the behaviour of depolymerized natural rubber.

It is known that the mooney viscosity of raw rubber which is a reflection of the molecular weight should be as high as possible for good physical properties. On the other hand, the viscosity should be low enough to make premastication unnecessary in consumer factories. Hence it would be a useful asset for the natural rubber producer if they were able to produce a controlled but economically viable reduction in viscosity of a batch without affecting the important physical properties.

Most of the currently available viscosity reducing processing aids are either mixtures of fatty acid derivatives, hydrocarbon oils or blends of synthetic or natural resins. Their use is mainly in non tyre applications due to a tendency to bloom with a consequent effect on adhesion.

As discussed in this paper, the process of blending of a considerable level of depolymerized natural rubber with natural rubber has the potential to make a significant contribution in the area of processing aids. Blending, using two or more polymers, has been used (Brydson, 1978) for many years to soften rigid materials, to stiffen up soft, flexible polymers. Usually if polymer blends are incompatible they result in two phase systems. However, polymers with similar thermodynamic properties or having specific functional groups are known to form blends that are compatible to some degree. In general, polymer blends (Brydson, 1978) offer many advantages such as easy processing, improvements in the end use properties and a low cost final product.

The present study was undertaken, first to develop a uniform system with easy processability during the early steps of mastication and breakdown and, second to produce a system that would improve the physical properties of the rubber. Depolymerized natural rubber would also act as a non - extractable viscosity modifier with reduced scorch, better mixing and low die swell characteristics during extrusion.

EXPERIMENTAL

The first phase of this study consisted of milling tests on a two-roll mill with cooling abilities. The depolymerized natural rubber used in these experiments were produced by varying the treatment conditions. Viscometric molecular weight determinations (M_v) were carried out by using the Ubbelohde viscometer at 25°C (Collins, 1973). The molecular weight variations resulting from different treatment levels in the latex stage are shown in figure 1.

Only one depolymerized grade with viscosity average molecular weight 66102 was used in natural rubber blends in this study since the incorporation of lower molecular weight material would only ease the processing step without giving the desirable physical properties required.

Total blending time was limited to four minutes and processing behaviour was assessed using a Brabender Plasticorder PL 2000 (Brabender Manual, 1989).

Samples containing various proportions of depolymerized natural rubber and natural rubber plus 5 phr processing oil (Table 1) were tested on the plasticorder for variations in energy (Figure 2). The make up of the samples and the results are

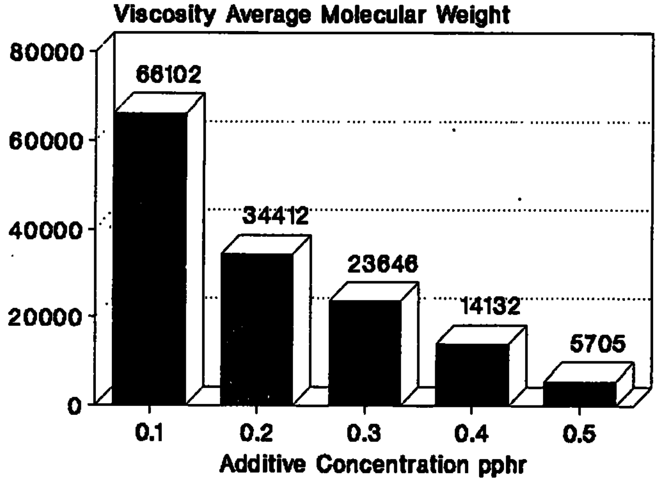

Fig. 1. Effect of additive concentration on average molecular weight

tabulated in Table 1. Figures 3,4 and 5 show the variations in Mooney viscosity, initial plasticity and P_0 and Plasticity Retention Index PRI of natural rubber and its blends with depolymerized natural rubber. The results are also tabulated in Table 2. These samples are also tested for gel content and the results are illustrated in Figure 6 and also tabulated in Table 2.

Samples containing different amounts of depolymerized natural rubber but with 100 parts of natural rubber and 5 parts processing oil kept constant were also tested (Table 3). Figure 7 illustrates the variations in energy on processing of these blends. Figures 8,9 and 10 show the variations in Mooney viscosity, P_0 and PRI values respectively of these samples with increasing depolymerized natural rubber based on 100 parts natural rubber.

The tensile properties of natural rubber/depolymerized natural rubber blend vulcanizates were tested with ACS 1 formulation (Table 4).

Table 1. *Processing properties in the Brabender plasticorder*

NR/Depol. NR	100/0	80/20	70/30	60/40	50/50
Processing oil	5.0	5.0	5.0	5.0	5.0
Energy (KNm)	98.6	85.0	84.0	78.3	69.6
Torque (Nm)	73.0	61.8	62.6	56.1	52.6
Specific energy (KNm/g)	5.1	3.1	2.6	2.0	2.6

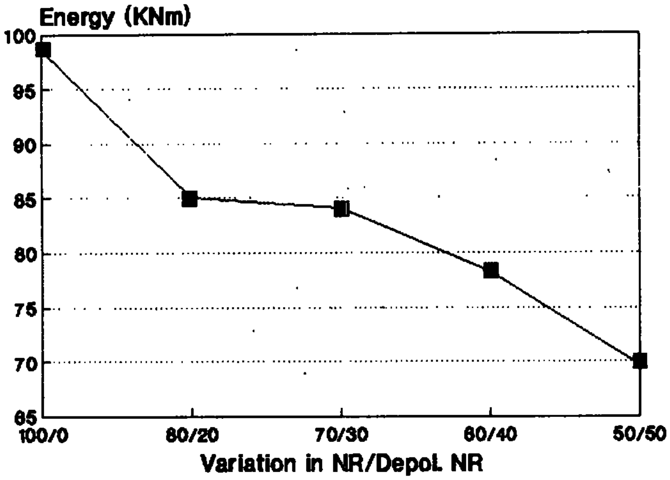

Fig. 2 Variation in energy

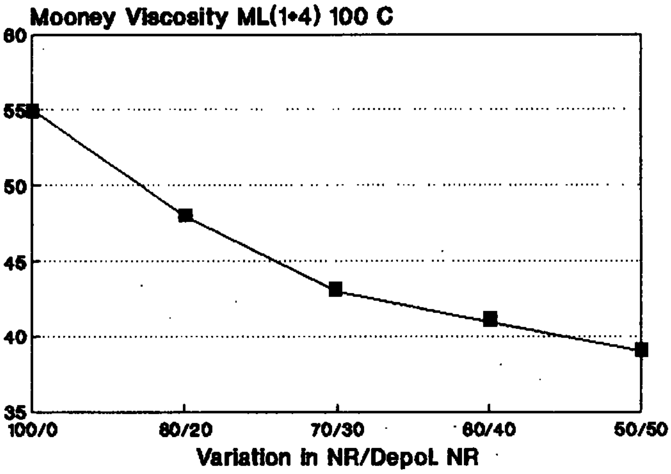

Fig. 3 Variation in monney viscosity values

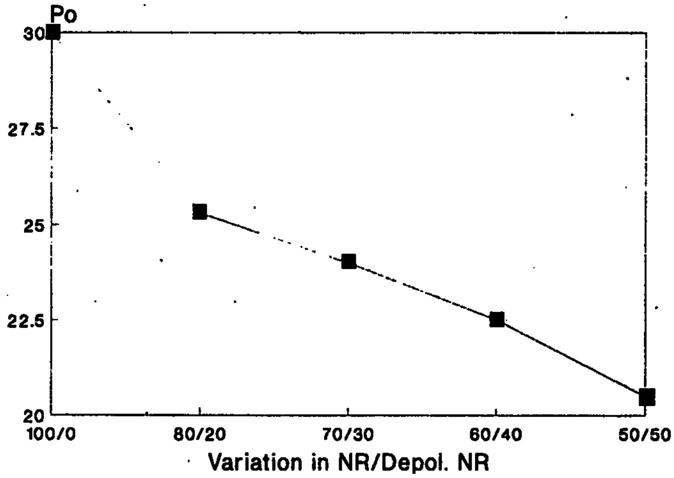

Fig. 4 Variation in Po values

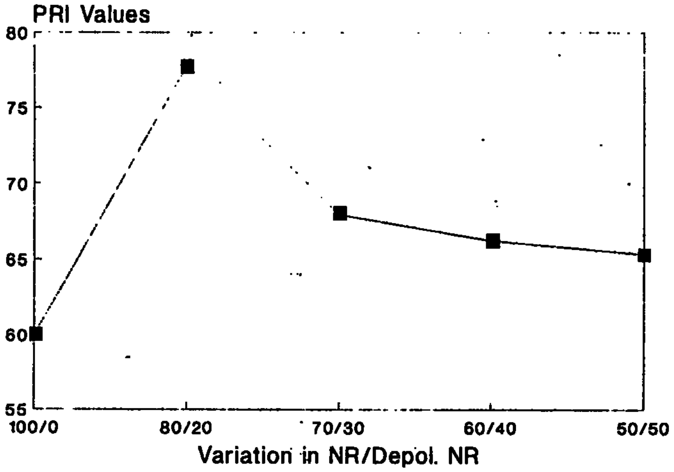

Fig. 5 Variation in PRI values

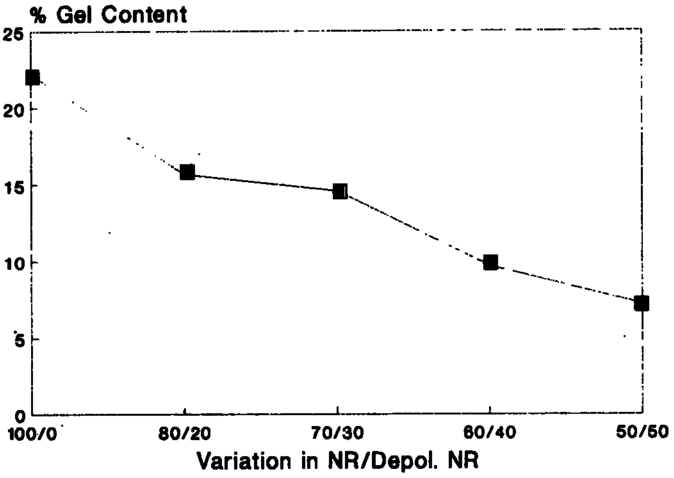

Fig. 6 Variation in % gel content

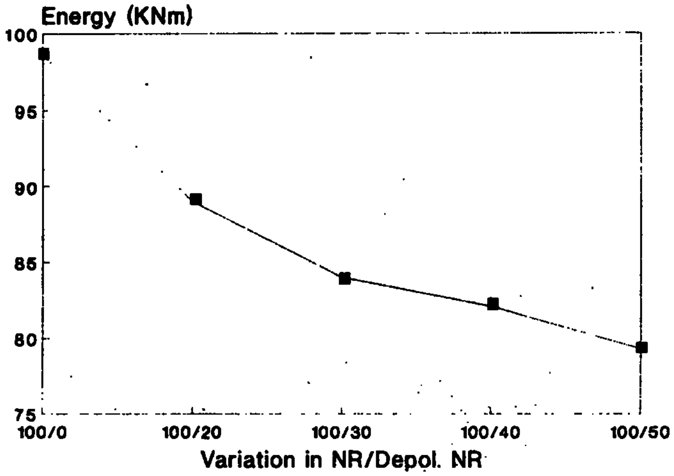

Fig. 7 Variation in energy

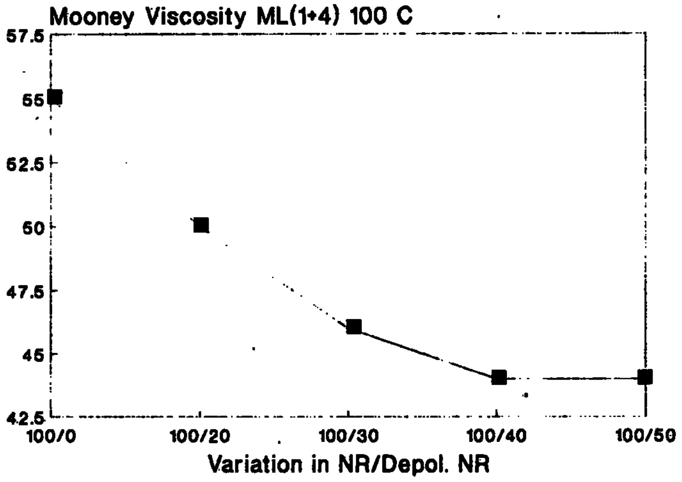

Fig. 8 Variation in mooney viscosity

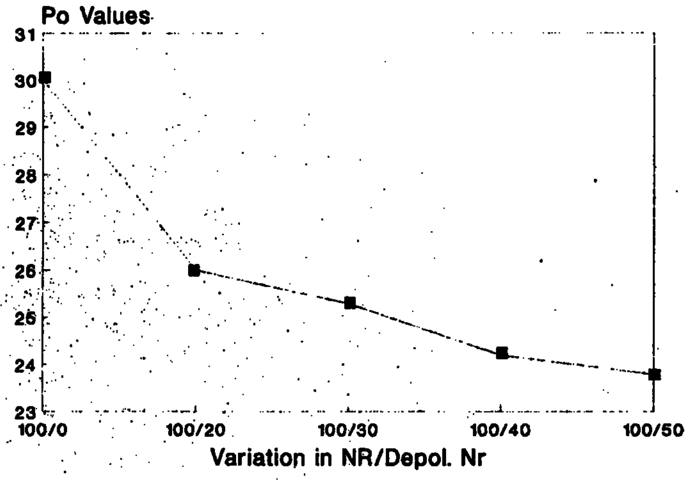

Fig. 9 Variation in Po values

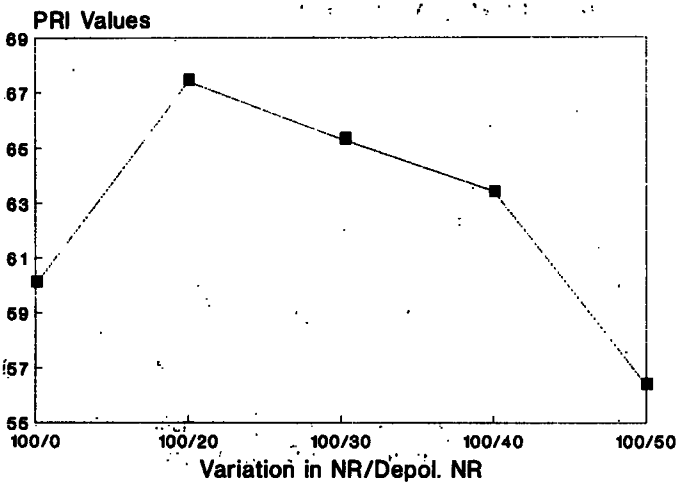

Fig. 10 Variation in PRI values

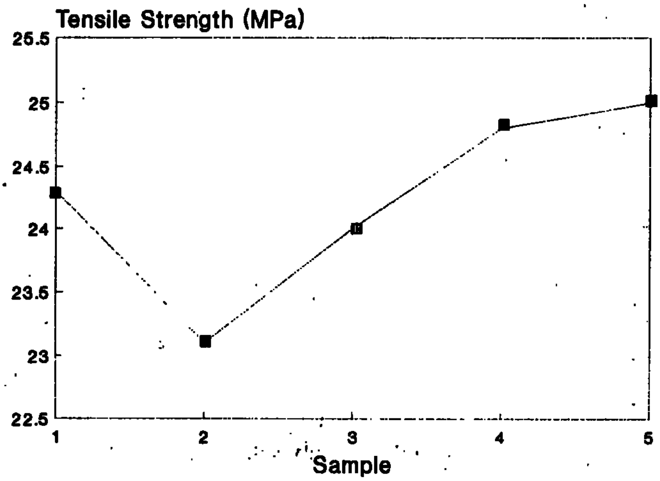

Fig. 11 Variation in tensile strength

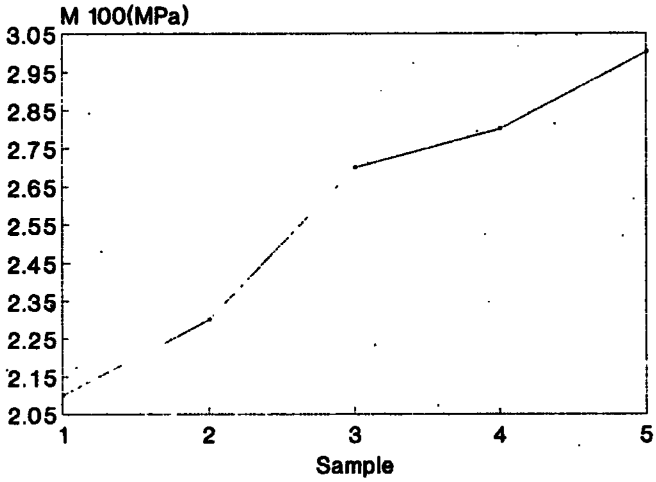

Fig. 12 Variation in M 100

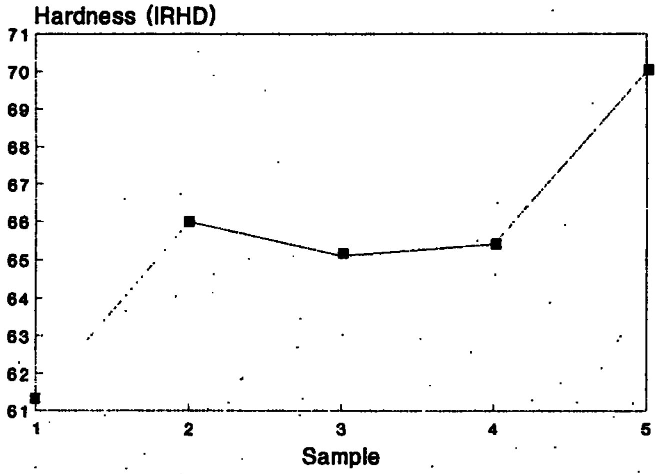

Fig. 13 Variation in hardness

Table 2. *Raw rubber properties*

NR/Depol. NR	100/00	80/20	70/30	60/40	50/50
Processing oil	5.00	5.00	5.00	5.00	5.00
Mooney viscosity ML(1+4) 100°C	55.00	48.00	43.00	41.00	39.00
P_0	30.00	25.30	24.00	22.50	20.50
P_{30}	18.00	17.60	13.80	14.90	13.80
PRI	60.00	77.80	67.90	66.20	65.30
% Gel content	22.20	15.70	14.60	9.70	7.20

To study the effect of depolymerized natural rubber in vulcanized products a typical tread formulation (Table 5 sample 1) and tread formulation with replacement of part of rubber with depolymerised natural rubber was used. (Samples 3,4,5 Table 5).

Physical properties of the above samples are tabulated in Table 6 together with abrasion resistance and die swell values. Variations in tensile strength, modules at 100% and hardness with different amounts of depolymerized NR are illustrated graphically in figure 11,12,13. The after ageing tensile properties of the above samples are given in Table 7.

Table 3. *Processing properties in Plasticoder with constant NR*

NR/Depol. NR	100/00	100/20	100/30	100/40	100/50
Processing oil	5.00	5.00	5.00	5.00	5.00
Energy (KNm)	98.60	89.00	84.00	82.10	79.30
Torque (NM)	73.00	65.40	69.00	63.40	60.20
Mooney Viscosity ML(1+4) 100°C	55.00	50.00	46.00	44.00	44.00
P_0	30.00	26.00	25.30	24.20	23.80
PRI	60.00	67.40	65.30	63.40	56.40

Table 4. *Physical properties of vulcanizates (ACS 1 Formulation)*

		Before Ageing			
NR/Depol NR (Mv=66102)	100/00	80/20	70/30	60/40	50/50
Tensile strength (MPa)	12.69	11.96	16.68	12.75	13.03
%EB	900.00	763.00	816.00	731.00	806.00
M 100 (MPa)	0.05	0.06	0.17	0.08	0.06
M 300 (MPa)	0.51	3.67	1.14	0.88	0.65
Hardness (IRHD)	32.00	33.00	36.00	34.00	36.00
Resilience	61.00	69.00	70.00	68.00	71.00
		After Ageing for 48 hrs at 70 °C			
Tensile strength (MPa)	12.52	14.31	14.68	14.79	17.04
% EB	712.00	665.00	706.00	644.00	675.00
M 100 (MPa)	0.05	0.16	0.26	0.22	0.27
M 300 (MPa)	0.94	1.17	1.35	1.33	1.34

Table 5. *Typical tyre tread formulation with depolymerized NR (Mv=66102) and processing aids*

	1	2	3	4	5
NR/Depol. NR	100/00	100/00	90/10	80/20	70/30
Processing Oil	5.00	5.00	5.00	5.00	5.00
Kuraray LIR 50*	-	10.00	-	-	-
Carbon Black	45.00	45.00	45.00	45.00	45.00
ZnO	5.00	5.00	5.00	5.00	5.00
Stearic Acid	3.00	3.00	3.00	3.00	3.00
IPPD	2.00	2.00	2.00	2.00	2.00
Sulphur	3.80	3.80	3.80	3.80	3.80
CBS	0.75	0.75	0.75	0.75	0.75

* Depolymerized synthetic polyisoprene rubber

Table 6. *Physical properties of vulcanizates (tyre tread formulation)*

	1	2	3	4	5
NR/Depol. NR	100/00	100/00	90/10	80/20	70/30
Tensile Strength (MPa)	24.30	23.10	24.00	24.80	25.00
% Elongation at Break	516.00	501.00	528.00	506.00	548.00
M 100 (MPa)	2.10	2.30	2.70	2.80	3.00
M 300 (MPa)	11.90	9.60	11.60	10.40	13.60
Hardness (IRHD)	61.30	66.00	65.10	65.40	70.0
Abrasion (cm^3 per 1000 rev)	00.094	00.074	00.062	00.047	00.035
% Die Swell-Slow (20 rpm)	36.30	33.60	34.30	30.50	30.10
% Die Swell-Fast (80 rpm)	30.90	21.40	20.30	16.30	14.50
Special Gravity	01.055	-	01.035	01.041	01.035

Table 7. *Tensile properties of the vulcanizates after ageing at 70 °C*

		After Ageing for 24 hrs at 70 °C			
	1	2	3	4	5
Tensile strength (MPa)	24.0	21.2	24.4	23.7	24.7
% Elongation at break	504.0	481.0	532.0	489.0	498.0
M 100 (MPa)	2.0	2.3	2.8	2.5	2.7
M 300 (MPa)	11.0	10.1	11.8	10.6	12.2
		After Ageing for 48 hrs at 70 °C			
	1	2	3	4	5
Tensile strength (MPa)	23.1	20.1	23.3	22.6	24.0
%Elongation at Break	493.0	475.0	518.0	480.0	485.0
M 100 (MPa)	1.8	2.0	2.3	2.1	2.6
M 300 (MPa)	9.8	9.5	10.0	9.3	11.0

RESULTS AND DISCUSSION

Results obtained with blends of natural rubber and depolymerised natural rubber show that depolymerised natural rubber is a suitable plasticizer for natural rubber compounds.

As a processing aid depolymerized natural rubber seems to have certain advantages over the other processing aids. It is compatible with natural rubber and could perform several functions. In uncured rubber the incorporation of depolymerized natural rubber facilitates processing with a savings in energy, hence reducing the time and machinery wear during the mixing of rubber compounds. It is non-extractable in addition to being vulcanizable.

It has the effect of reducing overall molecular weight and thus reduce viscosity. All of the proceeding trials show the usefulness of depolymerized rubber as a processing aid and confirm that it plays the role of a viscosity modifier. However, choice of a suitable formulation is essential to suit the needs.

Effect of depolymerized natural rubber on uncured rubber properties

In general, the addition of depolymerized rubber to natural rubber leads to plasticization of the blend by means of intramolecular action, discussed below, with a reduction in viscosity without developing slippage in the two-roll mill.

The effect of gradual incorporation of depolymerized natural rubber to replace part of natural rubber was studied on the plasticorder and the data on variations in energy and torque values are tabulated in Table 1 and the variation in energy is also illustrated graphically in Figure 2.

As can be seen from these results, and as expected the natural rubber without depolymerized natural rubber has the highest energy and torque values. However, when natural rubber is replaced with 30% depolymerized natural rubber, a slight increase in energy occurs when compared to blends containing 40% and 50% depolymerised natural rubber. This can be seen in Figures 2.

A possible explanation for this difference in processing behaviour could be related to differences in the mobility of the high and low molecular components in this blend in this case natural rubber and depolymerized natural rubber. In the case of blends (Brydson, 1978). It is known that when two polymers are brought into contact the chain ends of the one polymer are able to diffuse into the other and that the rate of diffusion depends on a number of parameters. In addition, effect will increase tack which is an useful property required by many rubber manufacturing operations.

When a higher percentage of depolymerized rubber is incorporated, *i.e.*- > 30%, the low molecular weight component is increased, as is the rate of diffusion, thus reducing the molecular weight of the blend resulting in a further drop in energy as can be seen in figure 2.

As can be seen in Table 2 and Figure 3, the Mooney Viscosity decreases with a gradual replacement of rubber with depolymerized rubber. The P_0 values (Figure 4) also decrease with increasing depolymerized rubber content in the blend. Compared to natural rubber, the PRI values (Figure 5) of the blends with low percentage of depolymerized rubber show a sharp increase. When the percentage is higher than 30% and up to 50% the variation of PRI with depolymerized rubber content is a negligible. The gel content also decreases with increasing depolymerised rubber as shown in Table 2, Figure 6. The lowest gel content was obtained with the blend containing 50% depolymerized rubber.

Hence, if depolymerized rubber is chosen to replace natural rubber as a viscosity modifier, the percentage to be incorporated should be chosen carefully in order to obtain properties required in the end product.

When the amount of natural rubber was kept constant and depolymerized rubber was incorporated in different amounts, (Table 3) a similar pattern of behaviour is observed. The molecular weight of the blends gradually decreases with the incorporation of depolymerized rubber and energy (Table 3, Figure 7) and torque values (Table 3) decrease accordingly. Figures 8,9 and 10 show the variations in Mooney viscosity, P_0 and PRI values respectively. The reduction in viscosity of the blends is of particular interest and appears promising for injection moulding operations and applications.

Effect of depolymerized natural rubber on vulcanized rubber properties

The tensile properties given in Table 4 based on ACS1 formulation show that natural rubber can be partly replaced with depolymerized natural rubber with some improvements in physical properties.

Trials conducted on formulations based on tyre tread compound but with depolymerized rubber in the blend (Table 5) show that most tensile properties are retained, (Table 6, Figure 11), with improvements in modules values (Figure 12). The hardness is highest when the depolymerized rubber content is 30% (Figure 13). The improvements in properties is probably due to the reactivity of the depolymerized rubber in the blend as a vulcanizable material, *i.e.* the low molecular weight component prevents tearing by allowing viscous flow whilst the high molecular weight component provides a degree of elastic strength. The trials carried out by adding depolymerized natural rubber and a depolymerized synthetic polyisoprene rubber. Kurary LIR 50 from Japan, oil in the formulation (Table 5) have also shown promising results. These are shown in table 6 in which it can be seen that more interestingly the abrasion resistance seems to improve significantly with 30% of depolymerized rubber in the blend whilst extrusion die swell is also reduced. The performance of the samples after aging is not much affected as shown in Table 7. Infact, properties such as modules at 100% seems to improve on ageing.

CONCLUSION

The incorporation of depolymerized natural rubber in natural rubber formulations is superior to conventional processing aids in conferring improved processability on natural rubber blends. The ability of a rubber compound to turn a tight band on the two roll mill, a useful processing attribute seems to increase significantly with the addition of depolymerized rubber. This also leads to plasticization and provides good tack in the blend. Blends containing depolymerized rubber appear to co - vulcanize with natural rubber. Compounds containing depolymerized rubber have reduced tensile values, though these remain within the acceptable limits, and the corresponding mod values are equal or slightly increased. Hardness and abrasion resistance increase with increase of depolymerized rubber. The use of more than 50% phr of depolymerized rubber as a viscosity modifier may not be attractive; compounds with more than 50% phr of depolymerized rubber have generally poor mechanical properties except for hardness.

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