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A STUDY OF SOME OF THE PROPERTIES OF BLENDS OF POLYPROPYLENE AND CHEMICAL INCORPORATED GRANULAR NATURAL RUBBER

K G Karnika de Silva, S L G Ranjith and S S Warnapura

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ABSTRACT

Thermoplastic elastomers of plastics and natural rubber (TPNR) are generally produced by blending plastics with natural rubber (in bale form) using traditional banbury type internal mixers and plastics extruders. This involves high energy consumption and also high capital costs of both rubber and plastics processing machinery.

The production of Thermoplastic elastomers on a continuous basis using extruder blenders has been less applicable to TPNR blends because natural rubber is not readily or widely available in the required granular form in natural rubber consuming countries.

The manufacture of different types of granular rubber in our laboratories has not only made possible the blending of thermoplastics with natural rubber on a continuous basis but also paved the way for producing TPNR blends with improved properties.

In this publication the production of different types of granular rubber, the processing characteristics of various compositions of polypropylene and natural rubber blends and the end product performance of these blends at different temperatures are discussed.

INTRODUCTION

Of the thermoplastic elastomers (TPE) those produced by blending of thermoplastics and elastomers, are becoming increasingly accepted in the polymer market. These blends, can best be appreciated as high impact resistant engineering materials and are one of the fastest growing sectors of the polymer market. The blends possess special molecular features that enable them to behave as strong elastic

vulcanizates at normal temperatures but to flow like plastics at processing temperatures. Contrary to traditional vulcanized rubbers TPE scrap is reusable without any operations and upto about 40% of recycled scrap may be added to virgin materials without much affecting the properties of the finished article.

The commercial importance of TPE can be attributed to both properties as well as end product performance of the material. Quality and design flexibility are equally important and the TPE producers have a major advantage over the traditional rubber manufacturers in that it is possible to maintain consistent quality in their products.

Numerous studies and developments have been carried out by (Campbell *et al* 1978 and Tinker 1987) thus creating the technical background and essential knowledge necessary to enhance end use development of TPE. More complex compositions with fillers and reinforcing agents with a special combination of stiffness and impact resistance over a range of temperatures have also been tried out to comply with more stringent end use requirements of some products. In order to improve processability and elastic properties of TPE and to decrease the cost of production, (Elliott 1982 and IRRDB report 1987) have reported many proposals to modify elastomer and plastics binary blends either by addition of a third polymer or by extention with processing oils. The basic factors which optimise the processability of the TPE blends are the intensive and homogeneous mixing creating high shear stress throughout the plastic mass and also sufficient mixing time. One way of achieving these requirements is to blend the plastic and elastomer in a traditional Banbury type internal mixer. During this operation dynamic vulcanization takes place if crosslinking agents are present in the medium; dynamic vulcanization (Fisher 1974) is the crosslinking of one of the polymers during its molten state mixing with another polymer or other polymers. However, carbon black and other fillers which act as true reinforcing agents, do not give rise to any modification apart from a general stiffning of the compounds as they do not chemically bond to rubber chains. The use of TiO_2 may provide benefits in terms of reduced mould shrinkage and surface hardening but elastic performance is in no way improved by this filler or any other (IRRDB report 1987).

Thermoplastic Natural Rubbers (TPNR) are generally produced by blending plastics with natural rubber using traditional Banbury type internal mixers or Francis Shaw mixer/exruder. However, so far there has been no significant production nor consumption of TPNR in natural rubber producing and consuming countries due to processing difficulties and high capital costs involved. Generally, internal mixers are only available with the rubber products manufacturers who in general do not have the ancillary thermoplastic equipment. But on the other hand plastics processing factory

in general would be suitably equipped with extruders, pelletizers or extrusion pelletizers and injection moulding machines and if the rubber is available in a suitable form, then the implementation of the manufacture of TPNR in a plastic processing factory is quite convenient and economical. Production of TPNR on a continuous basis using an extrusion pelletizer is the method adopted (Coomarasamy *et al* 1988) by the Rubber Research Institute of Sri Lanka.

The most characteristic feature in our work is the use of granular rubber, produced by incorporation of fillers, crosslinking agents and/or processing oils in the latex stage. To improve the processability characteristics of the blends.

The manufacture of different types of granular rubber in our laboratories has now opened up the prospects of TPNR blends being made on a continuous basis with additional economies in terms of man power and production rates.

This paper is mainly concerned with the properties of such blends manufactured using these new types of granular rubber. The final product related properties which are so different from those of traditional natural rubber vulcanizates have also been evaluated. These blends have the potential for high impact resistant uses which should enable the market for natural rubber to be expanded.

These developments will encourage potential consumers to make use of the raw materials available from Sri Lanka. *eg* The filler, crosslinking resin and/or processing oil incorporated granular rubber (with induced crystallinity) in easy – to handle masterbatch form for the manufacture of TPNR materials with different properties, and homogeneous TPNR blends with different percentages of dynamically crosslinked rubber in pelletised form for the manufacture of TPNR products.

It is therefore pleasing to be able to report that a breakthrough has been achieved in the manufacture of potentially viable low cost TPNRS. This knowledge is already being intergrated into promotional work which has enabled the producers to introduce a better quality material to the consumer market.

EXPERIMENTAL

Preparation of Granular Rubber of Different Types

Granular rubber used in our experimental trials were prepared by first converting the natural rubber coagulum into sole crepe and then by passing the sole crepe through a granulator.

Different types of granular rubbers used in our study are listed below.

The rubber type A and B were obtained by processing the coagulum obtained from formic acid coagulation into sole crepe granules. Rubber C–G were prepared by incorporation of fillers, carbon black or TiO_2, crosslinking agent, phenol formaldehyde resin, SP 1045, (schenectady) and/or processing oil, naphthanic oil in the latex stage in the form of dispersions or emulsions before coagulation with formic acid and processed into sole crepe granules. The granules have regular rectangular or cubical shape.

type	**latex used and materials incorporated**
A	Fractionated field latex
B	Unfractionated, diluted field latex
C	7.5 phr resin with fractionated latex
D	7.5 phr resin, 5 phr processing oil with fractioanted latex.
E	5 phr carbon black with fractionated latex
F	7.5 phr resin, 5 phr carbon black and 5 phr processing oil with fractionated latex
G	5 phr TiO_2 with fractionated latex

The blends required to study the physical properties were prepared as 5 kg samples on a twin screw extrusion pelletizer available at a plastics processing factory. A specially fabricated multi-cavity mould was used for the preparation of injection moulded test pieces. A horizontal 7 oz plastijet injection moulding machine was used for moulding of test pieces at 180°C.

Yield stress values were measured at 23°C according to ISO 527 with an Instron Model 1136 Universal Testing Machine for testing injection moulded dumb-bell shaped test pieces.

Some useful information on processability of the blends were obtained from Melt Flow Index (MFI) measurements. The method used to find the falling weight impact strength was based on BS 2782 – method 306 B. Test specimen used were injection moulded as circular discs of 60 mm diameter and 1.5 mm thickness.

RESULTS AND DISCUSSIONS

Effect of crosslinking agent and rubber composition

The blends were prepared on a twin screw extruder according to the formulations (Table 1). Injection moulded test pieces were used to find the physical properties, yield stress, hardness and impact strength, of the blends (Tables 2 and 3).

Table 1. *Formulations of blends with variations in crosslinking resin and rubber composition*

Sample	1	2	3	4	5	6
Materials parts						
Polypropylene	80	80	80	80	60	60
Rubber/Type[1]	20-A	20-A	21.5-C	20-A	40-A	43-C
Resin[2]	1.5	3.5	-	-	3.0	-
Peroxide	-	-	-	1.5	-	-
ZnO.	1.0	1.0	1.0	1.0	1.0	1.0
A.O[3]	1.0	1.0	1.0	1.0	1.0	1.0

1. A – Granular rubber from fractionated latex
   C – 7.5 phr resin incorporated granular rubber
2. Phenol formaldehyde resin, SP 1045, (Schenectady)
3. Antioxidant BKF (Bayer)

Yield stress and modulus increase with increasing amount of vulcanizing agents (Table 2, sample 1 and 2) and by the use of a low percentage of resin incorporated granular rubber (type C) in the blends (sample 3). Accordingly, the yield stress of the blends seems to vary from 31.8 Mpa to 18.7 Mpa; for the blends containing 20 parts of rubber in the blend. The highest value was obtained with the blends containing a high percentage (3.5% on blend) of resin. The next highest value of 30.7 MPa was obtained with a blend containing a lower percentage of (1.5% on blend) resin incorporated granular rubber (sample 3).

Table 2. *Effect of crosslinking agent on tensile properties*

Sample	1	2	3	4	5	6
Tensile property						
Yield stress MPa	26.3	31.8	30.7	18.7	29.6	34.8
%E.B.	263	221	230	178	365	345
Modulus MPa	208	295	307	228	256	263

Table 3. *Effect of crosslinking agent on impact strength, hardness and MFI values*

Sample	1	2	3	4	5	6
Property						
Impact strength J at 23°C	7.37	8.56	10.37	5.36	11.57	12.5
Hardness	86	89	90	80	86	87
MFI (Condition L)	11.9	10.3	10.4	12.3	8.5	8.3

A similar effect was observed for impact strength of these blends (Table 3). The peroxide cured blend has the lowest value of 5.36J at 23°C whereas the blends with resin incorporated granular rubbers show higher values. The MFI values seems to decrease slightly with the increasing amount of resin in the blends (Table 3). The incorporation of resins in the latex phase has not made a significant difference in these values. Further, it was noted that the impact strength improves with the increase in the rubber composition in the blends up to 40% (Table 3).

Effect of rubber type

The main advantages of using sole crepe granules are two fold. Firstly, the method of manufacture of sole crepe facilitates easy alignment of rubber molecules along the direction of milling resulting in partial crystalization of rubber laces and

hence easy granulation. Secondly, the induced crystalization on stretching and lamination during the manufacture makes it somewhat compatible with polypropylene.

The formulations of various blends with different rubber types (Table 4).

The yield stress of the blends (Table 5) with different rubber types seems to vary from 30.7–17.0 MPa; highest value was obtained for the blends prepared with 20 parts of resin incorporated granular rubber (type C) containing 1.5% resin in the blend. The blend with 20 parts of resin incorporated granular rubber containing 1.5% resin and 1.0% processing oil (type D) in the blend gave a value of 29.1 MPa with a better surface appearance. The lowest value of 17.0 MPa was obtained for RSS and a slightly higher value was obtained for crepe rubber.

Further, it appears that the granular rubbers are the most suitable grades of natural rubber even without prior incorporation of resin when compared to the other grades (Table 5).

Table 4. *Formulations of blends with different rubber types*

Sample Materials parts	1	2	3	4	5	6
Polypropylene	80	80	80	80	80	80
Rubber\Type[1]	20–A	20–B	21.5–C	21.5–D	20–RSS	20–Crepe
Resin[2]	1.5	1.5	–	–	1.5	1.5
ZnO	1.0	1.0	1.0	1.0	1.0	1.0
A.O.[3]	1.0	1.0	1.0	1.0	1.0	1.0

1. A – Granular rubber from fractionated latex
   B – Granular rubber from unfractionated latex
   C – 7.5 phr resin incorporated granular rubber
   D – 7.5 phr resin and 5 phr processing oil incorporated granular rubber
2. Phenol formaldehyde resin, SP 1045, (Schenectady)
3. Antioxidant BKF (Bayer)

Table 5. *Effect of rubber type on tensile properties*

Sample Tensile Property	1	2	3	4	5	6
Yield stress (MPa)	26.3	21.1	30.7	29.1	17.0	18.2
% E.B	263	197	230	223	167	183
Modulus MPa	208	243	307	302	214	230

With these improvements it has now become possible to prepare homogeneous PP/NR blends with increased impact strength. The blends with granular rubber from unfractionated latex, RSS and crepe rubber (Samples 2,5,6) showed low impact strength values (Table 6) of 6.36J, 6.75J, and 6.97J respectively at 23°C.

Table 6. *Effect of rubber type on impact strength, hardness and MFI values*

Sample Property	1	2	3	4	5	6
Impact strength J at 23°C	7.37	6.36	10.37	11.80	6.75	6.97
Hardness	86	83	90	85	76	78
MFI (Condition L)	11.9	–	10.4	12.0	11.0	10.3

Effect of fillers and processing oils

Partial modification of blends is generally limited to relatively small amounts of fillers for specific properties although moderate amounts of cheap fillers may be used to reduce cost. The extent of incorporation of fillers and processing oils in the hopper with the raw materials (Table 7) is shown to have a decisive influence on the processability of the rubber, polypropylene blends.

The physical properties show no significant improvements with the incorporation of fillers as with the conventional natural rubber vulcanizates (Table 8).

However, there is a slight improvement in the impact strength in the blends with filler incorporated granular rubber.

Table 7. *Formulations of blends with variations in fillers, and processing aids*

Sample	1	2	3	4	5	6	7
Materials parts							
Polypropylene	80	80	80	80	80	80	80
Rubber\Type[1]	20–A	20–A	22.5–D	21–E	23.5–F	21–G	20–A
Resin[2]	1.5	1.5	–	1.5	–	1.5	1.5
Carbon black	1.5	5.0	5.0	–	–	–	–
Processing oil	–	1.0	–	–	–	–	–
EVA	–	–	–	–	–	–	1.5
ZnO	1.0	1.0	1.0	1.0	1.0	1.0	1.0
A.O.[3]	1.0	1.0	1.0	1.0	1.0	1.0	1.0

[1] A – Granular rubber with fractionated latex
D – 7.5 phr resin and 5 phr processing oil incorporated granular rubber
E – 5 phr carbon black incorporated granular rubber
F – 7.5 phr resin, 5 phr carbon black and 5 phr processing oil incorporated granular rubber
G – 5 phr TiO_2 incorporated granular rubber
[2] Phenol formaldehyde resin, SP 1045, (Schenectady)
[3] Antioxidant BKF (Bayer)

The addition of only processing oil in the latex stage gives some reduction in viscosity which is noticeable to improve processablity during extrusion and gives smoother extrudates.

The addition of a polymeric filler such as EVA was also carried out for comparison (Table 8).

Table 8. *Effect of fillers, processing aids on tensile properties*

Sample	1	2	3	4	5	6	7
Tensile property							
Yield stress MPa	21.3	20.1	23.7	25.1	27.0	24.2	33.8
%E.B.	203	170	216	213	218	188	219
Modulus MPa	189	143	203	204	223	228	237
Impact strength J at 23°C	7.41	7.58	8.05	9.43	>12.6	9.31	9.07

Effect of crosslinking agent, fillers and processing oil

Processing properties

The variations in flow properties were studied on the Capillary Rheometer to examine the rheological behaviour of polymer melts.

The effect of crosslinking agent on viscosity, shear stress and die swell are illustrated (Figures 1–3) to show that the flow characteristics are affected by the percentage and the way of addition of resin to the blend. The effect of fillers and processing oil on the processing behaviour (Figures 4–5). The addition of fillers in to the mixing hopper has shown poor processability. However, this tends to improve when the addition of fillers is done at the latex stage (Figure 4). Viscosity tends to decrease with the incorporation of processing oil as expected (Figure 4).

Therefore, by varing the proportion of the added ingredients, it is possible to get compounded blends with different flow and physical properties.

CONCLUSIONS

The main objective of this study was to find out a technically sound and commercially profitable process to manufacture thermoplstic blends with natural rubber, by looking at the technological properties of polypropylene and natural rubber blends. It is clear that the use of continuous mixing extruder for the preparation of thermoplastic blends has several advantages; *eg* convenience in raw material and product handling, easy control and monitoring of the mixing process during preparation of the blends *etc*.

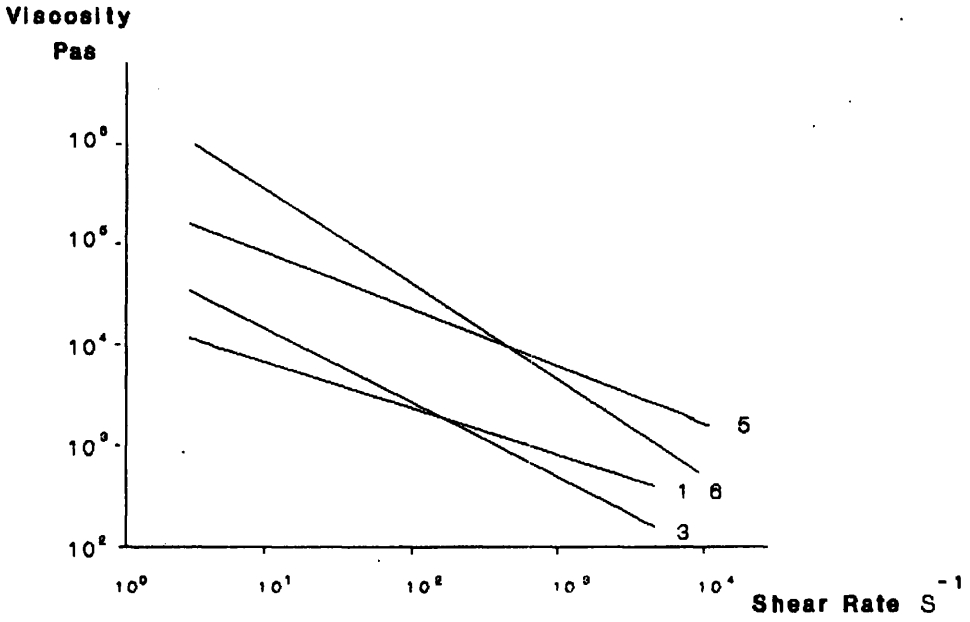

Fig. 1. Effect of crosslinking agent on viscosity vs shear rate curves at 180°C

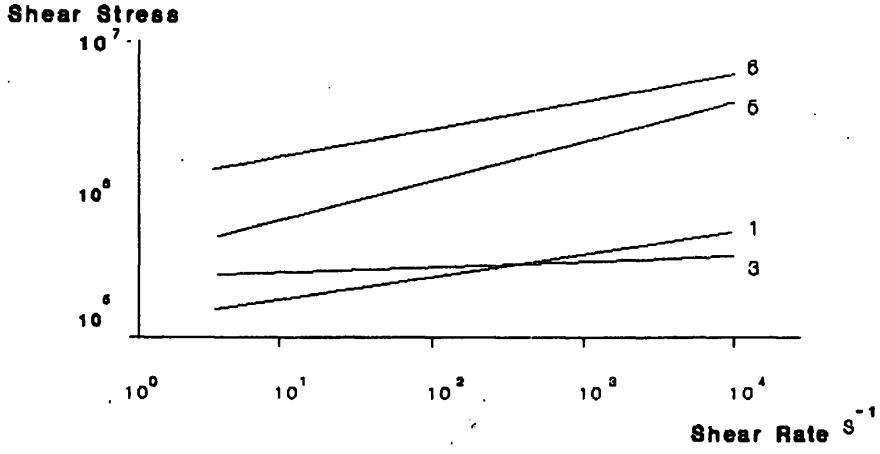

Fig. 2 Effect of crosslinking agent on shear stress Vs shear rate curves at 180° C

In Figures 1 and 2;

1 – 80:20 PP:NR with 1.5% resin

3 – 80:21.5 PP:NR with 1.5% resin incorporatee granular rubber

5 – 60:40 PP:NR with 3.0% resin

6 – 60:40 PP:NR with 3.0% resin incorporated granular rubber

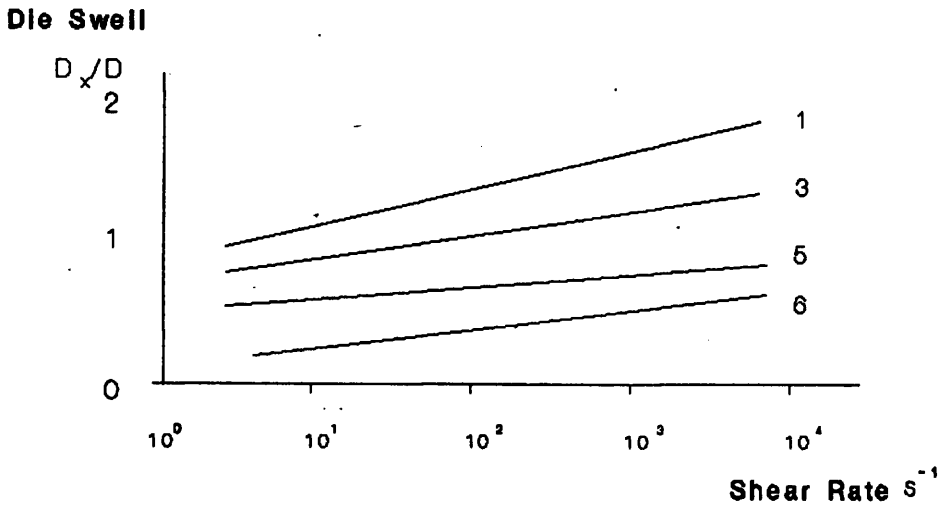

Fig. 3 – Effect of crosslinking agent on die swell vs shear rate curves at 180° C

In Figure 3:

1 – 80:20 PP:NR with 1.5% resin
3 – 80:21.5 PP:NR with 1.5% resin incorporated granular rubber
5 – 60:40 PP:NR with 3.0% resin
6 – 60:40 PP:NR with 3.0% resin incorporated granular rubber

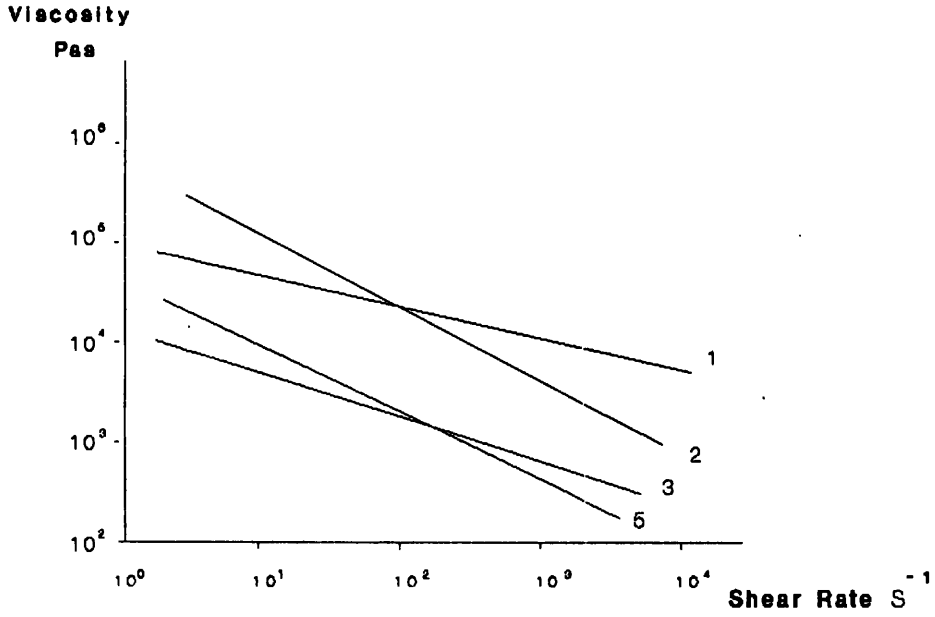

Fig. 4. Effect of fillers and processing oil on viscosity vs shear rate curves at 180° C

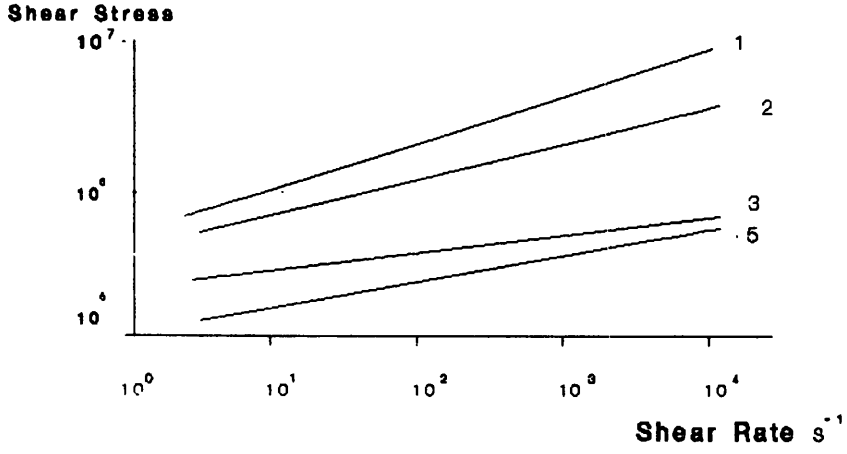

Fig. 5. Effect of fillers and processing oil on shear stress vs shear rate curves on at 180° C

In Figure 4 and 5:

1 – 80:20 PP:NR with 1.5% resin and 1.5% carbon black

2 – 80:20 PP:NR with 1.5% resin, 5% black and 1% oil

3 – 80:22.5 PP:NR with 7.5 phr resin and 5 phr oil incorporated granular rubber with 5% black (22.5 parts of rubber contain 1.5 parts of resin & 1 part of oil)

5 – 80:23:5 PP:NR with 7.5 phr resin, 5.0 phr black and 5.0 phr oil incorporated granular rubber (23.5 parts of rubber contain 1.5 parts of resin, 1 part of each oil and black)

The results show that the preparation of rubber has a significant effect on the properties of the thermoplastic blends. As a result, granular sole crepe made from coagulation of fractionated and phenol formaldehyde resin incorporated latex has been found to be the most suitable grade of sole crepe for this purpose. The oil extention in the latex stage seems to improve the processability of the thermoplastic belnds. Addition of fillers (small percentage only) too can be done in the latex stage for better incorporation of fillers. Injection moulded and extruded products of improved quality can be obtained by using the thermoplastic blends prepared with resin incorporated and oil extended granular rubber and by the processing of these blends at carefully controlled temperatures.

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