MANUFACTURE OF THERMOPLASTIC NATURAL RUBBER IN SRI LANKA

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INTRODUCTION

Thermoplastic rubber is the name given to a class of materials which possess rubber — like properties of an elastomer with the easy processing characteristics of thermoplastics. Unlike the conventional rubbers they do not need to be compounded or vulcanised. Their main advantages are, lower capital cost of processing machinery, lower labour requirements and better material utilisation, since scrap and rejects can be recycled. Several types of thermoplastic rubbers are now available commercially.

The first thermoplastic elastomers were the polyurethanes but these suffered from the disadvantage of high cost. This was overcome by the discovery and commercialisation in the mid 60's of styrenic block copolymers, by Shell, Phillips, ANIC and others. The application of these block copolymers though large is limited to certain sectors due to the lower softening temperatures.

In the mid 70's intensive work on physical blends of polyolefine plastics especially the homopolymer grades of polyolefine with EPDM rubbers led to the development of olefinic thermoplastic rubbers. The first commercial production of this type of thermoplastic rubber was by Uniroyal inc. U. S. A.

On the other hand a thermoplastic processing factory, in general, would be suitably equipped with injection moulding machine, extruders, pelletisers and granulators. Therefore it would be quite easy to implement the manufacture and use of thermoplastic rubber in a thermoplastic processing factory. The continuous mixing/blending machines that are available in such factories could be used for blending, if natural rubber is made available in free flowing powder/granular form.

This paper is mainly concerned with the manufacture of TPNR from granulated natural rubber, its properties and possible applications that are being investigated by us for these materials in Sri Lanka.

EXPERIMENTAL

Preparation of Granulated Natural Rubber

Granulated rubber used in our experimental trials was prepared by, first converting the natural rubber coagulum into sole crepe and then by passing the sole crepe through a granulator. These granules can be easily mixed with polyolefine granules and other additives.

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It is possible to manufacture different grades of granulated crepe rubber. The following grades of natural rubber were used in our trials :- The granular crepe rubber was made;

(*A*) from coagulum obtained by formic acid coagulation of diluted whole field. latex. The latex crepe from this coagulum is similar to SLR L-Grade — GC 1A.

(*B*) from coagulum obtained by formic acid coagulation of fractionated field latex. It is known that the yellow fraction contains a high amount of gel and the removal of the yellow fraction results in a whiter latex crepe with low gel content. — Grade — GC 1B.

(*C*) from coagulum obtained by formic acid coagulation of fractionated field latex with added bleaching agents such as totyl mercaptan in it. This method gives a grade of latex crepe with water white colour and almost no gel in it — Grade — GC 1C.

(*D*) Ribbed Smoked Sheet (RSS) has also been used in our trials. • The RSS was however wet milled into latex crepe laces. Grade — GS 1.

(*E*) Oil Extended Natural Rubber (OENR) in the form of Granulated Crepe Rubber (OEGC).

Oil Extended Granulated Crepe was prepared by first adding the required quantity of oil (10% on rubber) as an emulsion to the field latex and mixing it thoroughly before coagulation.

In our experiments, petroleum jelly and paraffinic oil have been used for the preparation of oil extended granular crepe.

(*F*) Oil extended Granulated crepe rubber containing silica Granulated rubber containing oil and silica was prepared by dding an emulsion of petroleum jelly (20 phr) and silica (10 phr) to the latex prior to coagulation and processing the coagulum as described below.

Milling procedures

The milling procedure adopted in our experiment is the same as that used in sole crepe rubber manufacture and this is done by wet milling through 3 sets of rollers with provision for internal water cooling. The rollers operate at friction speeds and the friction speed of the last set of rollers (which are smooth rollers) is about 1: 1.6. This facilitates easy alignment of rubber molecules along the direction of milling which results in partial crystallisation of the rubber laces. The sole crepe laces are usually made to a thickness of either 0.4 mm or 0.53 mm. The laces after drying at 35°C were laminated first manually and then by passing through a laminator to give a sole crepe of the desired thickness of either 3 mm, 4.5 mm, 6 mm.

Preparation of Thermoplastic Natural Rubber (TPNR) Blends from Granulated Natural Rubber

Granulated natural rubber, polypropylene granules, antioxidants, curing agents (if used) and other additives in the form of either powder or pellets, of the required composition, are hand mixed or tumble mixed and fed into the hopper or an extruder type of mixer with facilities for heating up to 200° —250° C. The temperature at the hopper end is maintained at about 165° C and at the die end is about 190°C. The extrudate can be obtained as small pieces and cooled or passed through a two roll mill, sheeted out and cooled, before feeding into a granulator for size reduction. The granulated Thermoplastic rubber can be used directly in injection moulding machines and extruders or it can be pellatised by passing through a commercially available pellatizer. The Thermoplastic Natural Rubber (TPNR) blend in pellatised form can be obtained directly, by feeding a pre-blended granulated NR & PP mix into a pellatiser. The extruded strands were cooled under water before pellatising.

TPNR blends ranging from, natural rubber (NR)/polypropylene (PP) 20/80 to 75/25, were prepared for evaluation. Non - staining antioxidants have been used at 0.05 - 1 php, in most compositions. Dicumyl peroxide, N-phenylene bis maleimide, phenolic curing resin and sulphur systems have been used in certain compositions as curing agents.

The demand for thermoplastic rubbers has been steadily increasing. This has led to an increase activity in this sector. The scientists at the Malaysian Rubber Producers' Research Association in U. K. started researching in the 70's and have developed two routes to convert/modify, natural rubber into thermoplastic rubbers.

The major development is the preparation of thermoplastic natural rubber blends from solid rubber and crystalline polyolefine such as isotactic polypropylene and/or high dendisty polyethylene (HDPE). The mixing was done in a robust internal mixer such as a Banbury or a Francis Shaw internal mixer.

A wealth of information is now available on morphology, structure and properties of thermoplastic natural rubber blends. The information which has been published clearly indicate that natural rubber based thermoplastic rubber blends have advantages such as (i). wider service temperature range than polyvinyl cholride, polyurethanes and styrenics (ii) low density, which makes them suitable candidates for height weight components (iii). low manufacturing costs than vulcanised rubber. The work carried out on optimisation of blending techniques on the preparation of thermoplastic natural rubber blends in internal mixing machines, has now led to the commercial production of TPNR blends, which are available, from two manufacturers one in the U. K. and the other in the U. S. A., in the hardness range 50 - 90 shore A.

However, so far there has been no significant production nor consumption of thermoplastic rubber in natural rubber producing countries like in Sri Lanka. One of the reasons may be that the internal mixers that are needed for the preparation of TPNR blends from solid rubber grades are expensive equipment and these machinery are only available with rubber products manufacturers who in general do not have the ancillary thermoplastic processing equipment.

Preparation of injection moulded test pieces and articles

Specially fabricated multi-cavity mould provided with ejector system was used for the preparation of injection moulded test pieces. A horizontal, 200 g Plastijet injection moulding machine was used for moulding of test pieces.

Injection moulded cups for latex collection and other articles were made using horizontal type injection moulding machines, of suitable capacity under the same set of conditions, except that the injection and cooling times were different.

Evaluation of physical properties

The tensile properties were measured on injection moulded dumb bell test pieces (type B) at 23°C using Instron Universal testing machine with a cross-head speed of 50 mm/min. Melt flow Index (MFI) was measured at 190°C under a load of 2.16 kg and at 230°C under a load of 2.16 kg. Falling weight, Impact strength data were obtained using injection moulded circular discs of 60 mm diameter and 1.5 mm thickness.

RESULTS

Tensile properties

The tensile properties and other physical properties of various blends are shown in *Table 1.*

Table 1. **Effect of Varying the NR Content on the Physical Properties of TPNR Blends**[1]

Composition NR GC-1B	*PP*	*MFI Condition L*	*Yield Stress MPa*	*Modulus MPa*	*E.B. %*	*Impact Strength*[2] *J*
20	80	11.9	29.8	300	40	6.71
30	70	10.0	21.7	255	430	7.32
40	60	8.5	19.1	195	365	> 12.2
50	50	8.7	16.2	203	250	—
60	40	7.9	10.9	133	250	—

1 — All compositions contain 0.5 php Vulcanox BKF (Bayer) as an antioxidant.

2 — For pure PP moulding — 3.78 J at 25°C.

The blends containing higher proportion of polypropylene have higher tensile stress values at yield and the tensile stress decreases progressively with the increase in the rubber content. Five test pieces which have been randomly selected from a large number of specimens have been tested for each sample. The results obtained were very consistent, which indicate uniform mixing/blending of the two polymers in the TPNR blends.

The melt flow index values indicate that the blending of granulated crepe rubber with polyolefine, has not significantly altered the flow properties. The die-swell has been found to increase with the increase in the rubber content in the blend. Falling weight impact data show the improvements in the impact properties in the blends. This too is an indication of a suitably dispersed elastomeric phase in the blends. However, the impact strength values obtained are only relative values.

Effect of curing agents added before moulding

Samples of pellatised TPNR NR/PP 30/70 prepared with Grade GC-1B granular crepe rubber and polypropylene (Profax 6331) were mixed with different curing agents and injection moulded test pieces were prepared from each of the mixes containing various curing agents, on a plastijet reciprocating screw injection moulding machine, under the conditions specified earlier.

The tensile properties and MFI values obtained are shown in Table 2. The addition of crosslinking agents prior to moulding has not made any improvement in tensile properties. However the MFI values obtained were lower particularly for the mix containing phenolic curing agent.

Table 2. **Properties of NR/PP 30/70 Tpnr Blends[1]**
Effect of Curing Agents Added Before Moulding

Curing agent Name or type	*Amount php*	*MFI Condition L*	*Yield Stress MPa*	*Modulus MPa*	*E.B. %*
None	0.0	7.6	23.2	256	60
DCP	0.5	—	15.3	209	13
Bis-maleimide[2] with DCP	0.5/0.05	6.4	22.5	283	50
Phenolic resin[3] with ZnO	1.0/1.0	2.4	23.0	312	50

1 — All compositions contain 0.5 php Vulcanox BKF (Bayer) as an antioxidant

2 — HVA-2 (Dupont)

3 — SP — 1045 (Schenectady)

Use of curing agents in the preparation of TPNR blends

Curing agents can be pre-mixed with granulated sole crepe polypropylene granules and other additives. The mix can be conveniently fed into the mixing extruder. The results of our initial trials on the use of phenolic curing resin/zinc oxide and a sulphur/zinc oxide system in the mix for the preparation of NR/PP 60/40 blend are shown in Table 3. Calcium oxide at 0.5 php was added as a descicant. An antioxidant at 0.5 php was also used in every batch.

Table 3. **Effect of Curing Agents on the Preparation and Properties of NR/PP 60/40 Tpnr Blends[1]**

Curing System	*Observations*	*Moulding Properties*	*MFI Condition L*	*Tensile Strength MPa*	*Modulus MPa*	*E.B. %*	*Hardness*
None	Good pellets very slight odour	Good	8.4	10.9	133	250	92
Sulphur system[2]	Porous pellets Pungent odour	Poor	—	5.8	80.5	100	86
Phenolic resin[3] with ZnO	Good pellets No noticeable odour	Good	2.4	13.3	133.3	265	91

1 — All compositions contain 0.5 php Vulkanox BKF (Bayer) as an antioxidant and 0.5 php CaO.

2 — Sulphur system — S — 1.2, TMTD — 1.2, MBTS — 0.6, St. A — 0.6 and ZnO 3.0.

3 — SP 1045 (Schenoctady).

The results indicate that the use of a phenolic curing agent has given noticeable improvement in the properties of the blends. TPNR pellets obtained with the blend containing sulphur system were quite porous. Immediately after preparation these blends had a pungent odour, due to the volatile sulphur compounds formed during blending.

Soft TPNR blends

Soft blends can find use in shoe soling applications and for making flexible extruded tubings. TPNR soft blends were prepared either by using higher proportion of rubber in the blend and/or by using oil extended grades of granulated crepe in the blend. Phenolic curing resin/zinc oxide system has been used to effect partial vulcanisation in most of the compositions. The results on the tensile properties and hardness values of the samples are given in Table 4.

Table 4. **Properties of Soft TPNR Blends**

Ingredients and properties tested	*TPNR Compositions and Properties*			
NR — GC 1B	—	—	—	75
PP	50	40	40.	25
ONER[1]	55	66	—	—
OENR with Silica[2]	—	—	70	—
Antioxidant[3]	0.5	0.5	0.5	0.5
CaO	—	0.5	0.5	0.5
Phenolic resin[4]	—	1.0	1.0	1.0
ZnO	—	1.0	1.0	1.0
Tensile Str. MPa	11.9	21.7	8.8	8.8
Modulus MPa	127.5	106.3	116.7	72.9
E. B. %	230.0	300.2	150	50
Hardness IRHD	94	92	85	75
MFI Condition E	2.9	1.7	—	0.2

1. — Acetone Extract — 11.5%.
2. — Acetone Extract — 18.17% and Ash = 10.92%.
3. — Vulcanox BKF (Bayer)
4. — SP 1045 (Schenoctady)

Experiment on the use of TPNR cups for latex collection

TPNR cups (350 ml capacity) prepared from NR/PP 30/70 and NR/HDPE 20/80 blends containing 0.5 php Antioxidant/and 3 php Carbon black, were used in the trials. In order to compare the performance of these cups with coconut shells which are used as latex collection cups in Sri Lanka, a statistically designed experiment was carried out using the above two types of TPNR cups along with used coconut shells and new coconut shells.

The main finding was that 'The coconut shells in general showed a highly significantly greater scrap weight than the TPNR 'cups'. It has been found that the volatile fatty acid (VFA) number of the latex collected in TPNR cups were quite low when compared to the VFA of the latex collected in coconut shells. There is no sign of weathering of the TPNR cups after nearly one year of use in the field.

DISCUSSION

The results obtained indicate that thermoplastic natural rubber (TPNR) blend of any composition of natural rubber to polyolefine can be prepared in an extruder mixer which can be heated up to the melting temperature of polyolefine used. For such blending, the rubber in granular form can be preblended with polyolefine granules (*e.g.* PP) for feeding into the extruder. The granular rubber grades made from sole crepe used in our experiments were of regular shape of uniform size and of almost uniform weight. Uniform mixing as evidenced by consistent physical properties could be attributed to the free - flowing characteristics of granulated sole crepe which facilitates uniform mixing.

In the banbury process, SMR-CV and SMR-L have been used. It has been stated[1] that gel in the NR resulting from storage hardening can in some circumstances be difficult to disperse and this can effect certain properties such as impact strength at low temperatures, adversely. SMR CV grades which disperse more readily, facilitate the preparation of TPNR. The grades GC-1A and GS-1 which were made from whole field latex rubber, are somewhat similar to SMR-L although coagulation of latex without much dilution and drying at 100°C during manufacture for SMR-L promote storage hardening to a certain degree. The grades GC-1B and 1C which are made from fractionated latex and fractionated bleached latex respectively, contain low amount of gel and these grades are most suitable for TPNR manufacture.

Since the humidity in Sri Lanka is high in the order of 80 to 90 storage hardening does not occur to some significant extent. Hence the grades of crepe rubber used in our experiments would be expected to contain low gel resulting from storage hardening. However, CV grade of crepe can be prepared by using viscosity stabilizing agents such as hydroxylamine salts or semicarbazide manufacture.

In agreement with the previous work, our results also show that it is advantageous to use curing systems to effect cross linking of the rubber phase. It has been shown in previous studies that the use of cross linking agents also promote interfacial adhesion between different phases. Of the cross linking systems that have been used, phenolic resin curing, has given most satisfactory results. This phenolic curing system (accelerated by zinc oxide) has been shown to improve the physical properties, particularly, the impact strength of hard TPNR blends. In the extrusion mixing process the cross linking/curing agents have to be added at the beginning in the pre-blend as it is not possible to add later during mixing, like in the case of banbury mixing. This limits the choice of curing agents that can be used. Sulphur systems produce gases and a vent in the mixing barrel is necessary for the release of gases and vapours. The results obtained in our initial trials on soft blends also show that our process could be adopted for the preparation of soft blends.

In Sri Lanka, coconut shells, which are cheap and readily available, are used as latex collection cups. The main disadvantages of coconut shells for latex collection are (i) the shells are porous causing bacterial contamination of the latex resulting in precoagulation (ii) cups cannot be kept clean and (iii) with high yielding clones becoming available, the capacity of the coconut shell is becoming inadequate. To overcome the problem of precoagulation, coconut shells with a thin coating of a resin or a binder on the innerside has been tried.

An experiment has already been conducted on the use of TPNR cups in Indonesia and promising results have been obtained. Our results also clearly show that the amount of scrap has been significantly reduced when TPNR cups are used. Therefore it is advisable to use TPNR cups in place of coconut shells at least for collection of latex for use in centrifuged latex manufacture.

The use of continuous mixing extruder for the preparation of TPNR has several advantages. Raw materials and product handling during preparation of TPNR can be conveniently done. It is also very easy to control and monitor the mixing process. TPNR can be obtained directly in pelletised form. However the choice of the process and the product would ultimately depend on the economic advantages.

In producing countries direct processing of powdered rubber/polypropylene dry blends by injection moulding or extrusion would have obvious attractions economically. The success with a new product requires a large home market and the new forms have to compete in a harsh world on the basis of cost-effectiveness.

Considering the export duty of approximately Sri Lankan Rs. 12/- per kilogram, the cost of granulated crepe rubber is within the price of equivalent grades of NR in the international market. The cost of conversion of preblended NR,PP and other additives to TPNR in pellet form by a custom compounder is about Sri Lankan Rs. 12/- per kilogram. Although Sri Lanka has a relatively small market, it is the only natural rubber exporting country within the SAARC countries. The other members in the SAARC region such as India, Pakistan, Bangladesh and Maldive Islands and neighbouring countries are potential markets for TPNR.

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