

THERMOPLASTIC RUBBER PRODUCTION

This invention relates to a process of the production of thermoplastic rubbers.

Conventionally, thermoplastic natural rubber is produced from natural rubber (NR) in the form of ribbed
5 smoked sheets or block natural rubbers. The rubber is blended with granules of a synthetic thermoplastic polymer (TP) such as polypropylene (PP) or high density polyethylene (HDPE). Typically, this is carried out in an internal mixer or in a continuous type of mixer which uses pelletised or
10 powdered rubber. Both these processes are expensive.

When an internal mixer is used the natural rubber has to be premasticated. Granules of, for example, polypropylene are added and the operation must be conducted at a high temperature, generally approximately,
15 170°C, in order to fuse the polypropylene and the rubber. The resultant blend is then extruded either as a strand which can be chopped into small particles or as a sheet which can then be passed through a granulator.

In the second process the natural rubber either
20 has to be granulated in the initial stage or purchased in the form of a powder. This powdered rubber or the granules are then blended with, for example, polypropylene granules and are continually mixed in a mixer/extruder such as the Farrel Bridge MVX or Werner Pfleiderer EVK.
25 Again, use of a high temperature is required to fuse the polypropylene and the rubber. The resultant blend is extruded. The cost of granulating the natural rubber initially or of producing the powdered natural rubber is additional to the overall cost of producing the thermo-
30 plastic natural rubber.

The two prior art processes suffer from several disadvantages. A very strict temperature watch must be maintained throughout each. Over-heating must be avoided to prevent oxidation of the rubber yet a high temperature is required to ensure that the polypropylene and the rubber
5 gel together satisfactorily. Typically the rubber and the polypropylene are blended together in proportions of 20:80 by weight NR:TP and it is impossible to guarantee consistently good dispersion of the polypropylene in the rubber.

Further, when a more rubber-rich product is required
10 containing the rubber and the polypropylene in a weight ratio of 60:40 NR:TP a partitioning agent must also be present in the blend. This leads to a decrease in the impact strength of the resulting product.

A new technique of producing a thermoplastic rubber
15 blend has now been developed in which a powder of a synthetic thermoplastic polymer is mixed with a rubber latex. The mixture is coagulated and heated to form a fused homogeneous blend of the synthetic thermoplastic polymer and the rubber. This process offers considerable advantages
20 over the prior art processes for the production of thermoplastic natural rubbers but is equally applicable to the production of thermoplastic synthetic rubber blends. The process is simple to effect and much less expensive than conventional methods.

25 Accordingly, the present invention provides a process for the production of a thermoplastic rubber blend, which process comprising mixing together a powdered synthetic thermoplastic polymer and a rubber latex, coagulating the resulting mixture, and heating the coagulated material
30 at a temperature sufficient to cause formation of a fused homogeneous blend of the synthetic thermoplastic polymer and the rubber.

The synthetic thermoplastic polymer is used in the form of a powder, rather than in the form of granules as in the prior art processes for the production of thermoplastic natural rubber. The powder can typically have a particle size of 150-450 μm , for example a nominal average particle size of about 250 microns. Any synthetic thermoplastic polymer grades conventionally used in the production of thermoplastic rubber blends may be employed. Suitable such polymers include HDPE, polypropylene homopolymer and ethylene/propylene copolymers. Examples of such polymers are sold under the trade names HOSTALEN (Hoechst) and PROPATHENE (ICI). Examples of suitable ethylene/propylene copolymers are PROPATHENE GW 601 M AND GW 701 M and of an HDPE powder is HOSTALEN GS 7660 P. HOSTALEN is an R.T.M.

15 The synthetic thermoplastic polymer powder may be mixed with a natural rubber latex. This can be a field latex, typically having a dry rubber content (DRC) of 28 to 35%. Indeed, it is one of the advantages of the present process that it is sufficiently simple to carry out that
20 it may be used on rubber estates, thus considerably cutting the cost of producing thermoplastic natural rubbers. Alternatively, a latex concentrate may be employed. Latex concentrates typically have a DRC of 60-62% and the concentrate is diluted to a DRC of, for example, 30-40% with
25 deionised water for use in the present invention.

The process of the present invention can also be applied to a synthetic rubber latex. A latex of any synthetic elastomer may be employed, for example a styrene-butadiene rubber (SBR) or a chlorobutadiene
30 latex. Typically, a synthetic latex will have an elastomer content of 50 to 68%. The latex is desirably diluted in the same way as a natural rubber latex concentrate for easier processing in the present invention.

The powder of the synthetic thermoplastic polymer
35 is added to the stabilized rubber latex and the two are mixed together by any suitable means. The proportions in which the synthetic thermoplastic polymer is added to the rubber latex depends upon the desired

proportions of the polymer and the rubber in the final product. This in turn depends upon, for example, the desired degree of hardness and of stiffness in the final product. The weight ratio of rubber:thermoplastic polymer in the final
5 product may vary from 15:85 to 70:30. A preferred blend for master batch production is approximately 60:40 NR:TP since no partitioning agent is required.

When a natural rubber latex and polypropylene or high density polyethylene powder is employed, products can be
10 obtained which vary in stiffness from a rigid material having a weight ratio of natural rubber:thermoplastic polymer of 15:85 to a softer material having a natural rubber:thermoplastic polymer weight ratio of 70:30. Again, a particularly preferred blend contains natural rubber and the polypropylene
15 or high density polyethylene in a weight ratio of 60:40. This product once pelletised, for example in an under-water granulator, does not require any de-tackifier. An increase in the natural rubber content will make the product tacky, necessitating slight dusting with a partitioning agent as
20 silica particles.

The mixture of the powdered synthetic thermoplastic polymer and rubber latex is coagulated. This can be achieved using a weak acid such as formic or acetic acid at a concentration of 25 to 50% by volume. The latex/thermoplastic
25 blend is brought to a pH of 4.5 to 5.2. The mixture is discharged into one or more troughs where it is allowed to coagulate, for example overnight. Field latex takes longer to coagulate than concentrated latex.

The coagulated material is generally washed by soaking
30 and flushing with fresh water. It is then heated at a temperature sufficient to cause fusion and formation of the homogeneous blend of the synthetic thermoplastic polymer and rubber. The temperature must not be too high otherwise oxidation of the rubber will occur.

35 Typically the temperature of the thermoplastic polymer/rubber blend is from 160 to 180°C, preferably from 170 to 180°C, but this will depend upon the synthetic thermoplastic polymer grade used. This high temperature is to ensure that the thermoplastic polymer melts and becomes satisfactorily

homogenised with the rubber. If the temperature is much greater than 180°C oxidation of the rubber will occur. However, rubber antioxidants are generally incorporated into the rubber latex before coagulation to ensure that minimal
5 oxidation of the rubber occurs.

The coagulated material is also generally dried and extruded. This may be effected prior to heating to a temperature sufficient to produce a fused homogeneous blend of the synthetic thermoplastic polymer and rubber. Preferably, the
10 drying and/or extrusion operation may be effected at a temperature sufficient to cause formation of the fused homogeneous blend.

In the later event, one way in which the drying and extruding step may be conducted is as follows. Excess water
15 is removed by passing the coagulum through rolls. The partially de-watered coagulum is then passed into an extruder/dryer such as that manufactured by Anderson Ibec. This extruder/dryer contains an expeller de-watering press which removes a large percentage of the water. The product is
20 then passed through an expander dryer. Here the temperature of the blend slowly increases and it expands as water evaporates. This leads to the blend having a slightly foamed appearance. The blend is then extruded. The extrudate has a water content of less than 1% and is free from porosity.
25 During the final stages of the drying operation and upon extrusion the temperature of the thermoplastic polymer/rubber blend is from 160 to 180°C.

Extrusion can be accomplished by attaching, for example, a strand die to the head of the extruder dryer. The die
30 is pre-heated. Strands of the thermoplastic rubber blend are produced which can then be pelletised to produce small granules for direct use in injection molding equipment. Alternatively, the thermoplastic rubber can be passed through an under-water pelletiser to give the required granules.

35 The homogeneous thermoplastic rubber blend which is produced can be used to produce a variety of articles, for example by molding, typically injection molding. These

include luggage, electrical plugs, shoe soling, floor tiling and automobile parts, such as car bumpers, which require high impact characteristics particularly at low temperatures.

5 Granules containing NR:TP in a weight ratio of 15:85 are particularly suitable for injection molding direct to give a thermoplastic NR product suitable for car bumpers. However, it may be preferable, particularly if the thermoplastic NR granules have to be exported, to
10 produce a rubber-rich product which can be blended with suitable synthetic thermoplastic polymers or copolymers prior to injection molding to obtain the required physical requirements, e.g. from soft and flexible to a rigid high impact low temperature resistant product.

15 Percentages throughout are by weight unless otherwise specified.

The following Examples illustrate the invention.

EXAMPLE I

257 gm of a thermoplastic pre-mixed powder
20 (Propathene GW 701 M, which itself contains a u.v. adsorbent) were added to 2000 gm of 30% DRC field latex. The mixture was stirred continuously to give a blend of 70:30, calculated on a dry weight basis, NR:TP. To the mixture, 2.4 gm of 50% Antioxidant 2246 (a non-staining
25 rubber antioxidant) dispersion was also added to protect the natural rubber during processing at high temperatures.

Acetic acid having a concentration of 25% by volume was added to the mixture slowly to adjust the pH to 4.5. The resultant mixture was allowed to coagulate.
30 The coagulum was washed by soaking and flushing with fresh water. Excess water was removed by passing the coagulum through rolls. The partially dewatered coagulum was then passed into an extruder/dryer fitted with a 2mm strand die at the head of the extruder. The die
35 was preheated to 170 to 180°C and the body of the extruder to 170°C in order to "fuse" the polypropylene and rubber.

The hot strands of thermoplastic natural rubber extruded were passed through a water trough to cool and pelletised using a strand pelletiser; small granules of approximately 2 mm in size were produced. The granules were then dried in a vacuum dryer to remove final traces of moisture.

The 70:30 NR:TP granules had slight tackiness and it was necessary to add 1% by weight of a partitioning agent (silica powder, Ultrasil VN3) to the granules to prevent reagglomeration.

EXAMPLE II

To 2000 gm of 30% DRC NR field latex was added 323 gm of Propathene GW 701 M and 2.4 gm of 50% Antioxidant 2246 dispersion to give a blend of 65:35, calculated on a dry weight basis, NR:TP. Granules were prepared by the same process as in Example I.

The resultant blend produced granules with only very slight tackiness but it was still necessary to use 1% by weight of a partitioning agent (silica powder, Ultrasil VN3).

EXAMPLE III

To 2000 gm of 30% DRC NR field latex was added 400 gm of Propathene GW 701 M together with 2.4 gm of 50% Antioxidant 2246 dispersion to give a blend of 60:40, calculated on a dry weight basis, NR:TP. The same process as in Example I was used to prepare granules. The granules were free-flowing. No anti-tackifying agent was required.

EXAMPLE IV

To 2000 gm of 30% DRC NR field latex was added 600 gm of Propathene GW 701 M and 24 gm of 50% Antioxidant 2246 dispersion to give a blend of 50:50, calculated on a dry weight basis, NR:TP. The same process as in Example I was used to produce granules. This resulted in granules with no tack and no partitioning agent was required to keep the granules free-flowing.

EXAMPLE V

To 2000 gm of 30% DRC NR field latex was added. 900 gm of Propathene GW 701 M and 24 gm of 50% Antioxidant 2246 dispersion to produce a blend of 40:60, calculated on a dry weight basis, NR:TP. The same process as in Example I was used to produce granules. This resulted in rigid free-flowing granules.

EXAMPLE VI

To 1000 gm of 30% DRC NR field latex was added. 700 gm of Propathene GW 701 M and 1.2 gm of 50% Antioxidant 2246 dispersion to produce a blend of 30:70, calculated on a dry weight basis, NR:TP. The same process as in Example I was used to produce rigid free-flowing granules.

EXAMPLE VII

To 1000 gm of 30% DRC NR field latex was added 1200 gm of Propathene GW 701 M and 1.2 gm of 50% Antioxidant 2246 dispersion to produce a blend of 20:80, calculated on a dry weight basis, NR:TP. The same process as in Example I was used to prepare rigid free-flowing granules. These granules were particularly suitable for direct injection molding of automobile parts such as car bumpers.

EXAMPLE VIII

To 1000 gm of 60% DRC concentrated centrifuged field latex was added 1000 gm of distilled water to dilute the latex to 30% DRC. 400 gm Propathene GW 701 M and 2.4 gm of 50% Antioxidant 2246 dispersion were added to give a blend of 60:40, calculated on a dry weight basis, NR:TP. The mixture was stirred continuously with the help of a stirrer. A rectangular container 30.5 cm x 61.0 cm x 15.2 cm (12" x 24" x 6") containing diluted acetic acid at pH 3.5 was prepared. The latex mixture was poured into the container. Instant coagulation occurred.

The coagulum was washed, extruded and dried in the extruder dryer as in Example I. A product was produced which was similar to that of Example III which used field

NR latex. No partitioning agent needed to be added to the resultant granules, which remained free-flowing.

EXAMPLE IX

To 500 gm of 60% DRC concentrated centrifuged field latex
5 was added 500 gm of distilled water to dilute the latex to
30% DRC. 1200 gm of Propathene GW 701 M and 1.2 gm of 50%
Antioxidant 2246 dispersion were added to produce a blend
of 20:80, calculated on a dry weight basis, NR:TP. Granules
were produced in the same manner as in Example I. Free-
10 flowing rigid granules were produced requiring no partitioning
agent.

EXAMPLE X

Pilot plant trials to produce 50 kg (65 Natural Rubber: 35
Polypropylene) rubber rich Thermoplastic natural rubber from
15 field latex Coagulation in a 228 dm³ (50 gallon) rectangular
aluminium tank

To 114 dm³ (25 gallons) of natural rubber field latex
(dry rubber content 29%) containing 0.3% ammonia, 0.15%
hydroxylamine neutral sulphate (added as a 20% solution) to
20 stabilise the viscosity of the natural rubber, and 0.13 kg of a 5%
dispersion of Antioxidant 2246 to protect the natural rubber
during processing at high temperatures; was added 17½ kilos
of polypropylene powder (GW 701 M (ICI) itself containing a
u.v. absorbent). The average particle size of the GW 701 M
25 is 250 µm).

The mixture was stirred until the powder was dispersed
and a 5% formic acid solution was added to give a pH of
between 4.0 - 4.5. The acid is added slowly and thoroughly
dispersed by stirring. The acid was added until the pH was
30 4.1.

Aluminium divider plates were inserted into the coagulating
tank to help facilitate the handling of the coagulum. The
latex was allowed to coagulate overnight (approximately 16
hours).

35 The sheets of wet coagulum were then fed through crusher
rolls to expel the serum to give a wet coagulated sheet
having a solids content of 58-60%. This coagulum was fed
into a granulator which reduces the size of the coagulum lumps
so that they can be more easily fed into a dewatering extruder.
40 The extrudate was in the form of fine strands about 3 mm in

diameter having a total solids content of about 70%. The temperature build up in the extruder was high and it was necessary to cool the die with a water spray.

The strands of coagulum were dried in a deep bed crumb rubber dryer at a temperature of 100°C for 3 hours.

The dried rubber/polypropylene blend was then passed through a Scott Reitz prebreaker at a temperature of 175°-180°C to homogenise and flux the natural rubber/polypropylene blend. The fluxed blend was then pelletised.

10 A quantity of rubber rich 65/35 Natural Rubber Polypropylene TP:NR was blended with polypropylene copolymer GWM 213 (ICI) to give a Natural Rubber content of 16%. Impact strength and falling weight tests were carried out on injection moulded test pieces. The results obtained shown
15 below were considered very satisfactory.

<u>IZOD Impact Strength</u>		- 20°C	-30°C	-40°C	
(BS Notch)	Joules/metre	>640	227	135	
<u>Falling Weight Test</u>		23°C	-20°C.	-30°C.	-40C.
<u>(MRPRA Test Method)</u>					
Relative Modulus N/mm		117	175	192	216
Energy J.		9.7	11.2	11.1	9.3
Deformation mm.		15.4	15.7	14.7	12.2

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CLAIMS

1. A process for the production of a thermoplastic rubber blend, which process comprises mixing together a powdered synthetic thermoplastic polymer and a rubber latex, coagulating the resulting mixture, and heating the coagulated material at a temperature sufficient to cause formation of a fused homogeneous blend of the synthetic thermoplastic polymer and the rubber.
2. A process according to claim 1 in which the synthetic thermoplastic polymer is high density polyethylene, polypropylene or an ethylene/propylene copolymer.
3. A process according to claim 1 or 2 in which the rubber latex is a natural rubber latex.
4. A process according to claim 3 in which the natural rubber latex is a field latex.
5. A process according to claim 3 in which the natural rubber latex has been prepared by diluting a latex concentrate to a dry rubber content of 30-40%.
6. A process according to claim 1 or 2 in which the rubber latex is a synthetic rubber latex.
7. A process according to claim 6 in which the latex is a styrene-butadiene rubber latex or chlorobutadiene latex.
8. A process according to any one of the preceding claims in which the coagulated material is dried and extruded prior to heating at a temperature sufficient to cause formation of the fused homogeneous blend.
9. A process according to any one of claims 1 to 7 in which the coagulated material is dried and extruded and the drying and/or extrusion are/is effected at a temperature sufficient to cause formation of the fused homogeneous blend.



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10. A process according to claims 8 or 9 further comprising pelletising the extrudate of the synthetic thermoplastic polymer and the rubber.

11. A process according to any one of the preceding claims
5 in which the coagulated material is heated at from 170 to 180°C to cause formation of the fused homogeneous blend.

12. A process for the production of granules composed of a thermoplastic rubber blend, said process being substantially as hereinbefore described in any one of Examples I to X.

10 13. A molded article prepared from a thermoplastic rubber blend produced by a process as claimed in any one of the preceding claims.
