

Natural Rubber–Isotactic Polypropylene Thermoplastic Blends

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Received 31 March 2003; accepted 27 October 2003

ABSTRACT: Thermoplastic elastomers, prepared by melt blending of natural rubber (NR) and isotactic polypropylene (PP) through a dynamic vulcanization technique, were developed during the later 1970s. However, they have certain drawbacks due to thermal degradation and higher molecular weight of NR. In the study reported here, NR was masticated to different levels prior its addition to isotactic polypropylene to improve the flow properties and to reduce the incompatibility resulting from molecular weight mismatch of NR/PP thermoplastic blends. Mixing energy curves of uncrosslinked blends and those of dynamically vulcanized blends crosslinked using different cure systems were compared. The mixing energy curves of blends containing NR of different molecular weight (\bar{M}_n) and two grades of PP (injection and film grades) were also compared. Technological and processing properties of the dynamically vulcanized (sulphur and peroxide cure systems) and unvul-

canized blends were compared with those of the samples containing unmastered NR. The results indicated that a number average molecular weight in the range 4×10^5 for NR increased the processability without significantly affecting the technological properties of NR/PP thermoplastic blends. Among the three cure systems studied Luperox 101 and dicumyl peroxide gave better technological properties than the sulphur-cured samples. Two antioxidants, viz. quinoline (TDQ) and imidazole (MBI) type, were tried in NR/PP blends. It was found that TDQ imparts better aging resistance compared to MBI. The improvement in processability due to the reduction in molecular weight of natural rubber by mastication is more noticeable in the case of peroxide vulcanized blends compared to sulphur vulcanized samples. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2063–2068, 2004

INTRODUCTION

Thermoplastic elastomers (TPE) are materials that can be processed like thermoplastics at the appropriate temperatures and that retain some of the flexibility and resilience of elastomers at ambient temperature. Compared with the conventional rubbers, thermoplastic elastomers have commercial advantages because they can be processed on thermoplastic machinery and require no separate vulcanization stage. Mixing is simplified as the number of additives necessary is considerably reduced. These processing advantages result in savings in time, energy, and capital costs of machinery. Another advantage is that material wastage is reduced because scrap and rejects can be recycled.¹ TPEs also give higher output rates in injection molding and extrusion than the conventional elastomers. With these advantages thermoplastic elastomers are currently finding markets in many applications where vulcanized rubbers have been traditionally used. TPEs are also used in products that require better performance than what can be obtained with

general-purpose thermoplastics such as polyvinyl chloride (PVC) and polyethylene (PE).

Of the commercially available thermoplastic elastomers some are expensive, special-purpose materials. The olefin types, which include blends of natural rubber with crystalline polyolefins¹ and those of ethylene propylene terpolymer (EPDM) with polyolefins, are cheaper, and similar in price to the styrene–butadiene–styrene (SBS) block copolymer types of thermoplastic rubbers. The olefinic types have potential uses in flexible automotive components such as bumpers, spoilers requiring materials in the range 90 shore A to 60 shore D.^{2–11} The thermoplastic natural rubber blends (TPNR) developed by the MRPRA could replace vulcanized rubber in products where high resilience and strength are not essential, and could also replace flexible plastics, such as plasticized PVC, ethylene vinyl acetate (EVA), low-density polypropylene copolymers.^{1,11} It has been reported that properties of thermoplastic elastomers prepared by melt blending can be improved by dynamic crosslinking.¹⁰ The use of phenol-formaldehyde (PF) resin and zinc oxide as a curative for hard blends of NR and PP has been studied in detail.^{12,13}

Most of the commercially available polymer blends have lower mechanical properties due to incompatibility of the component polymers. Three types of incompatibility have generally been noted: incompati-

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bility due to viscosity mismatch, which prevents or generally delays the distribution of intimate blends; thermodynamic incompatibility, which prevents the mixing on the molecular scale and incompatibility due to cure rate mismatch in which virtually most of the ingredients that are available in a composition are predominantly consumed by the faster curing polymer component.¹⁷

Viscosity mismatch-derived incompatibility can be overcome by several methods such as improving the blending process, adjusting extender oil and filler concentrations in the dissimilar polymers, or by adjusting the individual raw polymer viscosities. When the component polymers have similar viscosities and concentrations, there is a greater chance for cocontinuity of the phase.¹ The molecular weight (\overline{M}_n) of natural rubber (NR) is very high ($\sim 7 \times 10^5$) compared to that of polypropylene (2×10^5). One of the possible methods to improve the compatibility of NR with PP is to reduce the molecular weight of natural rubber. Moreover, the flow properties of the masticated rubber incorporated blends are expected to be better. Several works have been reported regarding the processing, vulcanization, and applications of thermoplastic natural rubber.^{11–13,15} In the present study natural rubber was masticated to different levels and blended with isotactic polypropylene. The properties of the unvulcanized and those of the dynamically vulcanized blends having sulphur and peroxides as crosslinking agents were compared. The effects of two types of antioxidants, namely quinoline and imidazole, on the aging behavior of the NR/PP blend were also evaluated.

EXPERIMENTAL

The NR used was ISNR-5 grade block rubber. NR of different molecular weight was prepared by masticating the rubber to 0, 5, 10, 15, and 20 min and determining the \overline{M}_n by GPC. Two grades of isotactic polypropylene, injection grade with MFI 11 and film grade having MFI 10 were used. The properties of these thermoplastics are given in Table I. Crosslinking agents, di-cumyl peroxide (DCP) and 2,5-dimethyl-2,5-di (*tert*-butylperoxy) hexane (Luperox 101) used were of commercial grade, having 40% active ingredients. Sulphur and other compounding ingredients used in this work were of commercial grade.

Blending

Mixing of NR with PP (60 : 40) was carried out in a Haake Rheocord (model 90) at a temperature of 180°C and a rotor speed of 60 rpm. The mixing cycle started with blending NR with PP after melting the PP.⁵ The blending continued for 2 min so that the rubber and the polyolefin form an intimate mixture.¹¹ In the case

TABLE I
Properties of Polypropylene

Property	PP (Injection grade)	PP (Film grade)
Melt flow index (230°C/ 2.16 kg) g/10 min	11	10
Tensile strength at yield, (50 mm/min) MPa	36	37
Elongation at yield (50 mm/min) %	8	6
Flexural modulus (1% secant, 1.3 mm/min) MPa	1415	1700
Notched Izod impact strength (23°C), J/m	27	5

of dynamically vulcanized samples, the curatives were added to the uniformly blended mix at the second minute, and the mixing operation continued for 3 more min. The antioxidant, if any, was added just 1 minute prior to the dumping (total mixing cycle—5 min). Late addition of the antioxidant is suggested because the peroxide crosslinking agent functions by a free radical mechanism. Finally, the material, while hot, was sheeted out on a mixing mill and blended for 1 more min in the Rheocord to ensure uniform mixing of the ingredients. The uniformly mixed samples were again sheeted on a mill, prior to granulation.

Test methods

Test specimens for the various mechanical properties were compression molded at a temperature of 190°C in a specially designed mold. Tensile test was carried out on a Zwick Universal Testing Machine (UTM Model 1474) at a crosshead speed of 500 mm/min at room temperature as per the ASTM D-412 test procedure. The other mechanical and processing properties such as hardness, melt flow index (MFI), etc., were evaluated as per the relevant ASTM test methods. Aging resistance of the samples was assessed by keeping tensile test specimens at 100°C in an air circulated oven for 96 h and then determining the change in tensile properties.

Designation of blends

NR samples having different molecular weight (\overline{M}_n) were prepared by masticating the rubber to 0, 5, 10, 15, and 20 min, and these were designated as NR₀, NR₅, NR₁₀, NR₁₅, and NR₂₀ respectively. Injection-grade PP and film-grade PP were designated by the letters I and F, respectively, and those vulcanized with DCP and sulphur were represented respectively by D and S. For example, DCP vulcanized blends containing NR and injection grade PP was denoted by NRPPID, and that

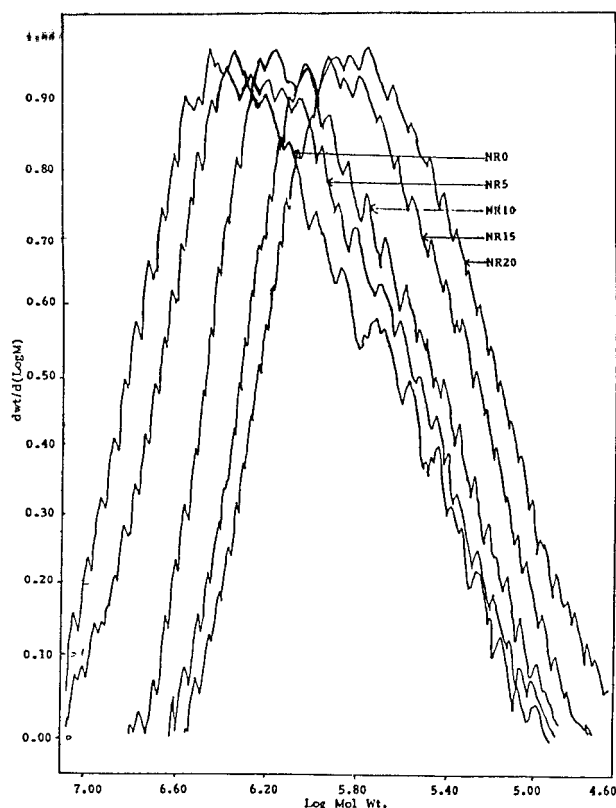


Figure 1 Gel permeation chromatographs of natural rubber masticated to different levels.

of film grade was NRPPFD. In the case of sulphur vulcanization these notations change respectively to NRPPIS and NRPPFS. Unvulcanized blends were represented by NRPPIC or NRPPFC according to the grade of PP.

RESULTS AND DISCUSSION

Processing properties

Natural rubber with different molecular weights was obtained by mastication of the rubber, and the molecular chain breakdown by this milling process can be better understood from the gel permeation chromato-

TABLE II
Molecular Weight of Natural Rubber (\bar{M}_n) after Mastication

Time of mastication, min	Molecular weight, $\bar{M}_n \cdot 10^5$	Tensile strength, ^a MPa
0	7.6	11.78
5	6.8	12.62
10	4.4	13.28
15	3.7	13.48
20	3.2	10.76

^a NR : PP (60 : 40) blend with DCP vulcanization.

TABLE III
Formulation of Mixes

Ingredient	Sulphur cure	Peroxide cure
Natural rubber ^a	60	60
Polypropylene ^b	40	40
Zinc oxide	5	—
Stearic acid	2	—
CBS ^c	1.5	—
TMTD ^d	1.5	—
Sulphur	0.5	—
DCP ^e /Luperox 101 ^f	—	1
TDQ ^g /MBI ^h	—	1

^a NR masticated to different levels

^b Injection and film grades of polypropylene

^c N-cyclohexylbenzothiazyl sulphenamide

^d Tetramethylthiuram disulphide

^e Dicumylperoxide

^f 2,5-dimethyl 2,5-di(tert-butylperoxy) hexane.

^g 2,2,4-trimethyl 1,2-dihydroquinoline polymerized.

^h Mercaptobenzimidazole.

graphs shown in Figure 1. As evident from the curve, natural rubber without any mastication has a molecular weight distribution peak at the higher molecular weight range. As mastication time increased, the peak shifted slightly to the right, indicating an increase in the proportion of smaller molecular weight fractions. This can be better understood from Table II. The number average molecular weight (\bar{M}_n) is reduced to half of the original value by about 15 min mastication of the raw rubber.

Formulation of the mixes used is given in Table III. Blending of natural rubber with polypropylene was done in a Haake Rheocord-90, and the change of mixing energy with time is shown in Figure 2. The uncrosslinked blend showed an initial sharp increase in torque followed by a similar decrease and thereafter an almost constant value with time, indicating a uniform dispersion of the components. The peak at the beginning of each curve represents the high amount of energy involved in the incorporation of rubber into molten PP. Progressive reduction in mixing energy is due to a reduction in size of the dispersed phase, followed by its uniform distribution in the matrix.

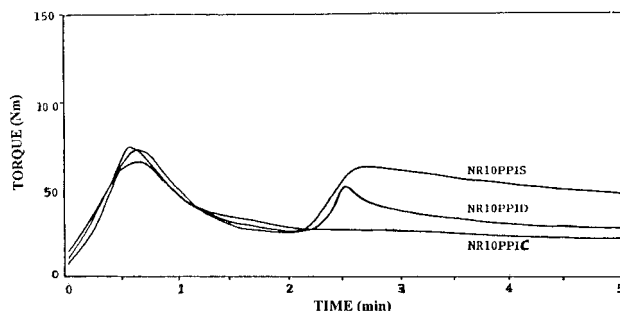


Figure 2 Mixing energy curves of NR/PP blends vulcanized with sulphur and the DCP cure system.

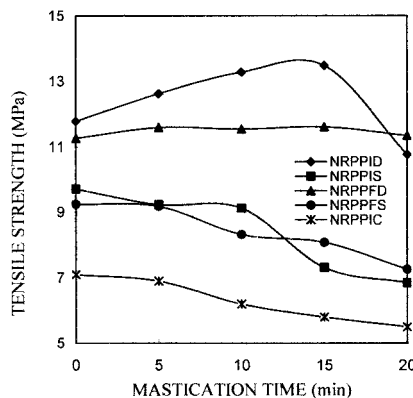


Figure 3 Variation of tensile strength with (a) time of mastication of NR, (b) type of cure system.

For dynamic vulcanization of the NR phase, sulphur and other ingredients were added to the mix 2 min after the start of the mixing cycle. Before adding the curative, formation of a homogenous blend of NR and PP was ensured, as evident from the constant torque. The increase in torque upon the addition of the curative is due to crosslinking. The torque reached a maximum and then showed a decrease before being stabilized. The decrease in torque after the second peak is due to a further reduction in size of the vulcanized rubber phase, which finally attained stable domain morphology by the end of the mixing cycle. The mixing energy curve of the blend having a DCP cure showed a somewhat similar nature to that of the sulphur-cured blends. However, sulphur vulcanization showed a higher torque value, indicating a higher level of crosslinking and less degradation of the NR phase of blend.

Reduction in torque values after attaining the maximum is expected to be due to the combined effect of reduction in size of the dispersed domains and degradation of the NR phase caused by higher mixing temperature. A comparatively low increase in torque and a sudden decrease after attaining the maximum of the DCP incorporated mix is due to the degradation of PP by DCP.^{11,13} It is known that small amount of DCP (0.1 phr) can cause considerable reduction in the melt viscosity values of PP. The mixing energy curves of the blend containing NR masticated to different levels showed an almost similar trend of the curves in Figure 2, but recorded less energy with time of mastication of the NR phase.

Tensile strength (TS) values of masticated rubber incorporated blends are shown in Figure 3. The unvulcanized blend showed a decrease in TS with the mastication of NR. Dynamically vulcanized blends had tensile strength values much better than the unvulcanized blend. Here also, as expected, the tensile values decreased with time of mastication of NR. Both the grades of PP followed this trend. In the case of

injection grade PP, with peroxide vulcanization, the TS increased slightly with mastication of NR and thereafter it decreased. However, in the case of film grade PP, TS remained almost constant with time of mastication of NR in the blend. Mastication of NR and degradation of PP by DCP would naturally be expected to decrease the tensile strength. However, the unexpected retention of tensile strength of the DCP cured blends indicated the possibility of interfacial crosslinking in these blends. The high TS values with injection-grade PP may be due to the better flow properties of the injection-grade PP that increased with decreasing the molecular weight of NR. This might also have helped to form a more uniform blend and improvement in properties. Film-grade PP also showed a similar trend, but the magnitude of the TS values is less. For both grades of PP the sulphur-cured blends showed lower TS values compared with the DCP-cured ones, probably because there is no chance for interphase crosslinking when sulphur is used. Another probable reason for the high TS values of DCP-cured blend compared to the sulphured one is the higher thermal stability of the C—C crosslinks formed during DCP curing against C—S—C or C—S_x—C crosslinks formed in sulphur curing.

Modulus values of the different blends are given in Figure 4. Modulus values of the uncrosslinked blends are not given, as they have very low elongation. Modulus of the peroxide-cured blends showed higher values than that of the sulphur-cured ones. The decrease in modulus with mastication of NR was more pronounced in the case of the sulphur-cured blends.

Elongation at break (EB), which is an index of the elastic property of the blend, showed a sharp increase with dynamic vulcanization (Fig. 5). However, the peroxide-vulcanized blends registered the maximum value. With time of mastication, EB values decreased, and this effect is more pronounced after 10 min of mastication. Among the five levels of masticated NR used, the unmasticated rubber had maximum EB,

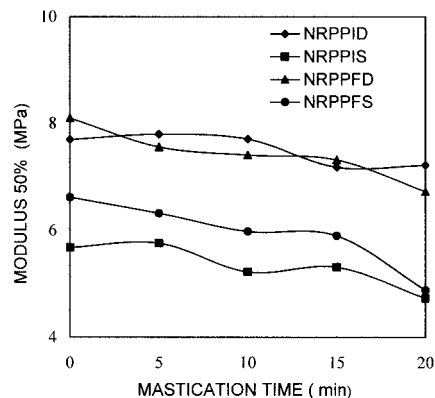


Figure 4 Variation of modulus with (a) time of mastication, (b) type of cure system.

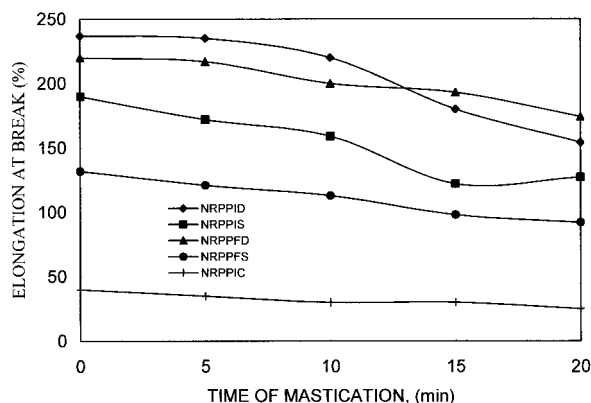


Figure 5 Variation of elongation at break with (a) time of mastication, (b) type of cure system.

whereas NR with 20 min mastication showed the least. EB values of sulphur cured blends of unmasticated NR and that with 10 min mastication are almost comparable. In the case of uncrosslinked blends, EB values decreased slowly with mastication time and the values are always less than the corresponding dynamically vulcanized samples. Variation of tear strength is shown in Figure 6. Tear strength values of DCP-cured samples decreased with mastication time of NR. The reduction is sharp for film-grade PP having sulphur vulcanization.

The melt flow index (MFI) values of the blends are shown in Figure 7. In all cases, The MFI values increased with time of mastication of NR used in the blend. MFI values of uncrosslinked blends are very high compared to those of the dynamically vulcanized blends. This is because of the unhindered flow of the polymer in the absence of any crosslinks. The reduction in MFI of the crosslinked blends is brought about by various factors.⁴ One of these is the crosslinking of the rubber phase. Another factor is the enhanced interfacial interactions of the two phases. Both these factors are expected to be operating in the case of the DCP-cured samples. However, the DCP-cured sam-

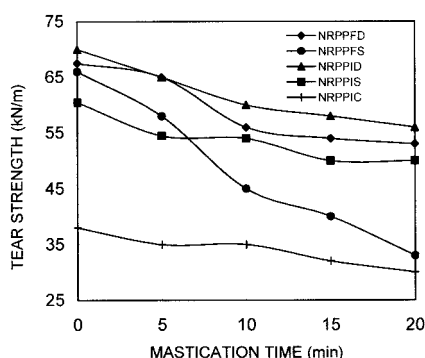


Figure 6 Variation of tear strength with (a) time of mastication, (b) type of cure system.

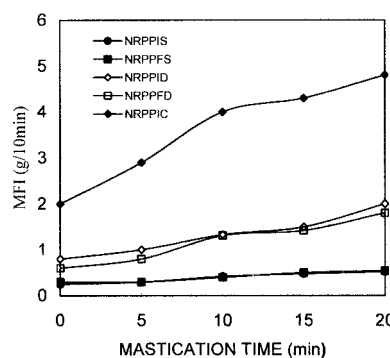


Figure 7 Variation of melt flow index with (a) type of cure system, (b) mastication time.

ples showed higher MFI values than those of the sulphur-cured blends. A low level degradation of PP caused by DCP helped in improving the melt flow of the blend. The MFI values of sulphur-cured blends are very low, but increases with mastication of NR. DCP-cured samples having injection-grade PP has high MFI value compared to film grade. However, with the sulphur system, there is not much difference in MFI between the two grades.

The variation in hardness of the blends with cure system and mastication time of NR is shown in Figure 8. Mastication has very little effect on the hardness of the vulcanized blends, and it ranges between 89 to 92 Shore A units. During the melt blending process and the subsequent molding operation, the PP phase being lower in viscosity (at the melt temperature) is reported to form a continuous phase. As a result, in the molded sample the NR phase is embedded in PP, leading to an almost constant hardness value.

Effect of different cure systems on the tensile strength of the blend containing injection-grade PP and natural rubber masticated for 10 min is given in Figure 9. Tensile strength of the different cure systems followed the order Luperox > DCP > Sulphur > Control. Luperox 101 is expected to form interphase

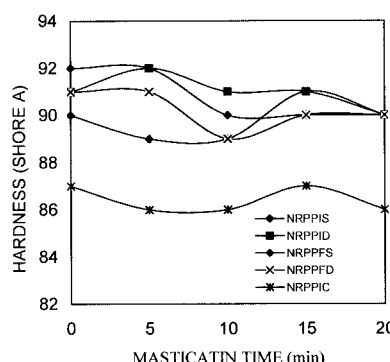


Figure 8 Variation of hardness with (a) type of cure system, (b) time of mastication.

crosslinks; hence, the tensile values of these samples are slightly higher than that of the DCP-cured ones. Moreover, samples vulcanized with Luperox 101 have no smell, which is very severe with DCP-cured samples due to peroxide residues.

Aging resistance

Two antioxidants (MBI and TDQ) were assessed for their activity in NR/PP blends (Fig. 10). It can be seen that the after aging tensile strength values are maximum for samples containing TDQ followed by MBI. The volatilization loss of antioxidant at the high processing temperature of the blend is expected to be less for TDQ because it is in the polymerized form, which may be the reason for its better antioxidant activity. The percentage retention of tensile strengths is also higher for sample containing TDQ antioxidant.

CONCLUSIONS

In NR-PP thermoplastic blends the molecular weight mismatch between NR and PP was minimized by masticating natural rubber. GPC analysis showed that a molecular weight 7.5×10^5 (\bar{M}_n) of natural rubber could be reduced to 4.3 and 3.7×10^5 , respectively, by 10 and 15 min of mastication. Use of NR having lower molecular weight can improve the MFI values of dynamically vulcanized NR/PP blends. The reduction in molecular weight of natural rubber by mastication and the consequent improvement in processability are more noticeable in the case of the peroxide-vulcanized blends compared to sulphur-vulcanized samples.

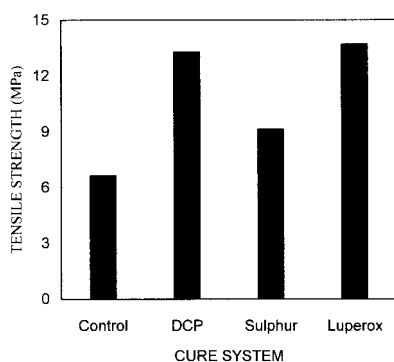


Figure 9 Tensile strength with type of cure system; blend of NR masticated for 10 min with injection grade PP.

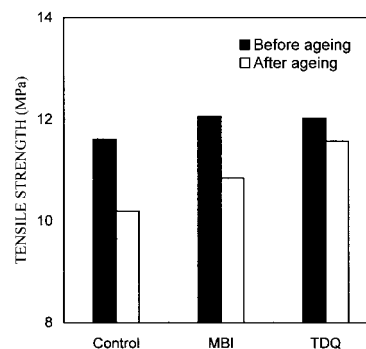


Figure 10 Effect of antioxidant before and after aging; blend of NR masticated for 10 min with injection grade PP.

Mastication of NR for 10 min ($\bar{M}_n = 4 \times 10^5$) is found to improve processability without significantly affecting the technological properties of the blend. However, reducing molecular weight of NR below 3×10^5 adversely affected the technological properties. The processability and technological properties are best balanced in blends containing NR having a molecular weight (\bar{M}_n) in the range of 4×10^5 . Between the two grades of PP used, the injection grade PP gave better properties, especially with the peroxide-cure system. Hardness was not affected much with the type of cure system, grade of PP, or with mastication time of NR. The blends showed better aging resistance with TDQ compared to MBI. Among the cure systems tried, DCP and Luperox-101 registered maximum properties. Moreover, blends vulcanized with Luperox 101 had no residual smell of peroxides.

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