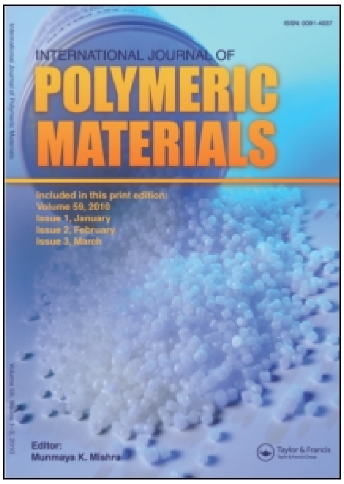

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Blends of Natural Rubber with Unsaturated Polyester Resin

M. G. Bhuvaneswary[ab]; Eby Thomas Thachil[a]
[a] Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kerala, India [b] Department of Chemistry, S.N.M. College, Kerala, India

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Blends of Natural Rubber with Unsaturated Polyester Resin

M. G. Bhuvaneswary
Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kerala, India; Department of Chemistry, S.N.M. College, Kerala, India

Eby Thomas Thachil
Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kerala, India

The effect of modifying natural rubber (NR) using unsaturated polyester resin (UPR), by compounding on a two-roll mill, is investigated in this study. Both commercial resin and resins prepared in the laboratory under controlled conditions have been employed. After testing several possible catalyst systems, the benzoyl peroxide/dimethyl aniline (BPO/DMA) system was identified as a suitable catalyst system for UPR for blending with NR. The extent of unsaturation in the UPR influences the physical properties of the blend negatively. The UPR is found to have a positive effect on the aging properties of natural rubber.

Keywords: compounding, modification, natural rubber, unsaturated polyester

INTRODUCTION

Natural rubber is a low cost material with excellent physical properties such as good resilience, high tensile strength, superior resistance to tear and abrasion, excellent tack and self adhesion. On the other hand, it has poor age resistance and oil resistance [1]. These limitations restrict its use in high temperature applications and hydrocarbon environments. Attempts have been made to improve the aging characteristics of NR by compounding or by blending with

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Address correspondence to Eby Thomas Thachil, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, Pin - 682022, Kerala, India. E-mail: ethachil@cusat.ac.in

rubbers that are inherently resistant to aging [2–3]. In this work we attempt to modify natural rubber by incorporating varying amounts of unsaturated polyester resins, an important thermoset material [4].

Unsaturated polyester resins (UPR) are a class of thermosets widely used by the fiber reinforced plastics (FRP) industry. These are prepared by the reaction of a saturated diol with a mixture of unsaturated and saturated dibasic acids or their anhydrides [5]. Commercially, the resin is available in the form of solutions containing 60–70 wt% of the prepolymer in a reactive solvent, usually styrene. Typical grades are orthophthalic, isophthalic and bisphenol A-fumarate polyesters. The widespread use of these resins can be attributed to their low cost, ease of processing, ease of combination with reinforcement, excellent dimensional stability and wide variety of available grades. UPR used for the present study was 1) procured from the market and 2) prepared in the laboratory under predetermined conditions. To our knowledge this is the first study undertaken to explore the effect of blending UPR with NR.

EXPERIMENTAL

Materials

GP grade UPR (HSR 8113 M) and styrene were commercial grades supplied by M/s Sharon Engineering Enterprises. Dimethyl aniline, benzoyl peroxide, 1,2 propylene glycol (PG), maleic anhydride (MA), phthalic anhydride (PA), xylene, hydroquinone, and triphenyl phosphate of laboratory reagent (LR) grade were supplied by E. Merck India Ltd., Bombay.

UPR Preparation

The resin preparation was done by polycondensation [6]. PG, MA, PA were taken in the molar ratio 1.1 : 0.60 : 0.40 in a 1 liter three-necked RB flask equipped with a mechanical stirrer, N_2 inlet and a reflux condenser. A slight excess of PG (10%) was provided to allow for evaporation losses. The reaction was conducted under an inert blanket of N_2. 0.05% triphenyl phosphate was added to obtain good color. The reaction mixture was heated at 210°C in a temperature-controlled heating mantle for several hours. The temperature was kept at 210°C, the optimum temperature at which MA in the cis configuration is isomerised to less strained and more planar trans fumaric acid [7]. About 10 ml of xylene was used to remove water of hydration azeotropically. The acid value was monitored every two hours. When the acid value reached 40, vacuum was applied to bring its acid value below 30 by removing unreacted reactants and the residual water of condensation. At this stage heating was discontinued. When the temperature of the reaction mixture cooled down to 100°C, 0.02 wt% hydroquinone and, subsequently, 40 wt% styrene were added and mixed thoroughly. The resin was cooled to room temperature and stored in containers. The unsaturation in the polyester chain arises from the MA employed in the esterification. Hence, the relative proportion of MA in the mixture of MA/PA can influence the properties of the final blend. To ascertain this, different UPRs are synthesized with varying MA/PA ratio, e.g., 0.3 : 0.7 and 0.9 : 0.1 and blended with NR.

Resin Addition

Since reports of blending UPR with natural rubber are not available in the literature, we conducted some preliminary experiments to determine the most suitable method of addition as well as the best catalyst system. The most popular catalyst system for UPR consists of a methyl ethyl ketone peroxide catalyst and cobalt naphthenate as promoter [8]. But this system was not selected for this study because of the deleterious effects of pro-oxidant cobalt on natural rubber [9]. Hence three other systems, namely, a) dicumyl peroxide (DCP) b) benzoyl peroxide (BPO) and c) benzoyl peroxide and dimetyl aniline (BPO and DMA) were selected for the study. Based on the properties of the rubber vulcanizate obtained by employing each of the above catalyst systems, BPO/DMA was selected for further studies.

Since UPR crosslinks to a gel within a few minutes after the addition of the catalyst and accelerator, it was necessary to find the optimum time interval before adding them to the rubber on a two-roll mill. The effect of varying the percentage of catalyst was also investigated.

Rubber Compounding

The rubber was compounded on a laboratory two-roll mill (16 × 33 cm) employing the formulation given in Table 1. The mixing was done according to ASTM D 3184-89 (2001). The rubber was masticated on the mill and the resin was incorporated into the rubber (2, 4, 6 and 8% of the rubber). Then the compounding ingredients were added in the following order: activators, accelerators, and sulphur. After mixing, the stock was passed six times through tight nip gap and finally sheeted out.

TABLE 1 Compounding Formulation

Ingredients (phr)[a]	Mixes A	B	C	D	E
Natural rubber	100	100	100	100	100
UPR[b]	0	2	4	6	8
Zinc oxide	4	4	4	4	4
Stearic acid	2	2	2	2	2
MBTS[c]	0.8	0.8	0.8	0.8	0.8
TMT[d]	0.2	0.2	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5	2.5	2.5

[a] Parts per 100 parts of rubber by weight.
[b] Unsaturated polyester resin.
[c] Mercapto benzothiazyl disulphenamide (accelerator).
[d] Tetra methyl thiuram monosulphide (accelerator).

Cure characteristics of the mixes were determined at 150°C using Rubber Processing Analyser RPA 2000 supplied by Alpha Technologies, USA as per ASTM standards D 2084-01. Vulcanization to optimum cure time was carried out in an electrically heated hydraulic press at 150°C. The moldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 h.

TESTING

The vulcanizates were tested for different mechanical properties according to relevant ASTM standards.

Tensile Properties

The tensile properties were measured using Shimadzu Universal Testing Machine Model AG-1 50 kN according to ASTM D 412. Samples were punched out from the molded sheets with a dumbbell-shaped die. The crosshead speed was maintained at 500 mm/minute.

Tear Strength

The tear strength was determined according to ASTM D-624 using angular specimens punched out from the molded sheet. The test speed was 500 mm/min.

Hardness

The hardness of the sample (Shore A) was determined using Zwick 3114 Hardness Tester according to ASTM D-2240.

Resilience

Resilience was determined by the vertical rebound method according to ASTM D-2832-88. In this method, a plunger suspended from a given height (400 mm) above the specimen was released and the rebound height was measured. The resilience scale was marked in 100 equally spaced divisions. The ratio of the rebound height and original height is referred to as the resilience (%).

Aging Tests

Aging tests were carried out for 72 h in accordance with ASTM 573-88 using an air oven at 70°C. Tensile properties and tear resistance of the samples were determined after 24 h of conditioning at room temperature. These tests were done only on commercial UPR samples in view of their better performance on blending with rubber.

RESULTS AND DISCUSSION

Table 2 lists the physical properties of natural rubber modified with 2% unsaturated polyester resin using different catalyst systems. These are compared with results obtained when 1) no catalyst is used for UPR, and 2) no UPR is used. From an examination of tensile strength, the combination of BPO and DMA gives the highest tensile strength to the blend. While in the absence of catalyst the addition of UPR leads to a comparable value of tensile strength, the combination of MEKP and cobalt naphthenate gives somewhat lower values. Oxidation and consequent chain scission of the rubber molecules due to the presence of cobalt ion may be responsible for this. The combination of BPO and DMA has been used in subsequent studies.

The effect of time elapsed after the addition of BPO/DMA to the resin was studied by choosing different intervals, namely 1, 2, or 3 min (Figure 1). Beyond 3 min the resin became too viscous to add to rubber. The highest tensile strength is shown when 3 min are allowed to elapse. Hence this procedure was followed for later studies. Similarly, the amount of BPO giving the best tensile strength to the vulcanizate for a constant DMA content of 0.5% of the resin was also estimated by following the tensile strength. The optimum value of BPO is found to be 1.5% (Figure 2).

TABLE 2 Properties of Natural Rubber Modified with Commercial UPR using Different Catalyst Systems

Properties	NR + UPR 0%	NR + UPR 2%	NR + UPR 2% BPO	NR + UPR 2% DCP	NR + UPR 2% BPO + DMA	NR + UPR 2% MEKP + CoN
Tensile strength (MPa)	22.56	21.2	23.58	24.6	25.25	22.46
Modulus (MPa)	2.186	1.6747	1.58	1.74	1.51	1.50
Elongation at break (%)	1001.8	1081	1297	1224.7	1281	1222
Tear strength (N/mm)	41.61	42.59	37	42.2	38.54	39.5
Hardness (Shore A)	35	36	35	37	35	35
Resilience (%)	63	68	68	74	70	64
Abrasion loss (cc/hr)	4.3304	5.704	5.6411	4.954	5.03	5.4689

NR-natural rubber.
BPO-benzoyl peroxide.
DMA-dimethyl aniline.
MEKP-methyl ethyl ketone peroxide.
CoN-cobalt naphthenate.

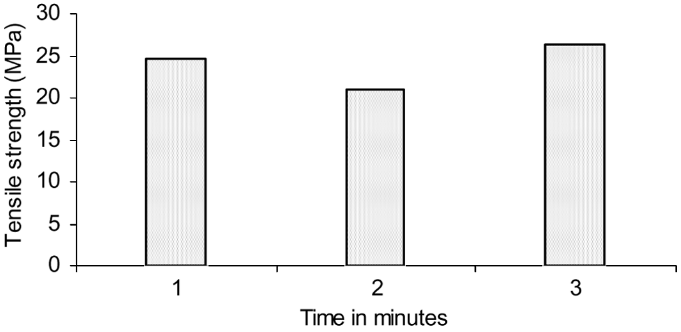

FIGURE 1 Effect of time elapsed after addition of catalyst.

Figure 3 shows the variation of tensile strength on the addition of various percentages of resin to the rubber. A moderate enhancement of tensile strength is observed at about 4% of UPR. Higher amounts of resin may interfere with the crystallization of rubber under stress. Stress crystallization is an important mechanism responsible for the strength of NR [10]. This may account for the reduction of tensile strength at higher resin contents. Figure 4 shows the change in tear strength on addition of resin. There is a gradual reduction in tear strength on addition of resin. Although there is a reversal of this trend on addition of 4%, there is a net reduction in tear strength. Since tear strength is a property directly affected by crystallinity, lower values of tear strength are to be expected.

UPR gets crosslinked via a free radical mechanism, whereby sites of unsaturation are linked through styrene crosslinks. In the presence of

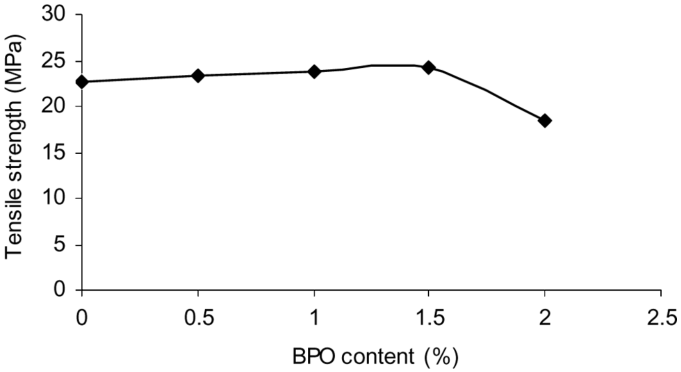

FIGURE 2 Variation of tensile strength of NR with BPO%.

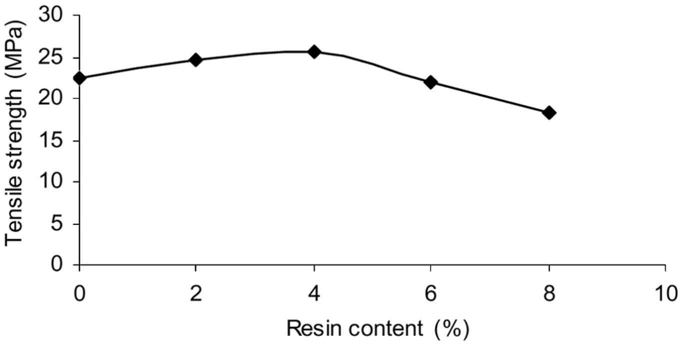

FIGURE 3 Variation of tensile strength of NR with commercial UPR.

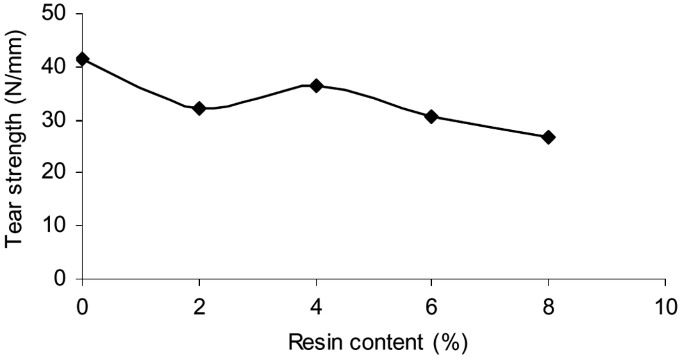

FIGURE 4 Variation of tear strength of NR with commercial UPR.

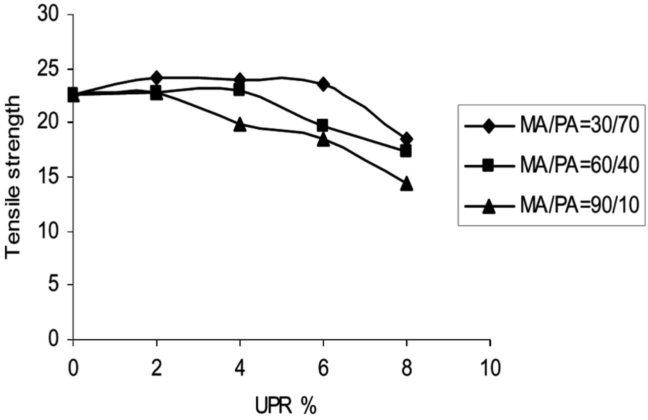

FIGURE 5 Variation of tensile strength of NR with synthesized UPR.

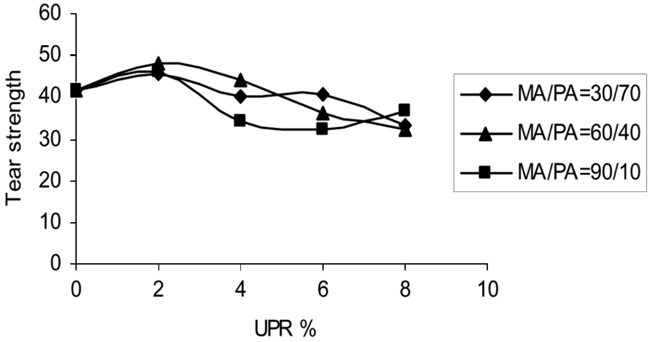

FIGURE 6 Variation of tear strength of NR with synthesized UPR.

natural rubber the involvement of the double bonds in the NR chain in the free radical reaction cannot be ruled out. The results of incorporating the three different synthesized resins (MA/PA = 30/70, 60/40 and 90/10) are depicted in Figures 5–7. Figure 5 shows the variation of the tensile strength of the blend when different percentages of UPRs are added. A slight fall in tensile strength is observed with increased amount of MA. Larger amounts of MA indicate greater unsaturation. This may lead to excessive crosslinking. The lower elongation at break with increased MA content (Figure 7) points to this. The elongation at break shows a general increasing tendency with percentage resin. This can also be a consequence of a lower level of stress-induced

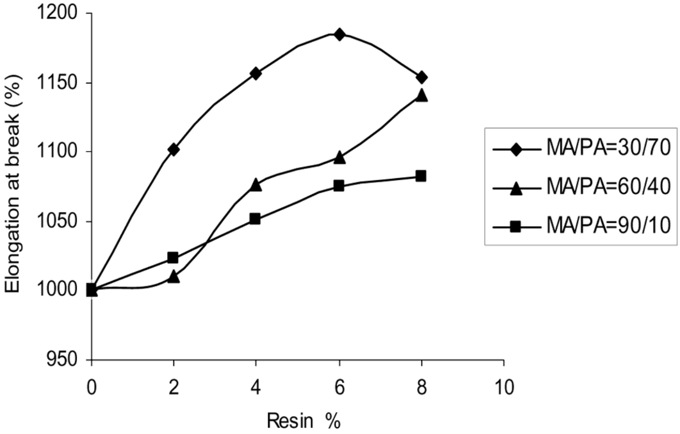

FIGURE 7 Variation of elongation at break of NR at break with synthesized UPR.

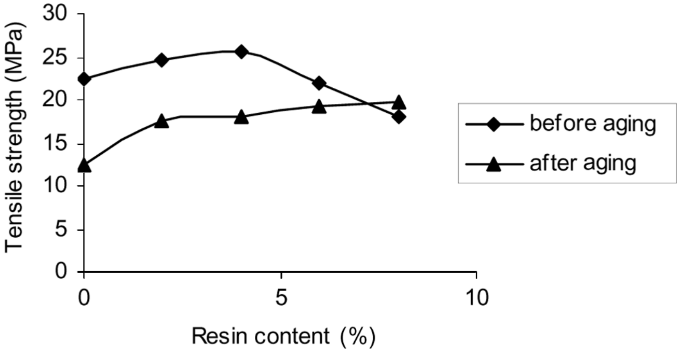

FIGURE 8 Tensile strength of NR before and after aging at 70°C for 72 h with commercial UPR.

crystallization in NR caused by the presence of the resin. Tear strength also largely follows the tensile behavior. The lowest tear strength is shown by samples containing the highest amount of MA.

Figures 8 and 9 show the effect of aging the blends in an air oven at 70°C for 72 h. The aging process causes loss of some tear and tensile strength at various percentages of resin. The addition of resin has a positive effect on the aging behavior with respect to tensile and tear strength. Figure 10 and 11 represent results obtained on testing resilience and the surface hardness of the modified samples. A lower crystallinity can reduce surface hardness and hence the fall in Shore A

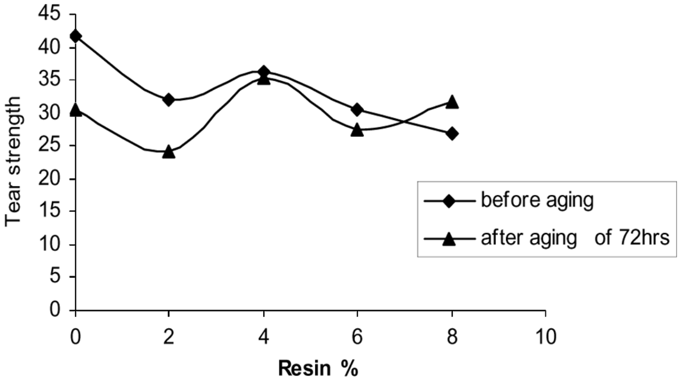

FIGURE 9 Tear strength of NR before and after aging at 70°C for 72 h with commercial UPR.

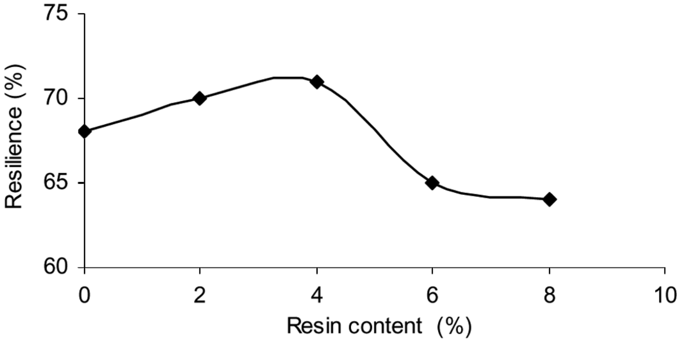

FIGURE 10 Variation of resilience of NR with commercial UPR.

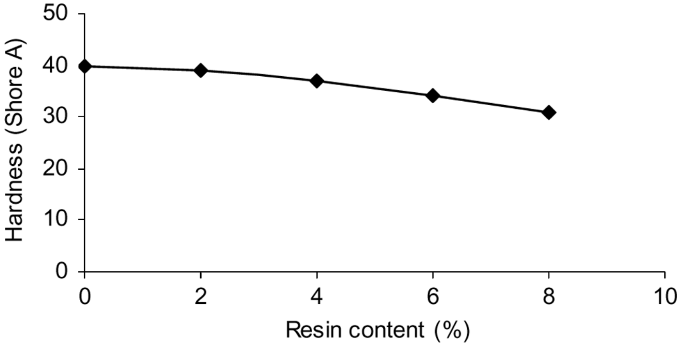

FIGURE 11 Variation of hardness of NR with commercial UPR.

values is understandable. The reduction in resilience can be the result of either excessive crosslinking or intercomponent grafting.

CONCLUSION

The study has identified the BPO/DMA system as a catalyst system for unsaturated polyester resin for modifying natural rubber. The properties of the modified rubber are somewhat negatively influenced by the extent of unsaturation in the UPR. Aging properties of the NR in terms of retention of tensile and tear strength shows improvement on modification with UPR.

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