

Alkylated Phenolic Resins as Antioxidants for Rubber

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ABSTRACT: Polymeric antioxidants based on *p*-nonyl phenol formaldehyde resin (PNPF) and *p*-dodecyl phenol formaldehyde resin (PDPF) were prepared by the condensation reaction of the respective phenols with formaldehyde in the presence of an acid catalyst. The reactions were monitored by thin layer chromatography, and the melting points of the products were determined. These compounds were incorporated in natural rubber mixes to evaluate their antioxidant properties. The compounded mixes were character-

ized for their rheometric properties. The compression-molded rubber sheets were tested for their mechanical properties. The effects of aging on the mechanical properties of these molded sheets were evaluated. Both PNPF and PDPF showed better antioxidant properties than the conventional styreneated phenol antioxidant. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2649–2651, 2006

Key words: antioxidants; PNPF; PDPF; NR

INTRODUCTION

Rubber goods find many uses as engineering materials because of their unique combinations of elastic and viscous properties. The service requirements of the finished products demand improved polymer stabilization. The oxidative aging of rubbers is one of the most important problems in rubber technology because the absorption of a small amount of oxygen causes a considerable change in their physical and mechanical properties.^{1–3} Such changes can be retarded but not completely avoided by the addition of antioxidants. The most common antioxidants are derivatives of aromatic amines and phenols.⁴ In most rubber systems, amines are more effective in preventing long-term oxidative degradation. However, amine antioxidants usually discolor^{5,6} with aging and may not be the system of choice for light and brightly colored rubber articles where color retention is important. Phenolic antioxidants, in contrast to amine antioxidants, do not discolor on aging but are generally less effective in preventing long-term oxidative degradation. Thus, a compromise may be necessary in the formulation of light or brightly colored rubber compounds. The various antioxidants used in the industry are low-molecular-weight compounds. However, because they are low-molecular-weight compounds, they lose their effectiveness over time. They are lost by evaporation, extraction, and migration. Sometimes, they bleed out of the system due to low compatibility. It is possible to extend the usefulness of these stabi-

lizers by increasing their molecular weights to make them less volatile and more compatible with the polymers.⁷ Polymeric antioxidants were prepared by the reaction between a monoalkylated phenol and formaldehyde in the presence of an acid. In this article, the synthesis, properties, and applications of polymeric antioxidants with different molecular weights are reported.

EXPERIMENTAL

Materials

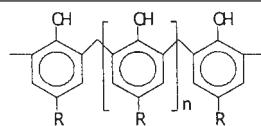
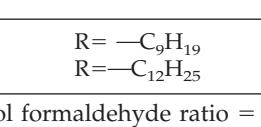
p-Nonyl phenol and dodecyl phenol were supplied by Schenectady Herdillia, Ltd. (Mumbai, India). Formalin (37%) and oxalic acid were procured from S. D. Fine Chemicals, Ltd. (Mumbai, India). Vulcanox styreneated phenol (SP) was procured from Bayer (I), Ltd. (Mumbai, India).

Synthesis

A calculated quantity of the monoalkylated phenol and formalin were charged in a three-necked flask equipped with a condenser, a Teflon-blade stirrer, a pulley, a motor, and a thermometer pocket. An oxalic acid solution (20%) was added slowly with stirring. Simultaneously, the temperature of the reaction mixture was slowly raised to 85°C. During processing, the pH of the reaction mixture was maintained at 2–3. The reaction was carried out for 5 h. Water was removed by vacuum distillation. The temperature of the reaction mixture was then raised to 120°C with simultaneous stirring. Condensation was carried out at this temperature for 5 h. Then, the obtained product was

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TABLE I
Structure of the Prepared Antioxidants

Name	Structure	mp (°C)
PNPF		74
PDPF		82

n = 12; phenol formaldehyde ratio = 1:0.85.

washed with hot water and dried in a vacuum oven. The hot condensation product was poured into a drying tray. The products were brown. The melting points of the compounds were determined. The structure of the prepared compounds *p*-nonyl phenol formaldehyde resin (PNPF) and *p*-dodecyl phenol formaldehyde resin (PDPF) are given in Table I.

Natural rubber (NR)-based composites

For the evaluation of the stabilizing action of PNPF and PDPF, NR composites were made with the recipe given in Table II. Rubber composites containing vulcanox SP, a commercial mixture of the SP antioxidant, were prepared to compare their antioxidant properties.

The rheometric properties of the rubber mixes were determined with a Monsanto oscillating disc rheometer (Monsanto & Co., USA).⁸ Circular-shaped specimens were cut with a punching machine and were used to study the rheometric properties. Rheometric study was carried out at a temperature of 150°C, arc \pm 3, for 30 min. The compounded sheets were cured with a compression-molding machine at 180°C for 10 min. The sheets were then cut into dumbbell-shaped specimens. The thicknesses and widths of the specimens were measured by a gauge. The tensile properties and hardnesses were measured on a Zwick tensile machine (Zwick GmbH, Germany) and a Shore A

TABLE II
Recipe for the Rubber Vulcanizates^a

Ingredient	phr
NR (IX)	100
Barytes	60
ZnO	10
Stearic acid	0.5
TiO ₂	10
Antioxidant	2
Sulphur	2
TMTD	0.5

NR (IX) = natural rubber (grade IX).

TMTD = tetramethyl thiuram disulphide.

^a Blank recipe without antioxidant.

TABLE III
Rheometric Data

Property	Sample			
	Blank	SP	PDPF	PNPF
Maximum viscosity of Li (kg)	7.5	7.0	6.5	8.0
Induction time (min)	2.25	2.37	2.25	2.12
Scorch time (min)	2.37	2.5	2.37	2.25
Torque at maximum cure of Lf (kg)	68.5	62.5	61.5	62.0
Optimum cure = 0.9 (Lf - Li) + Li (kg)	62.4	56.9	56.0	56.6
Optimum cure time (min)	4.12	4.12	4.12	4.0

durometer (Blue Steel, India), respectively.⁹ The aging of the test samples was carried out at 700°C for 7 days in an air-circulated oven.¹⁰ On aging, the tensile strength, percentage elongation at break, 300% modulus, and hardness of the samples were measured.

RESULTS AND DISCUSSION

Rheometric properties of the rubber compounds

As shown in Table III, it was clear that PDPF reduced the Mooney viscosity of the composites, whereas PNPF increased the viscosity. PDPF did not alter the scorch time much, whereas PNPF reduced the scorch time. However, the magnitude was less compared to the commercial antioxidant. The induction time and scorch time of the compounds did not differ much. All of the antioxidants showed reduced crosslinking compared to the blank, which was evident from the values of torque for the optimum and maximum cure. Despite this, the curing cycle of the NR compounds was not affected by the addition of the phenolic antioxidants.

Evaluation of the prepared compounds as antioxidants

The tensile properties and hardnesses of the rubber composites are shown in Table IV. The elongation at

TABLE IV
Mechanical Properties Before Aging

Property	Sample			
	Blank	SP	PDPF	PNPF
300% modulus (kg/cm ²)	40	36	36	36
Tensile strength (kg/cm ²)	218	214	203	215
Elongation at break (%)	630	630	630	640
Hardness (Shore A)	50	48	48	46

TABLE V
Mechanical Properties After Aging

Property	Sample			
	Blank	SP	PDPF	PNPF
300% modulus (kg/cm ²)	37.5 (6.2%)	49.9 (-38.5%)	47.1 (-30.9%)	48.9 (-25.8%)
Tensile strength (kg/cm ²)	186.8 (14.3%)	193.4 (9.6%)	181.3 (10.7%)	195 (9.3%)
Elongation at break (%)	620.5 (1.5%)	620.5 (1.5%)	618.9 (1.8%)	629.1 (1.7%)
Hardness (Shore A)	49 (2%)	49 (-2%)	50 (-4.2%)	50 (-8.7%)

The numbers in parentheses indicate the percentage change in the properties.

break, 300% modulus, and hardness of all of the batches were almost the same. Except for PDPF, which showed a lower tensile strength, the batches showed more or less the same tensile strength. The properties of the rubber composites after aging at 70°C for 7 days are shown in Table V; the numbers in parentheses indicate the percentage change in the properties after aging.

Except for 300% modulus, all of the physical properties of the rubber composites were retained on aging. Compared to the blank, all of the composites containing antioxidants showed a decrease in 300% modulus on aging. Among the three antioxidants, PNPF showed the best property retention. From these data, it was clear that the prepared compounds could replace SP with advantages; PDPF also reduced the Mooney viscosity, which should aid in processability.

CONCLUSIONS

The alkylated phenolic resins PDPF and PNPF can be effectively used as antioxidants in NR compounds. Both of the compounds did not affect the cure characteristics of the rubber compounds. Of the two antioxidants, PNPF showed the better retention of mechanical properties on aging.

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