Graft Copolymers from Peroxidized EPDM Rubber

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Synopsis

The transition metal catalyzed peroxidation of the pendant allylic functionality in EPDM rubbers with tertiary butyl hydroperoxide results in elastomeric, high polymer peroxides. The peroxidized EPDM rubbers are useful as free radical initiators for the polymerization and grafting of vinyl monomers in the preparation of comb-type structures. The grafted EPDM rubbers are efficient impact modifiers for thermoplastic resins so long as the polymer grafted onto the EPDM is identical to or is thermodynamically miscible with the composition of said thermoplastic resin.

INTRODUCTION

Studies of methods for preparing thermoformable graft structures have been numerous. Typically, an elastomeric structure is functionalized or reacted in such a fashion that monomer units are polymerized to form random graft polymers. The elastomer and graft polymer are selected on the basis of targeted properties. High impact polystyrene technology[1-8] represents the most well known example of graft polymer formation. Other elastomers such as ethylene/propylene/dicyclopentadiene (EPDM) rubber have been functionalized, and subsequently grafted via the functional moiety; e.g., epoxidation,[9-12] halogenation,[13,14] nitrosation,[15] photooxidation,[16] and carbon-carbon bond formation via the ene reaction.[17,18]

This communication details a method for peroxide functionalization of pendant allylic sites in EPDM rubbers and the utility of these modified EPDM structures for graft polymer formation.

EXPERIMENTAL

Reagents and Materials

Monochlorobenzene (Fisher Scientific Company) was used as received. Styrene, 4-t-butyl styrene, methyl methacrylate, methacrylic acid, and vinyl acetate (Aldrich Chemical Company) were purified by storage over alumina sieves followed by distillation. *N*-Phenylmaleimide monomer was prepared according to literature procedures[19,20] and recrystallized from heptane. Cobaltous naphthenate and cobaltous acetyl acetonate (Pfaltz and Bauer, Inc.) were used as received. The t-butyl hydroperoxide/toluene solution (35–40 wt% t-BHP) was prepared according to literature procedure.[21] The ethylene/propylene/dicyclopentadiene rubber (EPDM) had 8.4 wt% dicyclopentadiene and an inherent viscosity (η Inh) of 2.8 in decalin at 135°C.

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Analytical Procedures

Molecular weight (Mn and Mw/Mn) was obtained with a Waters 150-C ALC/GPC instrument calibrated with monodisperse polystyrene.

Glass transition (T_g) temperature was obtained by differential scanning calorimetry using a Perkin Elmer DSC-2 equipped with a thermal analysis data station.

EPDM-bound peroxide functionality was determined by iodometric titration[22] and adjusted for competing side reactions in the base EPDM rubber by iodometric titration of a blank containing the base EPDM rubber.

Half-life determinations for EPDM-bound peroxide were made by heating the functionalized EPDM rubber in chlorobenzene and analyzing peroxide concentration by iodometric titration.

General Reaction Procedures: Peroxidation Procedure

Approximately 200 g of EPDM rubber was dissolved in 800 g of monochlorobenzene in a pressure reaction vessel at 70°C with stirring. Once the EPDM rubber dissolves, a quantity of anhydrous tertiary butyl hydroperoxide/toluene solution (37.5 wt% t-BHP) was added and the polymer solution was stirred rapidly for 30 minutes. A monochlorobenzene solution of cobaltous naphthenate (6 wt% cobalt in mineral spirits) and cobaltous acetyl acetonate was prepared and metered into the reactor while maintaining the reaction mass at 72°C for eight hours. The peroxidized EPDM rubber was isolated and purified by precipitation into a fourfold excess of methanol.

Grafting Procedure

The peroxide functionalized EPDM rubber (200 g) was dissolved in monochlorobenzene (700 g) at 75°C in a pressure reaction vessel. A high torque motor was required to maintain stirring throughout the polymerization. The monomer or comonomer solution (1 : 1 w/w versus EPDM) was added to the reactor and the temperature raised to 137–144°C for six hours. The polymer mass was purified of unreacted monomer and recovered in crumb form by precipitation into a fourfold excess of methanol using a Waring blender. The sample was dried to constant weight and monomer conversion was determined.

The level of polymer grafted to the EPDM rubber was determined via Soxhlet extraction procedures. Methyl ethyl ketone (MEK) was selected as the extraction solvent because it is a solvent for the nongrafted styrene and acrylic polymers while being a nonsolvent for EPDM species. A sample of the graft polymer was placed in a Soxhlet extraction device for a minimum of 110 hours. The MEK-soluble component was recovered by precipitation into methanol. The percent of styrenic or acrylic polymer grafted to EPDM rubber (A) was determined by the following equation;

$$\frac{\begin{array}{l}\text{Total wt (g) of styrenic}\\ \text{or acrylic formed}\end{array} - \begin{array}{l}\text{Total wt of MEK-soluble}\\ \text{styrenic or acrylic}\end{array}}{\text{Total wt of styrenic or acrylic formed}} \times 100 = \text{A}$$

All graft polymers formed using the peroxide-functionalized EPDM rubber were completely soluble in chlorobenzene, eliminating crosslinking as a factor for consideration in the graft analysis.

Melt Blending Procedure

To assess the utility of the graft structures as impact modifiers, blends involving homo- and copolymers with graft structures were prepared. The two components were physically mixed, then melt compounded at 80–90°C above the T_g of the single-phase thermoplastic (non-EPDM) component on a Sterling single-screw extruder. The blend pellets were molded into test specimens on a Battenfeld BSKM30HK injection molding machine.

Physical Property Evaluation

Physical properties of the test specimens were evaluated in accordance with the following ASTM procedures, elongation (D-638) and notched Izod impact (D256). Gardner falling weight index was established using a 1/2″ diameter orifice, an 8 pound weight and a 1/2″ diameter Tup.

RESULTS AND DISCUSSION

EPDM Peroxidation and Characterization

Allylic carbon centers have been oxidized to the corresponding allyl alkyl peroxides with transition metal salt/alkyl hydroperoxides redox systems.[23-26] This same chemistry applied to ethylene/propylene/diene rubbers (EPDM) results in rubbers with pendant allyl alkyl peroxide functionality. In the presence of vinyl monomers, thermal activation of the elastomeric, high polymer peroxide initiates polymerization of the vinyl monomer resulting in the formation of EPDM graft structures.

Selection of the solvent in which peroxidation of the EPDM rubber occurred required a solvent of low polarity allowing for high solid solutions of EPDM rubber and noncomplexation with the transition metal catalyst. The solubility factor is obvious, but more subtle is the solvent catalyst interaction. Previous work had demonstrated that transition metal/alkyl hydroperoxide oxidation of organic substrates in low polarity solvents exhibits an induction phenomenon at the point in the redox cycle where the concentration of alkyl hydroperoxide drops below that of the transition metal catalyst.[27-28] The induction period was proposed to result from inactive catalyst micelles which form once the alkyl hydroperoxide concentration reaches the critical point. In order to maximize the level of bound EPDM peroxide and prevent further catalyst-EPDM peroxide reactions once the concentration of t-butyl hydroperoxide dropped to the critical level, numerous solvents were screened, with chlorobenzene being identified as the solvent of choice.

Singular transition metal catalysts as previously noted have been shown to effectively oxidize (peroxidize) allylic organic substrates with alkyl hydroperoxides.[23-26] It has been found that binary transition metal catalysts enhance both the rate of formation and the overall level of EPDM bound peroxide (Fig. 1). Singular cobalt, copper, and manganese catalysts were evaluated but, in comparison to binary cobalt catalysts, were less efficient. A twofold increase

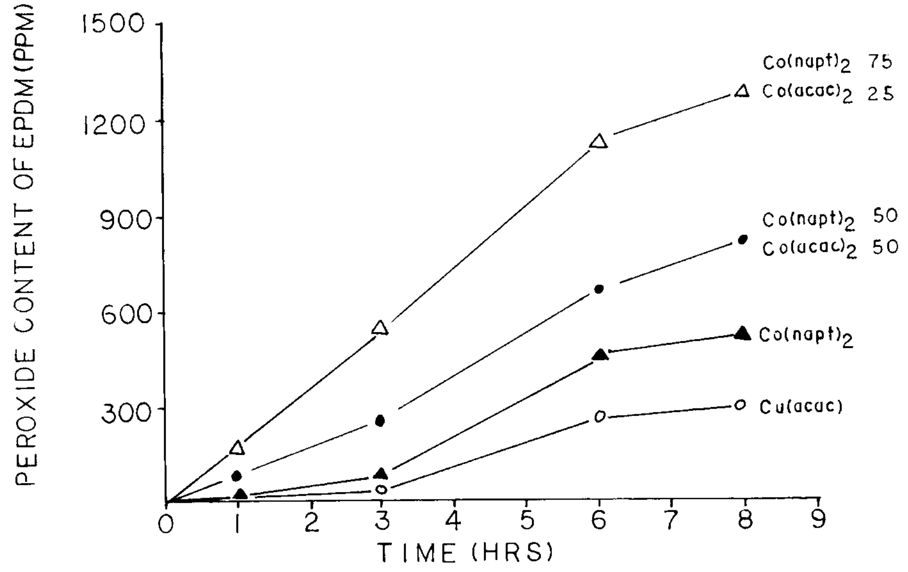

Fig. 1. Peroxidation catalysts.

in both rate and level of peroxide formation was achieved with a 75 : 25 molar ratio of cobaltous naphthenate : cobaltous acetyl acetonate. Optimum peroxide functionality was achieved with the molar ratio of cobaltous metal salts to EPDM diene content to t-butyl hydroperoxide of 0.008 to 1 to 3.8.

The level of EPDM peroxide functionality as determined by iodometric titration ranged from 950 to 1472 ppm. The nature of the peroxide is proposed to be an allyl alkyl derived from peroxide formation by the transition metal-mediated reaction of the pendant dicyclopentadienyl radical and t-butyl hydroperoxide. Infrared absorption at 1185 cm^{-1} not present in the base EPDM rubber supports the proposed allyl alkyl nature of the peroxide. The absence of absorption at 3550 cm^{-1} and 3380 cm^{-1} eliminates the possibility of hydroperoxide functionality.[29]

The half life of the EPDM-bound peroxide was determined according to the aforementioned procedure. The $t_{1/2}$ *and* K_d values were determined at three temperatures (Table I). A temperature of 140°C provided for four half-life cycles with a reasonable rate and extent of polymerization when the peroxidized EPDM rubbers were used as polymerization initiators for graft polymer formation.

TABLE I
Kinetic Determinations for EPDM-Bound Peroxide

Temperature (°C)	K_d [s^{-1}]	$t_{1/2}$ (min)
130	4.1×10^{-5}	281
140	1.4×10^{-4}	82
150	6.3×10^{-4}	16

EPDM Graft Polymerization

The polymerization of a variety of vinyl monomers with the peroxidized EPDM forms both grafted and nongrafted polymer molecules. In all cases, the nongrafted polymer was separated from the EPDM graft structure by extraction as described in the experimental procedure. Characterization of the graft polymer was carried out by assuming that the kinetic chain length and microstructure of the nongraft species closely approximate those of the grafted material, so that the molecular weight and molecular weight distribution of the nongraft species (Table II) as measured by gel permeation chromatography can be assumed to approximate the values for the grafted species. The molecular weight and molecular weight distribution of the nongraft species did not deviate from that which is typical for free radical polymerization.

The grafting efficiency was high for all the vinyl monomers evaluated. The quantification of the grafting level is considered to be accurate within the scope of the extraction process. Control samples were prepared by two methods to validate the reliability of the extraction process. One control sample (A) was prepared by mechanically blending methyl methacrylate/*N*-phenylmaleimide copolymer with base EPDM rubber in a Brabender plastograph at 260°C for 5 minutes, the other control sample (B) was prepared according to the experimental procedure substituting base EPDM rubber and ditertiary butyl peroxide for the peroxide-functionalized EPDM rubber in the

TABLE II
EPDM Graft Polymer Characterization

EPDM-bound peroxide (ppm)	Monomer(s)	% Monomer conversion	% Polymer grafted	T_g (° K) of grafted polymer	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$
960	S	93	47	379	107,700	2.2
1172	4-t-BuS	86	42	405	100,200	2.3
1120	MMA	91	54	375	90,100	2.4
1190	S (90) MAA (10)	95	56	400	91,800	2.3
1120	MMA (76) N-PMI (24)	93	47	425	86,400	2.2
1085	VAc	83	35	305	125,300	2.6

TABLE III
Methyl Ethyl Ketone Extraction of EPDM-g-MMA/N-PMI

	Weight % of available MMA/N-PMI extracted	Mn	T_g (° K)
Control A	96	201,700	415
Control B	94	102,700	415.5
Peroxide-functionalized EPDM	53	111,200	416.5

TABLE IV
Impact Modified Blends

Thermoplastic resin	EPDM graft, Table II	Wt% EPDM[e]	Notched Izod (J/m)	GFWI (N-m)	Elongation break (%)
Polystyrene[a]	EPDM-g-PS	8	272	13.7	15
Poly(methyl methacrylate)[b]	EPDM-g-PMMA	18	245	20.1	42
Styrene/maleic anhydride[c]	EPDM-g-PMMA	18	224	28.9	34
Styrene/ acrylonitrile[d]	EPDM-g-MMA/ N-PMI	18	384	40.6	47

[a] Dylene® 8 resin, ARCO Chemical Company.

[b] Plexiglas® V-052 resin, Rohm and Haas Company.

[c] DYLARK® 332 resin, ARCO Chemical Company; 14 wt% maleic anhydride.

[d] Lustran® SAN-31 resin, Monsanto Chemical Company; 24.5 wt% acrylonitrile.

[e] This is the overall EPDM rubber content of the (EPDM-g-polymer and thermoplastic resin) composition.

polymerization of methyl methacrylate/*N*-phenylmaleimide copolymer (Table III). Extraction of the MEK-insoluble EPDM-g-MMA/*N*-PMI with heptane shows only minor amounts ($< 2\%$) of EPDM rubber without MMA/*N*-PMI copolymer grafts.

Impact Modification

The high grafting efficiency available through the peroxidized EPDM rubbers allowed for tailoring graft copolymers to function as coupling agents between the rubbery EPDM polymer and a thermoplastic resin targeted for impact modification. The polymer grafted to the EPDM must be (1) identical in composition to the thermoplastic resin or (2) thermodynamically miscible with said thermoplastic resin. The resulting (EPDM-g-polymer and thermoplastic resin) composition characterized as having a single continuous phase and a noncontinuous dispersed phase (EPDM) by transmission electron microscopy. A wide variety of thermoplastic resins were impact modified with the peroxidized EPDM approach (Table IV). The thermodynamic miscibility of styrene/maleic anhydride copolymer with poly(methyl methacrylate)[30] and of styrene/acrylonitrile copolymer with methyl methacrylate/*N*-phenylmaleimide copolymer[31] has been documented. All the thermoplastic resins employed in this study exhibited notched Izod values ≤ 37 J/m, GFWI values < 1 N-m, and elongations at break $\leq 5\%$. The data in Table IV substantiates the effectiveness of the graft structures formed via the elastomeric EPDM peroxide as impact modifiers, since simply blending virgin EPDM rubber with any of the thermoplastic resins in Table IV results in notched Izod and GFWI values of less than 50 J/m and < 2 N-m, respectively.

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