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Innovative Coatings from Low Molecular Weight EPDM

By Zhiyong Zhu\* and Solomon H. K. Tang  
Lion Copolymer Geismar, LLC  
Baton Rouge, LA

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\* Speaker

## Abstract

EPDM rubber is a desirable material in many coating applications due to its weather/ozon resistance, water repellence and low temperature flexibility. Two innovative coatings have been developed from low molecular weight EPDM polymer employing either a sunshine UV crosslinking mechanism or a peroxide crosslinking mechanism. The formulations display good paint application properties in viscosity, crosslinking speed, and pot life. After crosslinking, the coating films maintained EPDM rubber properties with high mechanical strength, good adhesion to polar substrates, high hydrophobicity and good flexibility. Factors influencing the crosslinking speed and coating properties have been studied such as crosslinking agent types, molecular structure of EPDM, crosslinking co-agents and choice of fillers. The formulations could be used in potential applications like roofing, industrial protective coating and decorative coatings.

## INTRODUCTION

EPDM rubber has seen significant growth in recent years in automotive, wire and cable, roof sheeting and thermoplastic vulcanizates (TPV) applications, due to the unique molecular structure and versatile processing properties.<sup>1,2</sup> These applications typically require a crosslinking process with either sulfur or peroxide to achieve specific shapes and desired mechanical strength, elasticity, insolubility and other beneficial physical and chemical properties.<sup>a</sup> Normally heat is applied to activate the crosslinking agents and accelerators in order to achieve crosslinking. However, there are situations in which crosslinking at low temperature is favored, where the heat cannot be applied or is difficult to apply. An especially interesting application is for coating, where rubbery properties of EPDM are delivered in the form of a thin layer, and the crosslinking process needs to be at room temperature. A coating from EPDM rubber should have excellent water, vapor, chemical and electricity barrier properties that differentiate it significantly from current widely used acrylic based coating products.

The unique properties of EPDM rubber are desirable in many coating applications. EPDM rubber has excellent weathering stability and water repellence, making the coating an outstanding candidate for roof coating, better than current acrylic latex based roof coatings. The very low moisture permeability, good mechanical strength and resistance to polar chemicals make EPDM coating suitable as anticorrosion protective coatings, especially at low temperature and highly humid environment. The elastic nature and low surface tension provide good hand feel, enabling applications as protective decorative coatings. Especially, the lower cost, better mechanical strength, and better adhesion with substrates, make EPDM coatings much superior to silicone rubber based coatings, the only other rubber based coating successfully commercialized currently.

For a viable coating formulation designed from EPDM rubber, both a crosslinking mechanism that vulcanizes EPDM rubber at room temperature and a proper viscosity range are critical. A key factor of coating application is that the polymer is applied in liquid form, in order for processing with rolling, brushing or spraying. This requires the starting molecular weight of EPDM to be sufficiently low; otherwise a large quantity of solvent has to be used and makes the coating unfavorable for volatile organic compounds (VOC) emission. Another key factor is a curing system that must have a reasonable crosslinking rate at room temperature to crosslink the low molecular weight EPDM, and in the presence of solvent. On the other hand, the crosslinking speed cannot be too fast such that,

<sup>a</sup> Phenolic resin cure often used in TPV applications.

significant crosslinking will not occur before solvent is fully evaporated, in order to allow sufficient application time window. Other considerations for coating formulation also include: leveling (flow ability before crosslinking in order to form a smooth surface), sagging resistance (degree of dripping before crosslinking), storage stability etc. To meet all these requirements and achieve a practical coating application has long been a challenge in industry, and generally needs a very carefully selected system consisted of proper type of EPDM, controllable crosslinking agents, and proper additives including fillers, pigments and crosslinking co-agents.

Studies have been made earlier in the EPDM rubber history in order to achieve a crosslinking system at room temperature. A photocuring system was reported using 2.0%  $\alpha$ - $\alpha$ -dimethoxy-phenyl acetophenone (BDK) and 2,4,6-trimethylbenzoyl phenyl phosphinio ethyl ester (APOE) as initiators, which could crosslink EPDM with a UV irradiation from a 2kW mercury lamp, to a thickness up to 2 mm, and has good adhesion with a steel panel.<sup>3</sup> However, the requirement of very strong UV source has limited its use in many applications. Peroxide chemicals were also tried to crosslink EPDM rubber at lower temperatures,<sup>4</sup> typically selected based on the ten hour half-life temperatures, ranging from di(2,4-Dichlorobenzoyl) peroxide at 54°C, to dicumyl peroxide at 114°C. EPDM compounds are typically mechanically mixed right before the processing, and allow very short time to operate in order for the fast crosslinking. In both situations, the EPDM polymer employed had molecular weight higher than 200,000; not favorable for a practical coating application.

In this study, we report two coating formulations from a commercially available low molecular weight EPDM, employing a sunshine UV crosslinking mechanism and a peroxide crosslinking mechanism, respectively.<sup>5,6</sup> The formulations maintain good EPDM rubber properties after crosslinking, such as high mechanical strength, good adhesion to polar substrates, high hydrophobicity and good low temperature flexibility. The formulations meet major industrial requirements as protective coatings in viscosity, solid content, crosslinking speed, pot life, shelf life, as well as cost level close to commercial acrylic coatings. The coatings were also tested as liquid roofing membranes, and showed advantages over solid EPDM sheets and other acrylic based coatings in terms of easy installation, high solar reflectance, better water resistance and good weather durability.

## EXPERIMENTAL

Table I lists the 2 base formulations used in this study. Formulation A employs a peroxide crosslinking system in the presence of Cobalt and Zinc catalysts. Formulation B used a photo initiator as the crosslinking agent. Sources of materials are also listed. The EPDM polymer sample was Trilene® T65 with 10.5% DCPD and E/P ratio at 50/50 from Lion Copolymer. The molecular weight of the EPDM polymer is derived from dynamic viscosity measurement to be around 50,000 Dalton, much lower than typical EPDM polymers used for bulk compounding applications. All raw materials were used without being further purified.

TABLE I EPDM Polymer BASED COATING FORMULATIONS

	Material	Manufacturer	A	B
<b>Part A</b>				
Trilene® T65	EPDM Polymer	Lion Copolymer	32.92	28.37
Ricon® 156	Co-agent	Cray Valley	2.74	2.36
SR-350 (TMPTMA)	Co-agent	Sartomer	0.69	
Mineral Spirit	Solvent	Lard Oil	20.67	16.55
SIH6115.0	Solvent	Gelest	10.00	21.28
Disper BYK® 118	Dispersant	BYK	1.10	0.70
Ti-Pure® R-706	White Pigment	Dupont	8.23	9.46
Coupsil® 6508	Filler	Evonik		9.46
Ultrax® 96	Filler	Kaolin	16.46	
Irgacure® 819	Photo Initiator	BASF		2.36
12% Co Ten-Cem	Catalyst	OMG	0.27	
18% Zn Ten-Cem	Catalyst	OMG	0.27	
Toluene	Co-solvent	Generic		9.46
<b>Part B</b>				
Peroxan® PIN	Crosslinking Agent	Pergan	1.65	
Mineral Spirit	Solvent	Lard Oil	5.00	
<b>Total</b>			<b>100</b>	<b>100</b>

For both formulations, EPDM polymer and dispersant were first dissolved in a portion of total solvent, then filler and pigment were added and mixed at 2,000 rpm with a FlackTek High Speed Mixer until a uniform paste was formed. The rest of the components were then added and allowed sufficient mixing at 1,000 rpm to form a final smooth liquid paint. Formulation A used a part B to separate

peroxide curatives to avoid premature crosslinking. The part B was a straight mixture of peroxide in solvent. The paint properties were then measured for specific gravity, solid content and viscosity. All tests were conducted following ASTM standards with standard lab equipment.

The paint was applied to desired substrates including steel, aluminum, wood, aged EPDM sheets, and release paper, using a Gardco wet film applicator to 0.8 – 1.0 mm thickness. Formulation A required a mixing of part A and part B before application. Coating of Formulation A was dried indoor at room temperature for 7 days. Formulation B was dried outdoor with typical sunshine for 7 days. During the drying process, the dry to touch time was measured following ASTM D1640 using a standard dry time tester. After drying, the coating film was used to measure physical properties including tensile strength, elongation at break, 100% Modulus, Shore A hardness, scratch resistance, contact angle, and moisture transmission resistance. All the tests were conducted following related ASTM standards with standard lab equipment.

## RESULTS AND DISCUSSIONS

### PROPERTIES OF BASE FORMULATIONS

Table II lists the properties of wet paint and dried coating film of base Formulation A and Formulation B, which were crosslinked by peroxide and photoinitiator, respectively.

TABLE II  
PHYSICAL PROPERTIES OF BASE FORMULATIONS

Item		A	B
Test Standard			
Solid Content (w/w%)	ASTM D3960	64.3	52.7
VOC (g/L)	ASTM D3960	243	247
Specific Gravity	ASTM D1475	0.95	0.95
Brookfield Viscosity (mPa•s)	ASTM D2196	4,600	5,400
Dry Time at 25°C (hours)	ASTM D1640	3.5	0.5
Tensile Strength (MPa)	ASTM D412	7.24	6.55
Elongation at Break (%)	ASTM D412	110	130
Hardness (Shore A)	ASTM D2240	40	35
Surface Contact Angle w/ Water (°)	ASTM D7490	92	91
Adhesion w/ Steel Panel (MPa)	ASTM D4541	15.2	13.6
MVTR (perm)	ASTM E96	0.10	0.10

Because of the low molecular weight of EPDM polymer, both Formulation A and Formulation B have high solid content, but still have low viscosity in liquid form, allowing them to be applied in the same manner as a typical paint using rolling, brushing and spraying. After crosslinking, both formulations displayed high mechanical strength and elongation at break, indicating a reasonable degree of crosslinking as a typical rubber material. Notably, both formulations have good adhesion to a steel substrate, and a very high moisture transmission resistance as well, typical of the nature of EPDM polymer.

These two formulations demonstrated that a practical coating formulation could be derived from a low molecular weight EPDM polymer using either the photo crosslinking mechanism or the peroxide crosslinking mechanism. Although a low viscosity liquid form is needed for coating application, crosslinking system could still be designed to achieve sufficient crosslinking and mechanical strength. Properties of the resulted coating film will not be substantially different from those of typical rubber compounds prepared by dry mixing.

#### PEROXIDE CROSSLINKING OF LOW MOLECULAR WEIGHT EPDM POLYMER

Peroxide is a classical method to crosslink thermoset rubber materials to achieve desired mechanical and chemical properties. The crosslinking is typically initiated from the decomposition of peroxides and the resulted free radicals then crosslink polymer chains through coupling reaction.<sup>7</sup> Although metal catalysts could be used to assist the crosslinking reaction in many situations,<sup>8</sup> the rate of crosslinking is usually dominated by the rate of peroxide decomposition, denoted by 10 hours half-life temperature. An elevated temperature is always favored in order to achieve fast crosslinking in many thermoset rubber applications.

However, in a coating application, the starting low molecular weight of EPDM polymer, the existence of solvent, and the necessity to crosslink at room temperature require selection of more reactive peroxide and application of peroxide at a higher loading. Table III lists the effect of using 3 types of commercial peroxides in Formulation A. It is noted that crosslinking speed is fastest for PPO which has highest reactivity indicated by the lowest 10 hour half-life temperature, but the final mechanical strength is highest for TBPB which has the lower reactivity, probably because of the formation of more crosslinking centers and thus a higher degree of crosslinking.

TABLE III  
CROSSLINKING WITH VARIOUS PEROXIDES

Peroxide	Chemical structure	10 hour half-life temp.	Dry time (Hour)	Tensile Strength (MPa)	Elongation at break (%)
PPO	<i>t-butyl 2-ethylperoxyhexanoate</i>	72°C	2.8	6.21	125%
PPIN	<i>t-Butyl peroxy-3,5,5-trimethylhexanoate</i>	94°C	3.5	7.24	110%
TBPB	<i>t-Butyl Peroxybenzoate</i>	104°C	4.5	7.68	105%

PHOTO crosslinking OF LOW MOLECULAR WEIGHT EPDM POLYMER

Although photo crosslinking of EPDM polymer was reported earlier,<sup>3,9</sup> the coating application requires a much more efficient photo initiator due to the starting low molecular weight of EPDM and the crosslinking at ambient temperature. The modern bisacylphosphine oxide (BAPO) type of photo initiator is found capable of curing EPDM polymer efficiently using the UVA wavelength (315-400nm) in natural sunshine. Figure 1 shows the splitting of BAPO under UV irradiation into free radicals to crosslink EPDM polymer chains. Formulation B employed Irgacure® 819, bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, as photo initiator, and showed a quick dry time of only 30 minutes. This photo initiator has both excellent surface crosslinking and through crosslinking, and is not inhibited by TiO<sub>2</sub> pigment. Several other types of photo initiators were also tested in Formulation B, but none has shown similar crosslinking efficiency.

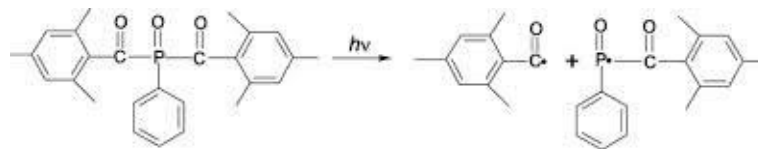


FIG.1. — Splitting of BAPO photo initiator under UV irradiation

Loading level of photo initiator also affects the crosslinking speed and the final coating film properties. Figure 2 shows that there exists a saturation point at about 1.5% in Formulation B, beyond which the final mechanical strength does not increase with more photo initiator.



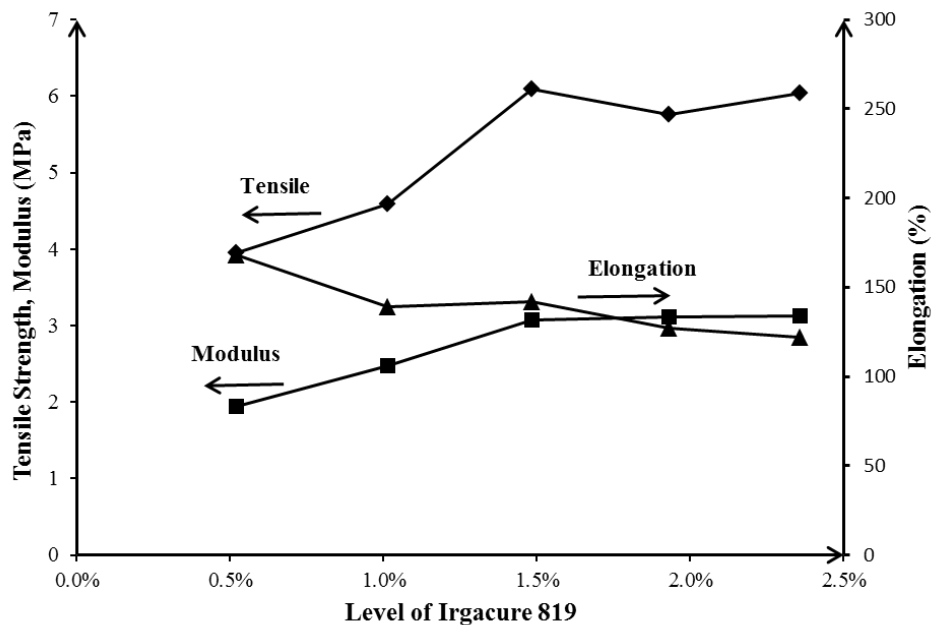


FIG.2. — Tensile properties with loadings of photo initiator.

#### EFFECT OF EPDM CHEMICAL STRUCTURE

The coating application requires the starting molecular weight of EPDM polymer to be sufficiently low. However, the chemical structure also affects the curing speed and mechanical strength of final coating film. Table V lists the use of several grades of EPDM in Formulation B with photo crosslinking. At very close molecular weight level, EPDM polymer with 5ethylidene-2-norbornene (ENB) monomer has slower crosslinking rate and weaker mechanical strength than EPDM polymer with dicyclopentadiene (DCPD) monomer (cf. T65 vs T67). It also seems higher level of propylene component in EPDM polymer tends to give better crosslinking (cf. T67 vs T77), probably due to the more available  $\alpha$ -H sites that are also reactive in free radical reaction.

TABLE V EFFECT OF EPDM CHEMICAL STRUCTURE

EPDM Type	T65	T66	T67	T76	T77
E/P Ratio	54/46	45/55	45/55	75/25	75/25
Diene Type	DCPD	ENB	ENB	ENB	ENB
Diene, wt. %	9.75	4.5	9.5	4.0	10.5
Mv (Daltons)	6411	8000	7700	7500	7500
Dry time (hours)	0.5	>5.0	>5.0	>5.0	>5.0
Tensile Strength (MPa)	7.49	2.25	4.08	2.83	3.60
Elongation at break (%)	114	43	100	44	86

The crosslinking of a low molecular weight EPDM also benefits from the addition of extra functionality derived from the co-agents added in both Formulation A and Formulation B. Trimethylolpropane Trimethacrylate (TMPTMA) belongs to Type I co-agent and polybutadiene (PBD) belongs to Type II co-agent, both of which provides extra reaction functionalities thus the crosslinking could be significantly accelerated.

#### EFFECT OF FILLERS

In curing the low molecular weight EPDM polymer, fillers play a significant role not only by physical reinforcement, but also through providing extra crosslinking centers so that polymer could build mechanical strength at a lower degree of crosslinking. While quite a few various types of fillers have been tested, it was found precipitated silica modified with vinyl based silane showed the best reinforcing effect and also good compatibility with EPDM polymer. This type of filler reacts with the diene in the pendant groups of the EPDM polymer during the crosslinking process, and forms extra covalent chemical bonds thus increases the degree of crosslinking. Figure 3 shows the effect of different loading levels of Coupsil 6508, silane-treated precipitated silica, in Formulation B.

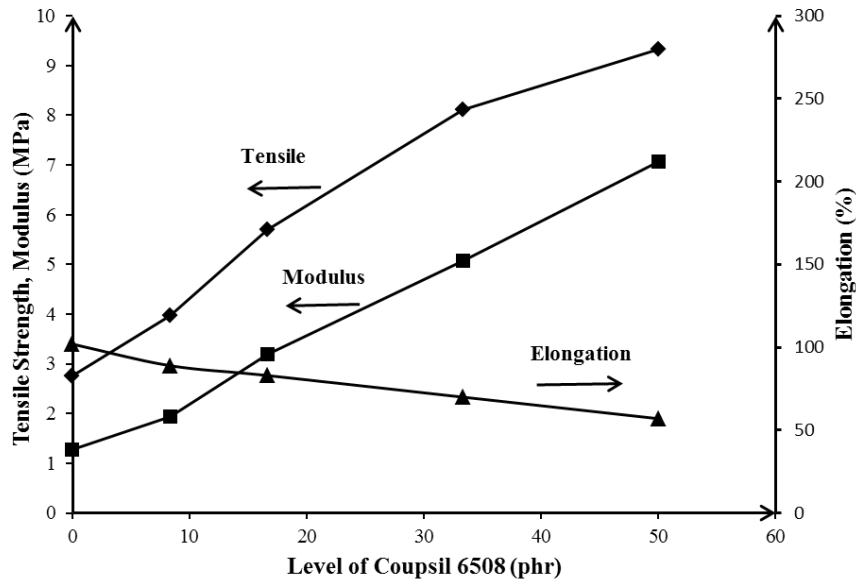


FIG.3. — Effect of loadings of filler.

### CONCLUSIONS

Despite the challenges that a coating application needs to cure a low molecular weight EPDM polymer at ambient temperature and in the presence of solvent, formulations were successfully developed, employing either a photo crosslinking mechanism or a peroxide crosslinking mechanism. The BAPO type of photo initiator was shown to induce fast crosslinking with the UV irradiation in natural sunshine, and carefully selected peroxide also provides crosslinking speed fast enough for a coating application. The formulations were tested to meet industrial coating application standards in viscosity, crosslinking speed, mechanical strength and adhesion etc. Especially, the coatings maintain unique properties of EPDM rubber, like weather resistance, heat aging resistance, low temperature flexibility, water repellence and high moisture vapor resistance.

A reasonable coating formulation should also take into consideration the influence of all components. Although the crosslinking package plays the dominant role in deciding the coating performance, the choice of EPDM polymer structure, crosslinking co-agents and fillers can also significantly affect the properties of final coating film.

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