

Contact metathesis polymerization (CMP)

Kenneth C. Caster*, Edward F. Tokas, Christopher G. Keck, Marlene E. Hontz

Materials Division, Lord Corporation, 110 Lord Drive, Cary, NC 27511, USA

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Abstract

Ring-opening metathesis polymerization (ROMP) has been used to investigate adhesive and coating formation via a general process called contact metathesis polymerization (CMP). This process involves applying a metathesis catalyst directly to the surface to be modified and initiating the polymerization by exposing this newly formed catalyst-coated surface to a monomer capable of undergoing ROMP, thereby creating an adhesive bond or coating. In this paper, we describe excellent primary adhesion results of bonding low surface energy elastomers to metals and themselves using ROMP as the operative chemistry. The elastomers natural rubber, EPDM, and Santoprene® are difficult to bond using conventional methods, particularly in their post-vulcanized state. CMP yields rubber-tearing bonds to pre- and post-vulcanized elastomers at room temperature under ambient conditions in air, in the presence of moisture, and with minimal surface preparation using well-defined olefin metathesis catalysts.

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1. Introduction

Olefin metathesis reactions are widely used to interconvert simple olefins via cross-metathesis, to prepare relatively complex natural products via ring-closing metathesis, and to make polymers via ring-opening metathesis polymerization (ROMP) or acyclic diene metathesis polymerization (ADMET). This chemistry has been used extensively in laboratories to synthesize single compounds, chemicals, or polymers with controlled structural features [1–3]. Likewise, olefin metathesis performed on the industrial scale [4] has been used to prepare chemicals and polymers for use in assorted products which range from simple detergent-range alkenes to polymers for oil recovery appli-

cations [5]. Metathesis polymerizations are done either in solution (ROMP) or in bulk (ROMP or ADMET).

Only recently, have researchers shown interest in using olefin metathesis, and ROMP in particular, to modify surfaces through surface grafting reactions. Surface modification by both physisorption and chemical reaction [6] has developed using methodologies such as Langmuir–Blodgett techniques [7] and self-assembly [8] to yield controlled surface structures which possess interesting architectures and properties. In addition, the literature abounds with examples of post-polymer surface graft reactions utilizing plasma [9], extrusion [10], radical [11,12], ATRP [13], cationic [14], anionic [15], condensation [16], photochemical [17,18], electrochemical [19], and ROMP (*vide infra*) polymerization methodologies. These grafting reactions work by attachment of a polymer to a surface “grafting to” (Fig. 1) and by initiation of a polymerization from a surface “grafting from” (Fig. 2). Both approaches use

* Corresponding author. Tel.: +1-919-469-2500x2375;

fax: +1-814-860-3593.

E-mail address: ken.caster@lord.com (K.C. Caster).

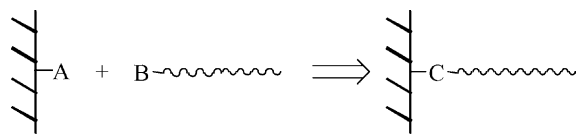


Fig. 1. Illustration of “grafting to” surface attachment of polymers. A and B represent reactive groups on a surface and a polymer, respectively.

a tether to attach functionality to the surface via a covalent bond. Grafting chemistry as applied to the formation of polymer brushes was recently reviewed [20].

A variety of tethers have been used to attach catalysts to surfaces, however ROMP approaches have been focused primarily on gold substrates. Grubbs and co-workers used the “grafting from” approach to prepare chemically diverse polymer brushes on a gold surface by ROMP of a tethered alkylthiophenyl-ethynylene substituted norbornene with a well-defined ruthenium catalyst. Surface analyses showed longer polymer chains protruding from shorter alkanethiol chains, which were applied to the surface in an earlier step [21]. Using a similar approach but a different tether and catalyst, Tremel and co-workers initiated ROMP from a catalyst covered colloid to investigate differences in homogeneous and heterogeneous activity [22]. Stelzer and co-workers recently reported on a ROMP in which a ruthenium catalyst had been covalently attached to a surface and used to graft polynorbornenes. However, this was limited to specially designed polymer substrates that contained exposed vinyl chains prepared specifically for this study [23]. A patterned polymer array has been applied to a silicon surface using microcontact printing of a siloxy norbornyl monomer followed by reaction with Grubbs’ catalyst and substituted norbornenes [24]. Covalently attached thin polynorbornene films have been grown from silicon surfaces [25]. Buchmeiser and co-workers prepared stationary monoliths for regular and chiral separations by grafting valine and phenylalanine containing polynorbornenes from norbornyl substitu-

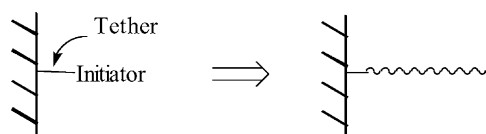


Fig. 2. Illustration of “grafting from” surface attachment of polymers.

ted polystyrene–divinylbenzene crosslinked solid supports [26–28]. Highly loaded polymer supports have been prepared for combinatorial chemistry [29] and catalysts [30]. Hybrid gold nanoparticles, composed of blocked ferrocene substituted norbornene segments, display interesting cyclic voltammetry behavior [31].

Our interest in surface modification is driven by adhesive design and manufacture, and an interest to understand how olefin metathesis, and ROMP in particular, would work in applications where adhesion was of primary importance. An examination of the literature revealed that others had used ROMP to affect adhesion. Saunders and Kent showed that block copolymers prepared by solution-phase ROMP are useful as adhesion promoters for bonding thermosets to solid materials and for glass-epoxy and copper-epoxy interfaces [32]. Others have used ROMP to promote adhesion to polyolefin substrates [33,34] and at glass-polymer interfaces [35]. Norbornene polymers have been reported to make transparent molding materials with good adhesion to aluminum films [36].

1.1. Contact metathesis polymerization (CMP) approach

So far, we have described surface modification that utilizes physisorption of bulk polymer from solution or a melt and grafting polymers chains from a surface. We would now like to turn to another method of surface modification “initiation off”. Here, the olefin metathesis catalyst is placed *directly on the surface to be modified and not attached via a tether as described earlier for “grafting from”*. The polymerization then initiates only when a ROMPable monomer comes in contact with the “activated” surface. Grubbs and co-workers used this type of approach to prepare polyacetylene films [37,38] and Goodall and Standish to coat reinforcing fibers with a classical ROMP catalyst to prepare molded polynorbornene articles [39].

CMP involves formation of a polymer film when a latent active surface, which is prepared by application of a well-defined initiator to any substrate, is exposed to a ROMPable monomer (Fig. 3). As new alkylidenes are formed during the polymerization, they serve as sites for further reaction with either the same or another monomer.¹ In this manner, coatings and films of

¹ [4], Chapter 3.

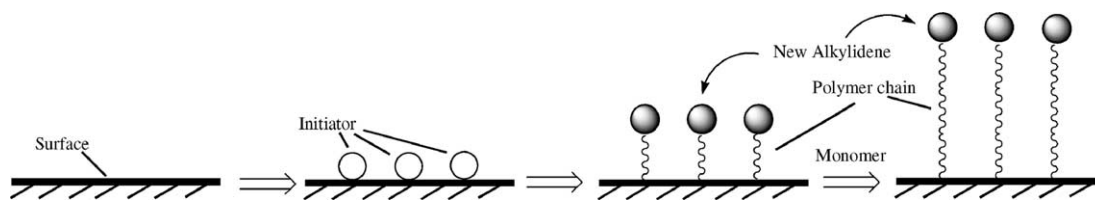


Fig. 3. Coating prepared by ROMP.

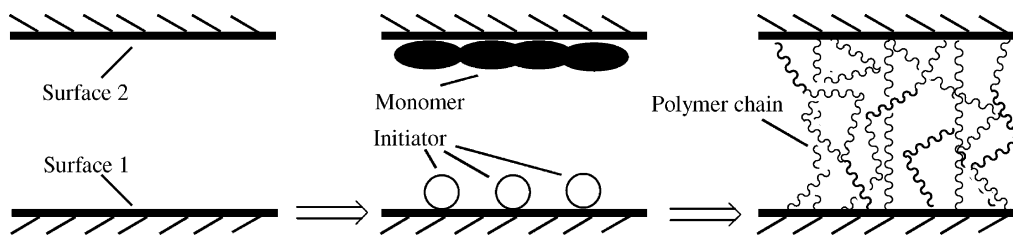


Fig. 4. Adhesive bond created by ROMP.

controlled thickness, functionality, and properties can be prepared.

Similarly, Fig. 4 illustrates how an adhesive bond is created by ROMP. One substrate is coated as above with catalyst to give a latent active surface and the other coated with a ROMPable monomer. When the two surfaces contact, ROMP ensues forming an adhesive bond between the substrates.

From the idealized depictions of each process, the generality of this method is clear. Likewise, it is also clear this methodology lends itself to highly complex examples wherein mixtures of monomers, fillers, extenders, and additives can be easily formulated and applied to give useful properties as required for the application. We envisioned that the olefin metathesis catalyst might react with unreacted C=C double bonds remaining on an elastomer surface (subsequent to our findings, such behavior with polybutadiene was reported) [40], and that this could lead to covalently bound alkydienes which could then react at a later predetermined time when a ROMPable monomer was placed in contact with this “catalyzed” surface. The results of our investigation show ROMP to be an enabling surface modification technology and that extremely strong adhesive bonds are created by the use of ROMP.

Catalyst reactivity and stability are key to this approach, and well-defined olefin metathesis catalysts

are ideal because of their high activity and longevity. Their chemistry is well-understood and has paved the way for designing new robust catalysts that are functional group tolerant and give polymers with controlled architectures, molecular weights, and narrow polydispersities [41]. Air- and water-stability has emerged as catalysts with better tolerance toward polar functional groups have been developed. This property is most apparent with the ruthenium-based systems that have appeared in the past 10 years or so. For example, Grubbs’ catalyst may be safely handled in the open atmosphere as a solid and only slowly oxidizes in solution (see Section 3.4). Recently, Grubbs has quantified the relative stability of several ruthenium alkydienes towards decomposition [42,43]. Highly active Schrock alkydienes lack the tolerance to air and water of the ruthenium systems.

2. Experimental

2.1. General

^1H and ^{13}C NMR spectra were recorded on a Bruker 250 MHz NMR at 250.13 and 62.9 MHz, respectively. All chemical shifts (δ) are positive and referenced downfield from tetramethylsilane (TMS);

coupling constants (J) are recorded in Hz. Grubbs' first generation catalyst **1** and Schrock's molybdenum *t*-butoxy catalyst **3** were purchased from Boulder Scientific and from Strem Chemicals, respectively, and were used as received. All manipulations with Schrock's catalyst were performed in a Vacuum Atmospheres drybox under an argon atmosphere. Grubbs' homobimetallic catalyst **2** was prepared following a literature procedure [44]. Ethylidenenorbornene **4** (CaH_2), dicyclopentadiene **5**, methylidenenorbornene **6**, and cyclooctene **7** were purchased from Aldrich and distilled using standard practices from the reagent specified. CHCl_3 and CH_2Cl_2 were obtained from Fisher or Pharmco and used as received, except for experiments involving Schrock's catalyst, where they were distilled from CaH_2 and degassed by three freeze-pump-thaw cycles prior to use.

EPDM elastomer (BTR 96616) was obtained from British Tire and Rubber under the designation 96616 and was molded into strips ($149.4 \text{ mm} \times 25.4 \text{ mm} \times 3.2 \text{ mm}$) and cured at 154°C for 9 min. Natural rubber (A225P) was obtained from M.A. Hanna Rubber Company, Burton, OH, USA, and was molded into strips ($149.4 \text{ mm} \times 25.4 \text{ mm} \times 3.2 \text{ mm}$) and cured at 163°C for 8 min. Santoprene[®] was obtained from Advanced Elastomer Systems, St. Louis, MO, USA, and was cut into strips ($147.6 \text{ mm} \times 25.4 \text{ mm} \times 1.6 \text{ mm}$). For bonding experiments, the elastomer strips were washed with acetone and allowed to dry for several minutes prior to application of catalyst or monomer. Natural rubber and Santoprene[®] strips were lightly abraded with either 120 or 220 grit sand paper in the bonding area ($34.9 \text{ mm} \times 25.4 \text{ mm}$) prior to washing with acetone and drying. Grit-blasted steel coupons were prepared by blasting 1010 fully hardened cold rolled steel ($60.3 \text{ mm} \times 25.4 \text{ mm} \times 1.6 \text{ mm}$) with GS40 steel grit and were obtained from Northcoast Tool, Erie, PA. They were washed with acetone and dried prior to application of catalyst solution. Older unused metal coupons were freshly grit-blasted with silica sand (grit size 30–100; obtained from McMaster Carr, Inc.) prior to bonding. Spray application of catalyst was done using a Badger hobby art sprayer and Badger PROPEL (1,1-difluoroethane and butane) as propellant.

Mechanical testing was performed on an Instron Model 4204 Materials Tester equipped with a 5 kN load cell. Extent of rubber cure was measured using a Monsanto Oscillating Disk Rheometer; the cure time

is designated by a subscript which correlates to percentage of full cure strength (e.g. T_{90} = time at 90% of full cure strength).

2.2. 180° Peel test for bonded specimens

Primary adhesion of bonded specimens was measured for self- and cross-bonded specimens by pulling them on an Instron in a 180° peel configuration according to ASTM-D 429 Method B. A typical test specimen was constructed from a grit-blasted steel coupon of dimensions $60.3 \text{ mm} \times 25.4 \text{ mm} \times 1.6 \text{ mm}$ bonded to a strip of elastomer $149.4 \text{ mm} \times 25.4 \text{ mm} \times 3.2 \text{ mm}$. Samples were pulled using a crosshead speed of 50.8 mm/min . The load-at-maximum load, energy-to-break, and displacement-at-maximum load were measured. Load-at-maximum load correlates to bond strength. While energy-to-break (the area under the force-displacement curve) relates to bond toughness and displacement-at-maximum load correlates to bond elasticity, both measurements also reflect the elasticity of the bonded assembly.

After being pulled apart, the samples were inspected to determine the mode of failure. The most desirable failure mode is rubber tear (rt), wherein a portion of the elastomeric material remains on the metal coupon. Rubber tear indicates that the adhesive was stronger than the elastomeric material. Deep rubber tear failure appears similar to rubber tear, but large chunks of elastomer are pulled from one or the other side. Another failure mode is cohesive failure (coh), wherein the failure occurs within the adhesive itself. Adhesive failure (adh) occurs when the adhesive comes off completely and remains on one of the substrates, leaving nothing on the other substrate. Thin-layer cohesive failure (tlc) occurs when most of the adhesive comes off one substrate, leaving a thin-layer of adhesive on the other substrate.

2.3. CMP polymer characterization

Formation of a ROMP polymer by CMP was confirmed by comparison of spectroscopic data obtained from poly(ENB) **8** isolated from ROMP in solution and CMP ROMP from a Teflon[®] surface. Analysis of each polymer's ^1H NMR spectrum revealed significant commonality between the two isolated polymers. Namely, proton resonances were observed at 1.29,

Table 1
180° Peel test data for self-bonded elastomers at different cure levels

#	Elastomer	Full cure (%)	Load-at-maximum load (N) ^a	Energy-to-break (J) ^a	Failure mode ^b
1	Natural rubber ^c	40	368	66.5	Deep rt
2	Natural rubber ^c	70	291	47.3	Deep rt
3	Natural rubber ^c	90	294	45.6	Deep rt
4	Natural rubber ^c	100	359	38.6	rt
6	EPDM	40	219	55.6	rt
7	EPDM	70	238	58.4	rt
8	EPDM	100	172	24.4	rt

^a Average result for three specimens.

^b Notation: rt, rubber tear.

^c Surface preparation included light sanding.

1.62 (CH₃), 2.00, 2.50, 2.8–3.5, and 5.2–5.6 (vinyl) ppm in each spectrum. Similarly, their FT-IR spectra revealed strong absorption at 1377 and 966 cm⁻¹ which are characteristic of a methyl group and a *trans*-disubstituted C=C bond, respectively.

2.4. Elastomer self-bonding at different extent of cure

A catalyst solution prepared by dissolving 0.031 g of catalyst **1** in 3.20 ml of CH₂Cl₂ was applied to three elastomer strips that were then self-bonded with **4** (0.10–0.18 ml) per strip as described in the brush procedure. Once this catalyst solution had been depleted, another identical batch was prepared and used to bond another three strips. EPDM and natural rubber strips were molded and cured to different extents of cure and evaluated on an Instron (Table 1).

2.5. EPDM self-bonding using catalyst **1** and ENB **4**

Lap shear specimens were assembled using the drip procedure described later, except the catalyst solution was prepared using 0.030 g of catalyst **1** in 2.00 ml of CH₂Cl₂ and applied to two EPDM strips. Each catalyst-coated EPDM strip was bonded to another EPDM strip with 0.02 ml of **4** per strip in a lap-shear configuration, and allowed to stand at ambient conditions for 3 months. Analysis by a lap shear tensile test on an Instron showed an average load at break of 419 N.

Peel test specimens were assembled using the brush procedure described later, except the catalyst solution was prepared using 0.027 g of catalyst **1** in 2.50 ml

of CH₂Cl₂ and applied to three EPDM strips, which were bonded to an EPDM strip with 0.07–0.10 ml of **4** per strip and analyzed on an Instron (Table 2).

2.6. EPDM self-bonding using catalyst **1** and DCPD **5**

Peel test specimens were assembled using the brush procedure described later, except the catalyst solution was prepared using 0.031 g of catalyst **1** in 3.10 ml of CH₂Cl₂ and applied to three EPDM strips, which were bonded to EPDM strips with **5** as described in the brush procedure for **5** and analyzed on an Instron (Table 2).

2.7. EPDM self-bonding using catalyst **2** and ENB **4**

Peel test specimens were assembled using the brush procedure described later, except the catalyst solution was prepared using 0.031 g of catalyst **2** in 3.10 ml of CH₂Cl₂ and applied to three EPDM strips, which were bonded to EPDM strips with 0.16 ml of **4** per strip and analyzed on an Instron (Table 2).

2.8. EPDM self-bonding using catalyst **3** and ENB **4**

Peel test specimens were assembled using the brush procedure described later, except that two separate catalyst solutions were prepared to self-bond unsanded and sanded EPDM strips. The first solution was prepared by dissolving 0.0216 g of catalyst **3** in 2.00 ml of CH₂Cl₂ and applied to two unsanded EPDM strips,

Table 2
180° Peel test data for self-bonded elastomers

#	Elastomer	Sanded	Catalyst	Monomer	Load-at-maximum load (N) ^a	Energy-to-break (J) ^a	Failure mode ^b
1	EPDM	Yes	1	4	166	25.6	rt
2	EPDM	No	1	4	176	27.0	Deep rt
3	EPDM	No	1	5	182	26.5	rt
4	EPDM	No	2	4	126	11.4	rt
5	EPDM ^c	Yes	3	4	13 ^d	0.8 ^d	tlc/adh
6	EPDM ^c	No	3	4	9 ^d	0.3 ^d	tlc/adh
7	Santoprene [®] 101-64	Yes	1	4	79	3.4	rt
8	Santoprene [®] 101-64	No	1	4	7	0.3	tlc
9	Santoprene [®] 201-64	Yes	1	4	72	3.4	rt
10	Santoprene [®] 201-64	No	1	4	7	0.4	tlc
11	Santoprene [®] 201-87	Yes	1	4	68	4.1	tlc
12	Santoprene [®] 201-87	No	1	4	6	0.3	tlc
13	Santoprene [®] 8201-90	Yes	1	4	28	1.6	tlc
14	Santoprene [®] 8201-90	No	1	4	5	0.2	tlc

^a Average result for three specimens.

^b Notations: rt, rubber tear; tlc, thin-layer cohesive; adh, adhesive.

^c Surface preparation included light sanding. Handled under an argon atmosphere (see Section 2).

^d Average result for two specimens.

which were bonded to EPDM strips with 0.08 ml of **4** per strip as described in the brush procedure later. The second solution was prepared by dissolving 0.0211 g of catalyst **3** in 0.70 ml of CH₂Cl₂ and applied to sanded EPDM strips, which were bonded to EPDM strips with 0.13 ml of **4** per strip as above. All specimens were analyzed on an Instron (Table 2).

2.9. Santoprene[®] self-bonding with catalyst **1** and ENB **4**

A catalyst solution prepared by dissolving 0.030 g of catalyst **1** in 2.50 ml of CH₂Cl₂ was applied to three strips of four types of Santoprene[®] (101-64, 201-64, 201-87 and 8201-90), which were self-bonded with **4** as described in the brush procedure. The amount of **4** applied to the surface depended on the surface treatment: 0.06 ml for unsanded and 0.16 ml for sanded strips. Once this catalyst solution had been depleted, another identical batch was prepared and used to bond another three strips. The bonded specimens were analyzed on an Instron (Table 2).

2.10. Typical CMP procedure whereby catalyst was applied to surface by drip

A catalyst solution was prepared by dissolving 0.021 g of catalyst **1** in 1.50 ml of CH₂Cl₂. A volume

of 0.50 ml of this solution was then applied to one grit-blasted steel coupon by pipette to just cover its bonding surface (34.9 mm × 25.4 mm). The solvent was allowed to evaporate for 3–4 min in the fume hood. To each EPDM strip (34.9 mm × 25.4 mm) was applied via syringe 0.03 ml of **4** while spreading the liquid evenly with the needle tip. The catalyst-coated metal coupon was immediately mated with the monomer-coated EPDM strip and loaded with a weight of approximately 100 g. Twelve specimens, which were prepared in this manner using fresh catalyst solution for every fourth coupon, sat at ambient conditions for 16–22 h before being evaluated on an Instron (Table 3).

2.11. Typical CMP procedure whereby catalyst was applied to surface by brush

A catalyst solution was prepared by dissolving 0.021 g of catalyst **1** to 1.50 ml of CH₂Cl₂ in a screw-cap vial under N₂. This solution was applied by brush to three grit-blasted steel coupons, and the solvent was allowed to evaporate in the fume hood during the brushing process, thus, leaving the catalyst powder evenly distributed over the bonding surface (34.9 mm × 25.4 mm). After drying, all prepared samples were weighed to determine the amount of catalyst which averaged 5.8 ± 1.8 mg per coupon. When the

Table 3
180° Peel test data for cross-bonding of grit-blasted steel to EPDM

#	Monomer	Catalyst	Catalyst application method	Load-at-maximum load (N)	Energy-to-break (J)	Failure mode ^a
1	4	1	Drip	273 ^b	37.9	rt
2	4	1	Brush	284 ^b	41.7	rt
3	4	1	Spray	352 ^b	61.2	rt
4	4	2	Brush	227 ^c	26.8 ^c	rt
5 ^d	4	3	Brush	47 ^e	1.5 ^e	tlc/adh
6 ^f	4	3	Brush	139 ^e	11.1 ^e	rt/tlc
7	5	1	Brush	291 ^c	44.4 ^c	rt
8	6	1	Brush	41 ^c	1.5 ^c	tlc/adh
9	7	1	Brush	–	–	–

^a Notations: rt, rubber tear; tlc, thin-layer cohesive; adh, adhesive.

^b Average result for twelve specimens.

^c Average result for six specimens.

^d EPDM strips had a 2 months residence time in the drybox.

^e Average result for three specimens.

^f EPDM strips were bonded within 1–2 h of placement into the drybox.

solution was depleted, another batch of fresh catalyst solution was prepared and applied as described earlier. A total of 12 samples were prepared in this manner. EPDM strips were prepared by washing the bonding surface with acetone, drying at room temperature for 3–4 min, and then applying via syringe 0.03 ml of **4** to each coupon and spreading it evenly with the needle tip. The catalyst-coated metal coupon was immediately mated with the monomer-coated EPDM strip and loaded with a weight of approximately 100 g. The samples sat at ambient conditions for 16–22 h before being evaluated on an Instron (Table 3).

2.12. Typical CMP procedure whereby catalyst was applied to surface by spray

A catalyst solution was prepared by dissolving 0.50 g of catalyst **1** in 20.00 ml of CH₂Cl₂. The catalyst solution was sprayed onto 12 grit-blasted steel coupons with a sweeping motion until evenly appearing coverage was obtained on the surface to be bonded (34.9 mm × 25.4 mm). The solvent was allowed to evaporate for 1.5 h in the fume hood. After drying, all samples were weighed to determine the amount of catalyst which averaged 9.0 ± 0.95 mg per coupon. EPDM strips were prepared by washing the bonding surface (34.9 mm × 25.4 mm) with acetone and drying at room temperature for 3–4 min. Then, 0.06 ml of **4** was applied to each coupon via syringe while

evenly spreading the liquid with the needle tip. The catalyst-coated metal coupon was immediately mated with the monomer-coated EPDM strip and loaded with a weight of approximately 100 g. The samples sat at ambient conditions for 16–22 h before being evaluated on an Instron (Table 3).

2.13. Cross-bonding of EPDM-to-grit-blasted steel using catalyst **1** and DCPD **5**

A catalyst solution was prepared by dissolving 0.031 g of catalyst **1** in 3.20 ml of CH₂Cl₂ and applied to grit-blasted steel coupons, which were bonded to EPDM strips with **5** as described in the brush procedure. The procedure for application of **5** varied slightly from that with **4**. The **5** was gently heated with a heat gun. Once liquid, it was pipetted and spread onto the EPDM surface. Once applied, the monomer-coated surface was gently heated with a heat gun to melt the solid; the metal and elastomer strips were immediately mated and loaded with a weight of approximately 100 g. The specimens were analyzed on an Instron (Table 3).

2.14. Cross-bonding of EPDM-to-grit-blasted-steel using catalyst **1** and methylenenorbornene **6**

A catalyst solution was prepared by dissolving 0.031 g of catalyst **1** in 3.20 ml of CH₂Cl₂ and applied

to three grit-blasted steel coupons, which were bonded to EPDM with 0.10 ml of **6** per coupon as described in the brush procedure. The bonded specimens were analyzed on an Instron (Table 3).

2.15. Cross-bonding of EPDM-to-grit-blasted steel using catalyst **1** and cyclooctene **7**

The typical procedure as described in the brush procedure earlier was used. No analysis was performed on the Instron as the specimens easily fell apart during handling. Visual inspection revealed the mated surfaces to be essentially free of adhered polymer.

2.16. Cross-bonding of EPDM-to-grit-blasted steel using homobimetallic catalyst **2** and ENB **4**

A catalyst solution was prepared by dissolving 0.030 g of catalyst **2** in 3.1 ml of CH₂Cl₂ and applied to three grit-blasted steel coupons, which were bonded to EPDM strips with 0.08 ml of **4** per coupon as described in brush procedure. The specimens were analyzed on an Instron (Table 3).

2.17. Cross-bonding of EPDM-to-grit-blasted steel using catalyst **3** and ENB **4**

In a drybox under argon, a catalyst solution was prepared by dissolving 0.021 g of catalyst **3** in 2.00 ml of CH₂Cl₂ and applied to three grit-blasted steel coupons, which were bonded to EPDM strips with 0.08–0.09 ml of **4** per coupon as described in the brush procedure. The original grit-blasted metal and rubber coupons had been stored in the drybox for 2 months to ensure com-

plete removal of any water or oxygen contamination. This was later found to be unnecessary as bonding was observed for samples with only 1–2 h residence time in the drybox. All specimens were analyzed on an Instron (Table 3).

2.18. Cross-bonding of natural rubber-to-grit-blasted steel using catalyst **1** and ENB **4**

Catalyst **1** was applied to grit-blasted steel coupons and bonded with 0.10 ml of **4** per coupon using the brush process. Four natural rubber samples were prepared: two sanded and two unsanded. After sitting for 2 days at room temperature, the two specimens prepared from sanded natural rubber easily pulled apart and failed by tlc, thus, leaving a thin poly(ENB) **8** film on the natural rubber strip. The two specimens prepared from unsanded natural rubber could not be pulled apart and were analyzed on an Instron using a 180° peel test showing a mean load at maximum load of 183 N and a mean energy-to-break of 12 J.

2.19. Cross-bonding of Santoprene®-to-grit-blasted steel using catalyst **1** and ENB **4**

A catalyst solution was prepared by dissolving 0.030 g of catalyst **1** in 3.00 ml of CH₂Cl₂ and applied to grit-blasted steel coupons following the brush procedure to give an average weight of 9.4 ± 1.2 mg of catalyst per coupon. The coupons were bonded to three samples of four types of sanded Santoprene® (101-64, 201-64, 201-87 and 8201-90) with 0.08 ml of **4** per coupon. The bonded specimens were analyzed on an Instron (Table 4).

Table 4

180° Peel test data for cross-bonding of grit-blasted steel to Santoprene® with catalyst **1** and monomer **4**

#	Type ^{a, b}	Load-at-maximum load (N) ^c	Energy-to-break (J)	Failure mode ^d
1	Santoprene® 101-64	104	3.4	rt
2	Santoprene® 201-64	92	4.3	rt
3	Santoprene® 201-87	88	3.6	tlc/adh
4	Santoprene® 8201-90	187	6.3	tlc/adh

^a Type refers the durometer number for the Santoprene® with hardness increasing as the last number increases. Thus, 8201-90 is harder than 101-64, 201-64.

^b All elastomers were sanded.

^c Average result for three specimens.

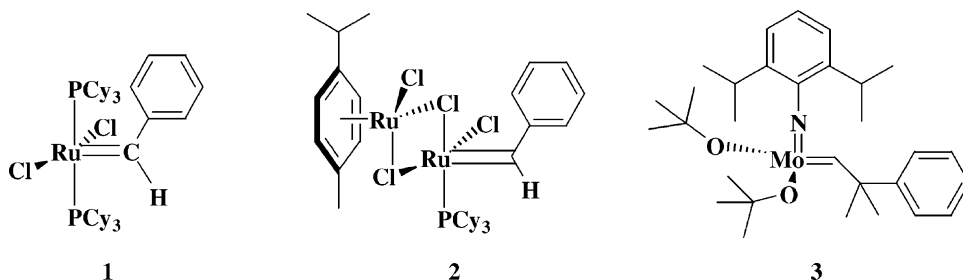
^d Notations: rt, rubber tear; tlc, thin-layer cohesive; adh, adhesive.

2.20. Activity of Grubbs' catalyst **1** in solution

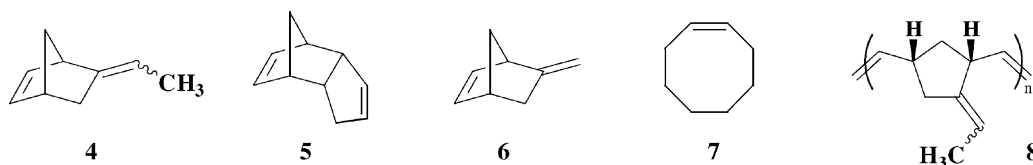
To a 250 ml round bottom flask with a single 24/40 ground glass joint equipped with a stirring bar was charged 0.053 g (0.0644 mmol) of catalyst **1** and 100.0 ml of CH₂Cl₂. The vessel, which was open to the fume hood atmosphere, was rapidly stirred so that a vigorous vortex pumped air into the solution. At a predetermined time interval, 5.0 ml of catalyst solution was added to a test tube that contained a wooden stirring stick. Immediately, 1.60 ml (11.9 mmol) of **4** was syringed into the catalyst solution. The solution was stirred until the first appearance of bubbles which defined the rate of polymerization. Typically, gelation and solidification occurred simultaneously with bubble formation.

3. Results and discussion

As described earlier, our surface-initiated polymerization utilizes an "initiation off" approach in which the catalyst is applied directly to the surface to be modified. Several well-defined catalyst systems were used in this study: Grubbs' first generation catalyst **1** [45], Grubbs' homobimetallic catalyst **2** [44], and Schrock's molybdenum *t*-butoxy catalyst **3** [46].



In this study, we concentrated on four monomers: ethylenenorbornene **4**, dicyclopentadiene **5**, methylenenorbornene **6**, and cyclooctene **7**. In principle, any monomer capable of undergoing ROMP is capable of being used in this process.



A variety of materials typically used by researchers in the adhesives industry including elastomers such as natural rubber (pre- and post-vulcanized), ethylene-propylene–diene–monomer (EPDM, pre- and post-vulcanized), Santoprene[®] (EPDM/polyethylene blend), and grit-blasted steel were used as substrates for adhesion testing.

3.1. Bonding properties versus extent of rubber cure

During initial bonding attempts using CMP, we determined that post-vulcanized elastomers strongly adhere to themselves and to other substrates. This was surprising since bonding to post-vulcanized elastomers is very difficult. Adhesive bonds to elastomeric substrates are usually made while the elastomer is in the pre-vulcanized state [47]. To understand how the extent of cure ($T_{\%}$) affected elastomer adhesion, a series of adhesive joints were prepared using catalyst **1**, monomer **4**, and pre- and post-vulcanized natural rubber and EPDM and analyzed by mechanical testing using a 180° peel test (Table 1).

Variability in load-at-maximum load (bond strength) was observed for the pre- and post-vulcanized bonded elastomer specimens. A trend to lower energy-to- was observed in going from pre- to post-vulcanized

specimens. At comparable bond strengths, the softer elastomer (# 1) will require greater energy to reach failure than the stiffer elastomer (# 4). As there was little change in bond strength with extent of cure of

the elastomer, the remaining bonding tests were performed with post-vulcanized elastomers only.

3.2. Elastomer self-bonding

Early in this study, elastomer self-bonding was examined to determine the generality of CMP. Before too much work had been done, surface pre-treatment affects on adhesion had to be ascertained. In practice, surface preparation may range from rough abrasion to simply to wiping any dust from the surface. Ideally, minimal procedures are desired. Several trends were noted during the course of this investigation. All elastomeric substrates required removal of any surface oils by wiping with acetone prior to bonding. This was particularly true for EPDM. Interestingly, EPDM required no surface abrasion for good adhesion. This is clear by examining EPDM self-bonding results shown in Table 2 (# 1 and 2; 5 and 6). There was also little bond strength difference between specimens bonded with **4** and **5** (# 2 and 3). While not statistically significant, adhesion appeared to be improved when bonding to the unsanded surface. Even though, both treatments showed rubber tear (rt), the unsanded specimens had large chunks of rubber removed from the surface suggesting this to be a better bond. Catalyst choice was extremely important for good results. Grubbs' first generation catalyst **1** clearly gave superior results (# 2 versus 4, 6). The difference in bond strength between Grubbs' catalysts **1** and **2** is unclear; however, the lower value results obtained with Schrock's catalyst **3** can be attributed to its lower tolerance to impurities in the reaction medium (i.e. additives formulated into the elastomer). With this in mind, it is surprising that the molybdenum catalyst performed at all under these conditions.

Post-vulcanized Santoprene[®] behaved differently. The best results were obtained when the elastomer surfaces were lightly abraded by sanding (Table 2; # 7, 8; 9, 10; 11, 12; 13, 14). For well-performing Santoprene[®] specimens, bond strengths dropped and the failure mode changed from rt to thin-layer cohesive (tlc) (# 7, 9, 11, 13). These changes are likely related to increased elastomer hardness, which results from increased polyethylene content in the blend. This trend to poorer bonding may reflect the difficulty to adhere to polyethylene [48,49].

3.3. Elastomer cross-bonding

Another parameter that was examined was the method of catalyst delivery to the surface. In these experiments, grit-blasted steel was bonded to post-vulcanized EPDM using catalyst **1** and monomer **4**. It was important to place the catalyst on the metal rather than on the elastomer surface otherwise sporadic adhesion resulted. Three modes of catalyst delivery were investigated involving CH₂Cl₂ evaporation from: (1) a catalyst solution applied dropwise to the surface via syringe; (2) a catalyst solution repeatedly brushed onto the surface; and (3) a catalyst solution sprayed onto the surface.

Even though, all bonds failed with rubber tear, bond strength depended heavily on the method of delivering Grubbs' catalyst to the grit-blasted steel surface (Table 3, # 1, 2, 3). Even with some variability in catalyst surface loading between the different application methods, this result is best explained by considering catalyst distribution on the surface of the coupon as bond strengths vary little at these catalyst loading levels [50]. Drip application produced uneven catalyst distribution by ineffectively covering both the high and low areas across the metal surface. Brush application, which was an attempt to correct this problem, resulted only in minor improvement in bond strength and energy-to-break. Spray application provided the most visually even coverage of catalyst on the surface. In addition, catalyst morphology was smooth and shiny compared to the brushed samples suggesting that particle size may be an important factor for superior adhesion.

As observed for EPDM self-bonding (Table 2), bond strengths are lower with catalysts **2** and **3** when cross-bonding to grit-blasted steel with **4** (Table 3, # 4, 5, 6 versus 2). Unexpected differences in bond strength were observed for catalyst **3** depending on the length of time the elastomer had been stored in the drybox prior to bonding (Table 3, # 5, 6). Originally, grit-blasted metal and elastomer coupons had been stored in the drybox for 2 months to ensure complete removal of any water or oxygen contamination. This was unnecessary as bonding occurred to samples with only 1–2 h residence time in the drybox. In both cases, surface oils were removed from the EPDM prior to application of the catalyst, so this behavior remains unexplained at this time. It was noted that the

coupons were immovable within 5–10 s after mating the two surfaces, suggesting that polymerization had occurred.

Finally, bond strengths for EPDM to grit-blasted steel were determined using Grubbs' catalyst and several other monomers (Table 3). Monomer **5** compares favorably with **4** (# 7, 2), but monomers **6** (# 8) and **7** (# 9) fall off dramatically, but not unexpectedly. With its exocyclic olefin **6** can act as a chain transfer agent in the ROMP, leading to lower molecular weight, lower modulus polymers in the adhesive bond. Monomer **7** polymerizes too slowly at room temperature and tends to evaporate before the polymerization can proceed to an extent to develop an adhesive bond.

Similar results were observed when cross-bonding natural rubber-to-grit-blasted steel using catalyst **1** and monomer **4** with one notable exception: specimens which were prepared by sanding the natural rubber prior to bonding easily pulled apart leaving a thin poly(ENB) **8** film on the natural rubber strip whereas specimens prepared from unsanded natural rubber could not be pulled apart. The 180° peel tests showed average maximum load of 183 N and energy-to-break of 12.2 J. This difference in bond strength as a function of surface preparation contrasts with those results observed for EPDM, where no difference was observed between sanded and unsanded

specimens (Table 2, # 1, 2). We have no explanation for these results at this time.

Finally, grit-blasted steel was cross-bonded to four types of sanded Santoprene[®] using catalyst **1** and monomer **4**. Good bond strengths were found for all specimens independent of elastomer type, which varied by durometer hardness (Table 4). However, the failure mode changed from rubber tear for the softer elastomers to thin-layer cohesive and adhesive for the harder elastomers revealing that cohesive strength is less than adhesive strength for the softer elastomers and just the opposite for the harder elastomers. This contrasts with the self-bonding experiments where the softer Santoprene[®] specimens displayed higher bond strengths than the harder ones (Table 2, # 7, 13).

3.4. Catalyst stability in air

In practice, the organometallic catalyst used in CMP would likely experience severe air exposure, so air-stability of Grubbs' first generation catalyst **1** was determined by following ROMP activity of ENB **4** with time while being stirred in a CH₂Cl₂ solution which was open to the air. After mixing an aliquot of rapidly stirring catalyst solution with **4**, gelation (solidification) time was recorded (Fig. 5). Although, these data reveal apparent drops in polymerization

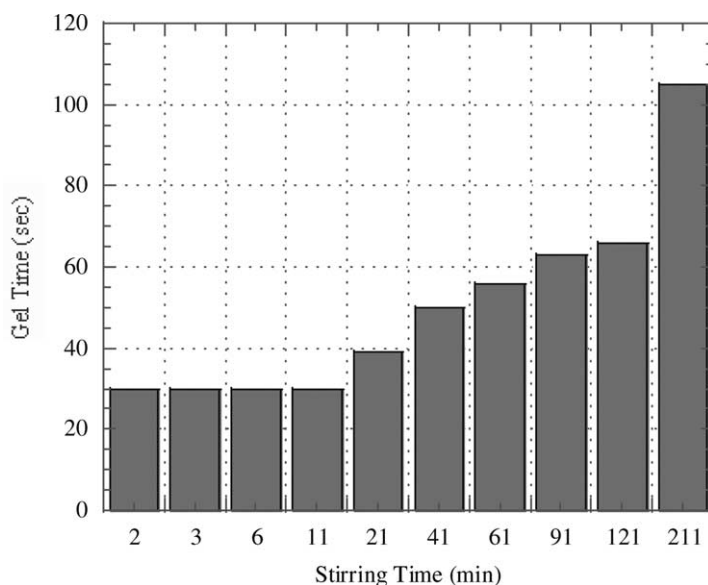


Fig. 5. Air-stability of Grubbs' first generation catalyst **1** in CH₂Cl₂ solution.

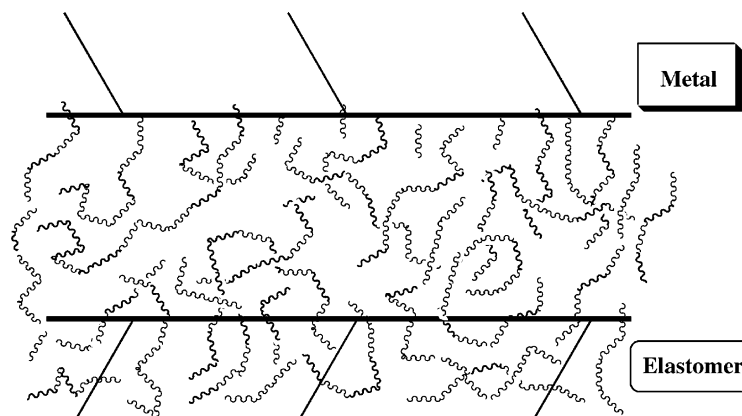


Fig. 6. Interpenetrating network formation in a CMP interface.

rate of 30% after 20 min, 87% drop after 60 min, and 250% after 210 min, the catalyst was extremely active considering these ROMPs were performed at 3719:1 monomer to catalyst levels. The catalyst activity eventually dropped to zero. During the experiment, the catalyst solution changed color from light-purple to gold to military-green.

3.5. Adhesion mechanism

Many rationalizations have been advanced to explain adhesion phenomena including electrostatic theory, diffusion, mechanical interlocking, wettability, acid–base interactions, and covalent bonding [51]. Understanding what is responsible for formation of an adhesion bond is complex as many of these rationalizations usually operate simultaneously. At this time, we have little direct evidence to attribute the excellent adhesion reported herein to one or another mechanism. On the metal side, adhesion appears to come primarily from mechanical interlocking of the growing polymer chains with the surface. Support for this hypothesis comes from elastomer-to-metal adhesion data wherein metals with different surface roughness show decreased bond strengths as roughness decreases [52]. Wetting of the elastomeric surface with a relatively nonpolar monomer is believed to be very important in adhesive bond formation. Furthermore, diffusion of the monomer into the surface followed by reaction with the invading ruthenium alkylidene and formation of a kinetically stabilized interpenetrating network is likely occurring (Fig. 6).

Monomer diffusion is rapid into these elastomeric substrates [53] and appears to be important to overall bonding. There is also potential for covalent bonding of the propagating alkylidene with any unsaturation remaining in the elastomer.

4. Summary

Contact metathesis polymerization is new technology with potentially broad application in adhesives, coatings, and materials technologies. By placement of a well-defined ring-opening metathesis polymerization catalyst directly on a surface and contacting this surface with another surface to which a ROMPable monomer has been applied, an adhesive bond between the two surfaces is created. Excellent primary adhesion results in self-bonding and cross-bonding modes with post-vulcanized elastomers such as EPDM, Santoprene®, and natural rubber. The chemistry uses commercially available materials, is a low energy process, works in the open air, and is a low to zero VOC system. Surface modification via this approach opens the door to producing polyfunctional coatings and adhesion activators through the use of functional monomers.

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