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Cross-Linkers for Improved High Temperature Performance of ROMP Adhesives

Christopher G. Keck,[a] Jonathan L. Kendall,[b,c] and Kenneth C. Caster[a,d,*]

[a] Lord Corporation, Materials Division, 110 Lord Drive, Cary, North Carolina 27511, USA
[b] Lord Corporation, Chemical Products Division, 110 Lord Drive, Cary, North Carolina 27511, USA
[c] Current address: Hanover Dental Company, P.O. Box 241301, Charlotte, North Carolina 28224, USA
[d] Current address: Center for Biologically Inspired Materials and Material Systems, Duke University, Durham, North Carolina 27708, USA
Fax: (+1)-919-549-4310; e-mail: ken.caster@duke.edu

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Abstract: Ring-opening metathesis polymerization (ROMP) has been shown to be an effective methodology to make adhesive bonds between various substrates. Excellent adhesion has been demonstrated on a variety of substrates including post-vulcanized elastomers, polyolefins, and metals. Strong adhesion results when one substrate surface is coated with the metathesis catalyst and the other substrate surface is coated with a ROMPable monomer. Concerns over using ROMP-based adhesion in dynamic applications where the bond-line could experience higher-than-ambient temperatures prompted this investigation. In this report, a variety of bis-norbornadiene cross-linkers were used to bond tire carcass, tire tread, post-vulcanized EPDM, and grit-blasted steel in a variety of self- and cross-bonded configurations. The resulting bonded assemblies were then evaluated using a 180° peel test in a temperature range from −40 °C to 66 °C at various cross-linker concentrations. Significant improvements in bond strength were observed at elevated temperature with little detrimental affect on low temperature strengths even at high cross-linker concentration. Self-bonding of polyolefins assemblies was also investigated. Addition of a peroxide radical initiator to the initial ROMP formulation and cross-linking the bonded assembly in a post-cure reaction was also found to lead to improved high temperature bond strength. Synthetic details for the preparation of several cross-linkers are reported.

Keywords: adhesion; cross-linker; metathesis; peroxides; polymerization; ROMP

Introduction

The increasingly wide range of industrial products that could best be fabricated or repaired using structural adhesives has created a continual need for new adhesive curing methods. These structural adhesives must withstand exceptionally high stresses and adverse environmental conditions that are placed on the adhesive joint. Adhesives that cure by ring-opening metathesis polymerization (ROMP) possess several particularly attractive traits compared to traditional commercial adhesives. Very fast cure speeds, resulting in high product throughput, can be achieved with well-defined catalysts such as Grubbs' 1st and 2nd generation ruthenium catalysts. Another important advantage results from the hydrocarbon nature of most available ROMP monomers, which readily wet low surface-energy substrates. Wetting is thought to be a key factor in obtaining good adhesion to these difficult-to-bond substrates, which include industrially-important materials like post-vulcanized rubber, EPDM-based elastomers, polyethylene, and polypropylene. Finally, ROMP-cured adhesives contain olefins that are suitable for secondary reactions within the adhesive or between the adhesive and the substrate.

ROMP has been found to be an effective polymerization methodology to create adhesive bonds between substrates. Strong primary adhesion has been demonstrated both with dispensed adhesives[1] and with surface-activated approaches. In the latter approach (contact metathesis polymerization, CMP), a well-defined catalyst is applied directly to one and the monomer to the other substrate surface – adhesion occurs when the two substrates come in direct contact. This grafting-off process was investigated for cold bonding of pre- and post-vulcanized elastomers, polyolefin-filled elastomers, and metal-elastomer composites using Grubbs' 1st generation ruthenium catalyst and dicyclopentadiene (DCPD), ethylidenenorbornene (ENB), and methylidenenorbornene (MNB) as monomers.[2] Room temperature bond strengths were very high, with rubber tear being the primary mode of substrate failure. Good bond strengths also resulted when a similar, but slightly modified, process was used to adhere natural rubber elastomers to different multifilament fibers including nylon, polyester, and Kevlar®.[3] This methodology also works well for generating coatings with excellent protective properties. Others have used grafting-off, whereby polymerization is initiated from a physisorbed initiator, to make polymer-coated pigment particles[4] and to functionalize poly(dimethylsiloxane).[5]

Because adhesively-bonded industrial products, especially those using natural rubber and EPDM elastomers, are often subjected to high temperature, adhesives for these purposes must have good high-temperature strength. We were concerned that adhesives based on the above-described technology might display low bond strengths at high temperature above the glass transition temperature of the linear polymer. To solve this problem we reasoned that cross-linking the *in situ* generated ROMP polymer should improve high temperature strength.

Two approaches to address this high temperature stability problem were considered. Initially, we concentrated on building cross-links into the polymer network as the polymer propagated. The key to this approach is to use ROMPable monomers that will cross-link into the system and not significantly change the reaction rate. Cross-linker solubility was expected to be important, so we focused on hydrocarbon based bis-norbornadiene systems as they should be more soluble in the hydrocarbon ROMP monomer and compatible with its resultant polymer. In the other approach, cross-linking of the network by a different chemistry was performed after the ROMP. Both approaches resulted in improvements in high temperature bond strength and are described below. Finally, we examined how adding cross-linking agents affected self-bonding of polyolefins.

Multiple approaches have been reported to cross-link ROMP polymers including post-cross-linking of methacrylate[6,7] and epoxide[7] side-chains which are attached to the ROMP polymer backbone; by addition of peroxide initiators to the ROMP polymer matrix;[8,9] by molecular recognition and self-assembly either by H-bonding;[10–12] or the formation of transition metal pincer complexes;[12] or through metathesis.

Numerous examples of metathesis-based cross-linking have been reported. Examples include polymerizing the secondary olefin in DCPD;[13] while others involve the preparation of monoliths from functionalized norbornenes and multicyclic dienes;[14–17] synthesis of molecularly imprinted polymers from DCPD and functionalized norbornenes;[18] ligand exchange with MMA by cross-metathesis;[19] the use of mono- and di-*N*-alkyldicarboxyimidonorbornenes of different chain tether lengths;[20,21] cross-metathesis of amphiphilic copolymers;[22] and the synthesis of novel cross-linking agents.[23,24]

The patent literature has many examples where multifunctional ROMPable monomers have been added to formulations to affect cross-linking and thus improve properties. Examples include systems for making storage-stable compositions that can be polymerized by action of actinic radiation or by short-term irradiation and subsequent thermal curing;[25] preparation of highly filled systems;[26] composites with sized reinforcement material;[27] fiber reinforced composites;[28] polymerizable compositions;[29] cross-linking compositions;[30,31] dental compositions;[32] improving solvent resistance;[8,33] producing molded articles;[34] making flame-retarding articles;[35] polymerizing low grade DCPD;[36] and improving heat distortion temperature.[37]

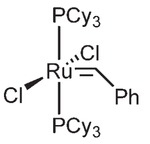
Results and Discussion

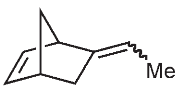
Cross-Linker Synthesis and Solubility

A variety of structures can be envisioned to be effective ROMPable cross-linking agents. For ease of availability and synthesis, we chose to examine structural types that all contained only two norbornene units per molecule. They were either available commercially, prepared from literature synthetic procedures, or newly synthesized bis-norbornadiene systems.

Initially, self-bonding of post-vulcanized EPDM using the grafting-off process was used to test the effect of cross-linker on bonding performance as we had considerable experience with this system.[2] In a typical procedure, Grubbs' 1st generation catalyst was applied to the steel surface and a mixture of cross-linker in monomer applied to the elastomer. After mating the surfaces, loading the assembly with a weight of approximately 100 grams, and allowing the assembly to stand at room temperature for at least 30 min, the assembly was subjected to a 180° peel test on an Instron test apparatus and failure analysis performed.

Adhesion is determined from the load-at-maximum load value, which is related to bond strength. While energy-to-break (i.e., 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 Instron testing, the specimens were inspected to determine the mode of failure. This subjective analysis provides information about the relative adhesive strength between the various interfaces. The most desirable failure mode is rubber tear, where a thick layer of rubber elastomer remains on one surface. Rubber tear indicates that the adhesive is stronger than the elastomeric material and that failure occurs within the elastomer and not at the elastomer-adhesive interface. Other failure modes are 1) adhesive failure (ad) which occurs between the elastomer and adhesive interface, 2) thin-layer cohesive failure (tla) in which a thin layer of adhesive remains on one surface, 3) cohesive failure occurs towards the center of the adhesive layer showing the adhesive interface to be stronger than the adhesive itself, and 4) stock break occurs when the bonded substrate fails. Typically in our systems, deep rubber tear was observed and was indicative of high bond strength and very strong primary adhesion.

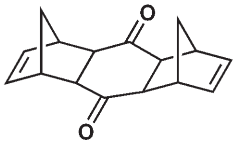




ENB

DCPD

Our first experiments involved using commercially available anthraquinone (**1**) as the cross-linker at two different concentrations (0.55 and 2.5 mol%) in ENB and Grubbs' catalyst as described above. High bond strength was observed when the assembly was peeled at room temperature, but after 30 min at 70°C, no improvement in high temperature strength was observed as all bonded specimens, which included control specimens that lacked cross-linker, could be peeled apart by hand. Attempts to dissolve relatively polar anthraquinone **1** in hydrocarbon ENB were problematic, so this result was not entirely unexpected.



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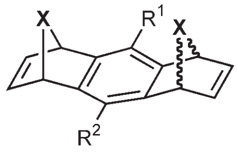

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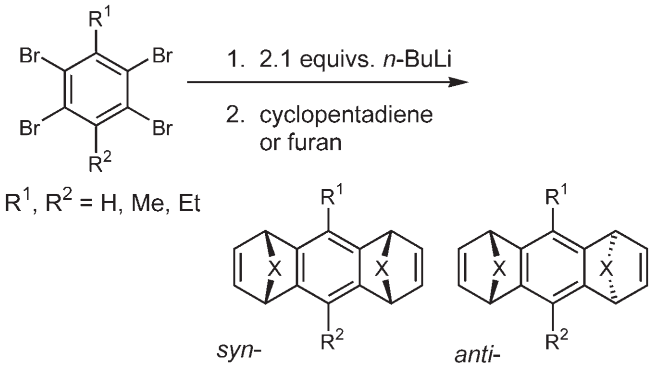
We expected that cross-linker solubility could be tuned by making slight modifications of the bis-norbornene structure, and thus turned our attention to bis-norbornadienes **2**, which are readily synthesized by Diels–Alder cycloaddition of benzynes with cyclopentadiene derivatives.[38] Structure **2** offers synthetic latitude in which polarity and symmetry can be manipulated to adjust solubility while maintaining the high ROMP reactivity associated with the benzonorbornadiene system.

The cross-linkers were prepared by dilithiation of tetrabromobenzenes followed by elimination of LiBr and subsequent trapping of the intermediate benzyne with furan or freshly cracked cyclopentadiene. While some tetrabromides were commercially available, *p*-ethyltoluene and 1,4-diethylbenzene had to be converted to their tetrabromoaromatics by bromination over Fe. The diethyl compound was prepared on a 10× larger scale with no difficulties except that addition of the benzene to the Br_2/Fe mixture was exothermic so the reaction temperature had to be carefully controlled during this step. Work-up involved removal of the excess Br_2 followed by recrystallization of the crude products from EtOH. Their structures were corroborated by ^1H and ^{13}C NMR analysis.

Starting with the appropriate tetrabromobenzene, metal-halogen exchange was done under the usual conditions[38,39] to generate the benzyne intermediate that was trapped *in situ* with freshly cracked cyclopentadiene or furan to give bis-norbornadienes **3**–**7** as white to cream-colored solids (Scheme 1). ^1H and ^{13}C NMR confirmed the products to be of high purity and to be a mixture of both *syn-* and *anti*-isomers. Furan-derived compounds **3** and **4** were found to have low solubility in the ENB, MNB, and DCPD at room temperature, but dissolved in all three at elevated temperatures. Unfortunately, they came out of solution on cooling. Less polar derivatives (**5**, **6**, **7**) were synthesized to allow control of hydrocarbon solubility (e.g., substitution on the aromatic ring to reduce symmetry, melting point, and increase hydrocarbon solubility). They readily dissolved in hydrocarbon monomers such as ENB at room temperature, but too showed differential solubility.



#	R^1	R^2	X	% yield
3	H	H	O	32
4	Me	Me	O	87
5	Me	Me	CH_2	73
6	Et	Et	CH_2	80
7	Me	Et	CH_2	57

Scheme 1. Formation of *bis*-norbornadiene cross-linkers by trapping of in situ generated benzynes.

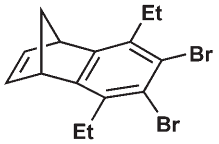
As more cross-linker was needed for these studies, compound **6** was prepared following the procedure worked out previously, but on a larger reaction scale. However, this time, the white powder contained a previously unobserved impurity. ^{1}H and ^{13}C NMR revealed the main product to be bis-norbornene (**6**, 87%) and the impurity to be dibromobenzonorbornadiene **8** (13%). Apparently, the reaction mixture was not stirred long enough at low temperature for complete lithiation of either the tetrabromobenzene or intermediate **8**. The product was easily separated from the intermediate by column chromatography.

In order to gain some insight into how other norbornadiene-based systems might behave as cross-linkers, two other compounds were synthesized from 2,5-norbornadiene (NBD). The first was 1,4-bis(2′,5′-norbornadienyl)butane (**9**), which contains two NBD units tethered with tetramethylene through one of their olefins. This compound is made by treating NBD with potassium *tert*-butoxide and *n*-butyllithium followed by 1,4-dibromobutane.[40] Purification by column chromatography (silica, hexanes) yielded a colorless liquid that is miscible with the hydrocarbon monomers used above.

The second cross-linking agent was made by the UV irradiation of NBD in the presence of a $(Ph_3)_2Ni(CO)_2$ catalyst.[41] This reaction produced a mixture **10**, which was shown by ^{1}H NMR spectroscopy to contain three dimers and one trimer in a 22:5:1:4 mole ratio. Other products were present at <1%. Because we were unsuccessful in separating the products by sublimation, as reported in the literature, we used the mixture for bonding experiments. The mixture was soluble at least up to 10 w/w% in ENB.

Variable Temperature Bond Strength Evaluation

As described earlier, we know that adhesive bonds produced by grafting-off of surfaces using ROMP chemistry performed very well at room temperature. However, many industrial applications require that an adhesive bond must be able to survive wide temperature swings and cycling. We wanted to ascertain how well a rudimentary cross-linked ROMP adhesive would perform at different temperatures in both self- and cross-bonded configurations. Tire carcass and tire tread stocks are industrially important substrates and were chosen for most of the cross-bonding work. Three different cross-linkers (**5**, **6**, **7**) were examined at different concentrations (**6**, **7**) at temperatures ranging from −40 °C to 66 °C. Cross-bonding of these stocks to grit-blasted steel was examined to develop understanding of how different elastomeric materials performed using grafting-off ROMP. Self- and cross-bonding of post-vulcanized EPDM to itself and to grit-blasted steel was also evaluated. In general, good performance was observed for nearly all conditions investigated.



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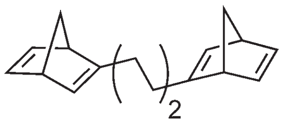

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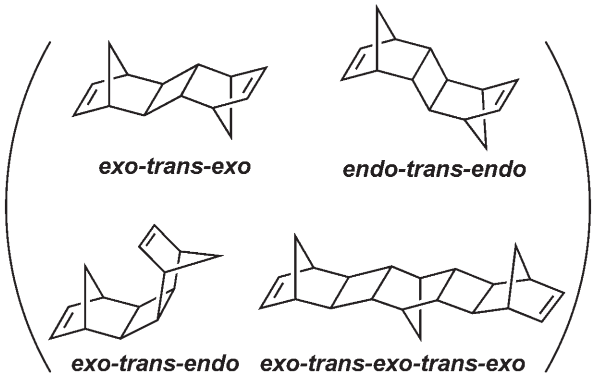

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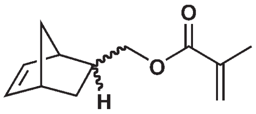

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Tire Carcass and Tread Stock Bonding

The initial studies on cross-bonding carcass-to-tread looked at temperature using cross-linkers **5**, **6**, and **7** at slightly different concentrations in ENB (2.8 to 7.9 mol%). Figure 1 shows that at −40 °C, the control (ENB without cross-linker) and the samples that contained cross-linker **6** had virtually the same load – they stretched on the Instron during testing whereas cross-linker **7** samples showed higher strength and stock failure. Unfortunately, no low temperature data were obtained for cross-linker **5** as this may have provided insight whether the higher bond strength was simply a function of cross-linker concentration. Significantly, at these high cross-linker concentrations, the adhesive bond would have likely been thought to be brittle. However, the bonded assembly remained elastic. The higher bond strength observed at the lower temperature may be explained by increased stiffness of the elastomer. The lack of joint failure is a more significant finding. As expected, all four specimens showed stock failure at room temperature. At 66 °C, incorporation of all three cross-linkers greatly increased bond strength. The control showed no rubber

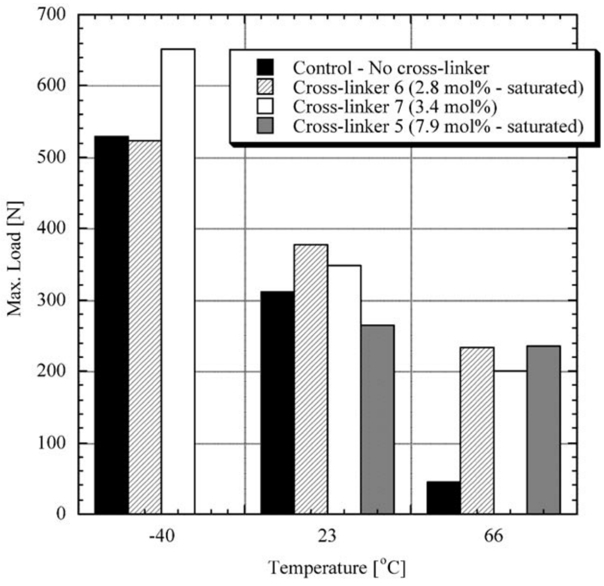


Figure 1. Comparison of bond strength for three different cross-linkers for bonding tire carcass-to-tire tread.

tear while the samples containing each cross-linker showed stock failure.

Cross-linker concentration was also examined (Figure 2). In these studies, we tried to push the limits of cross-linker solubility in ENB to see how wide changes in concentration affected bond strength. Each cross-linker sample exhibited stock failure at room temperature, independent of concentration. However, at 66 °C, failure was concentration-dependent. Cross-linker **7** samples showed no rubber tear at very high concentration (19.6 mole %), but stock failure was observed at a lower concentration (3.4 mole %). However with cross-linker **6**, bonded samples showed no rubber tear at 0.5 mole %, whereas at 2.8 mole %, stock failure was observed. While two different cross-linkers were used in this study, Figure 2 clearly shows trends in cross-linker performance: a) at room temperature, bond strength decreases at very high cross-linker concentration and b) at elevated temperature, bond strength increases to a maximum and then decreases again.

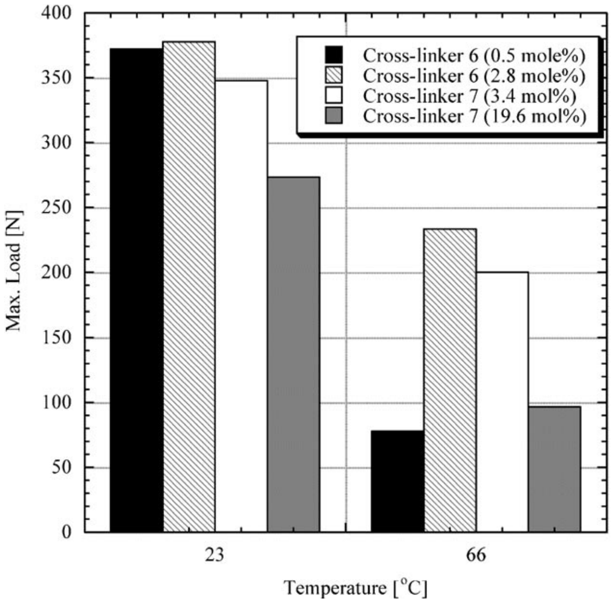


Figure 2. Effect of concentration on bond strength at elevated temperature for bonding tire carcass-to-tire tread.

In order to further our understanding of the mechanical performance of ROMP-based adhesive systems and to add to our elastomer bonding findings reported earlier,[2] elastomer-to-metal bond strength data were also obtained for both carcass and tread stocks; however, no cross-linkers were used in this study. Unsanded and sanded versions of both carcass and tread stocks were bonded to grit-blasted steel coupons with Grubbs' 1st generation ruthenium catalyst and ENB (Table 1). The carcass-to-metal specimens showed primarily adhesive failure to the metal side with only a small amount of rubber tear seen on one sample. All tread-to-metal specimens showed excellent rubber tear. In fact, the tread broke before peeling fully apart in all three samples. Bond strengths were lower for the sanded surfaces for both elastomers. The carcass-to-metal specimens showed only a very small amount of rubber tear along the perimeter of the coupons. Otherwise, the polymer film was left on the carcass surface after pulling apart. Surprisingly, the tread-to-metal specimens produced similar results – rubber tear was somewhat greater along the perimeter of these coupons but greatly reduced when compared with the unsanded tread. The lower bond strengths observed with the carcass are expected as this elastomer is considerable softer than the tread.

Table 1. Elastomer-to-metal bonding for unsanded and sanded carcass and tread stocks.

Elastomer	Sanded	Load at Max. Load (N)[a]	Energy to Break-Point (J)[a]	Failure mode[b]
Carcass	No	120	5.2	adh
Tread	No	280	40.5	stock break
Carcass	Yes	80	3.2	adh
Tread	Yes	214	24.6	adh

[a] Average result for three specimens.

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

EPDM Bonding

The results were very different when cross-linker **6** dissolved in ENB was used to self-bond EPDM using Grubbs' 1st generation catalyst. At room temperature, bond strength was essentially unaffected by cross-linker (196 N, 0.5 mol%) vs the control (178 N). Similarly at 66 °C, no improvement in bond strength was observed for the cross-linked systems (107 N, 0.5 mol%; 98 N, 2.8 mol%) *vs.* the control (98 N). However, there was an increase in bond strength when cross-linker **6** (0.5 mol%) was used to cross-bond EPDM-to-grit-blasted steel. Compared to the control (285 N), a slight improvement in bond strength was seen even at low levels of cross-linker (320 N, 0.5 mol%) at room temperature. All samples displayed good rubber tear; in fact, some of the cross-linker **6** samples showed stock failure. There was an even more dramatic effect at 66 °C. Here, the control samples (85 N) showed little rubber tear while samples formulated with cross-linker **6** (133 N) showed good rubber tear.

Polyolefin Adhesion

The tethered cross-linker 1,4-bis(2′,5′-norbornadienyl)butane **9** was used neat to bond unsanded polypropylene coupons as lap shear samples. This compound took several times longer to cure than the ENB control. However, it gave the same mean break values at room temperature: 302±40 N versus 294±76 N.

The NBD dimmer/trimer mixture **10** was used to bond sanded polypropylene lap shears assemblies at a series of concentrations. Compared with the control specimen (1548±169 N), a 17% improvement in room temperature bond strength was observed for samples that contained cross-linker (2 w/w%, 1806±214 N; 5 w/w%, 1802±102 N; 10 w/w%, 1810±142 N). The two NBD-based cross-linkers have not yet been tested at elevated temperatures.

Post-Cross-Linking Reactions

As described above, examples of cross-linking ROMP polymers in a post-polymerization reaction have been reported.[8] Improved solvent resistance was observed by thermally post-curing a poly(DCPD) resin which contained a peroxide [e.g., Luperox® 130; 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)hex-3-yne] that had been added to the initial monomer/catalyst mixture prior to ROMP. Higher cross-link densities likely resulted from this treatment than would occur by metathesis only. In practice, once the ROMP polymer has formed, then a separate post-bake cycle would be used to kick off the peroxide initiator and further cross-link the poly(DCPD) to get improved performance.

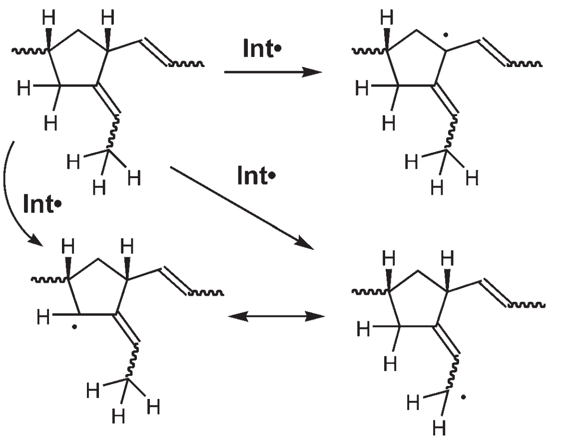
While DCPD is known to cross-link during metathesis through a secondary reaction of the cyclopentenyl ring,[13] we wanted to determine whether post-cure cross-linking could be used to improve high temperature adhesion using monomers that give linear polymers and that do not readily undergo secondary reaction. Bonding experiments were done to determine adhesion performance for specimens where cross-linking was performed by post-reaction using radical initiators that had been added to ENB prior to ROMP with Grubbs' 1st generation ruthenium catalyst.

Before attempting to bond any assemblies however, effort was spent to identify the radical initiator and reaction conditions that would be used during the post-bake cycle. In these tests, mixtures of ENB and Wako azo radical initiator V-65 ($T_{1/2}=51\,°C$) were heated under N_2 in a glass vial for different time periods. Changes in viscosity were used as evidence of reaction. Unfortunately, no polymerization was noted under any conditions for any reaction mixture [at 60 °C for 5 h at 1 w/w% V-65 in ENB and 9.2 w/w% V-65 in ENB; 110 °C for 2 h at 5 w/w% V-65 in ENB]. In each case a light-yellow liquid remained with no apparent polymerization.

The initiator was tested for activity by heating a 1 w/w% solution of V-65 in Cyclol Methacrylate® **11** at 110 °C under N_2. Indeed, the solution bubbled into a hard mass within a few minutes after placing it into the heated atmosphere thus demonstrating that the initiator was indeed active. While disconcerting that no reaction appeared to occur with ENB alone, it was decided that poly(ENB) should be used in place of ENB as this would represent more realistic bonding conditions. A polymer solution was then prepared from ENB and Grubbs' catalyst in toluene (M:I=3000:1). Once the polymer had been prepared, the V-65 was added to an aliquot of solution and heated at 90 °C for two hours under N_2. Again, no polymerization appeared to occur as evidenced by lack of insoluble product.

An explanation for this apparent lack of reactivity likely involves chain-transfer from ENB or poly(ENB) allylic protons to the radical initiator and formation of allylic and doubly allylic radical species through radical abstraction reactions (Scheme 2). In addition to chain-transfer limiting the cross-link density, the stabilized allylic radicals would be less reactive than normal alkyl radicals.

If the above hypothesis is operative, then other radical initiators should also be unsuccessful. However as described above,[8] the peroxide initiator Luperox® 130 has been shown to be effective at cross-linking bulk poly(DCPD). Thus, freshly grit-blasted steel cou-



Scheme 2. Abstraction of some of the allylic and doubly-allylic hydrogens on poly(ENB) by a radical initiator.

pons were bonded to post-vulcanized EPDM using Grubbs' 1st generation catalyst and a mixture of ENB that contained 2.9 w/w% (1.2 mol%) of Luperox® 130. Thirty minutes after bonding, the specimens were post-cured in an oven at 120 °C for 1.5 h (purged with N_2). The specimens were evaluated on the Instron using the 180° peel test at room temperature and 66 °C (Figure 3). These data show increased bond strength for the post-baked specimens over both control and cross-linker **6** bonded specimens at both room and elevated temperatures. Failure analysis, however. showed small amounts of metal-adhesive and rubber-adhesive modes to be present, which were absent with the bis-norbornadiene cross-linker **6**. Such mixed failure modes are common.

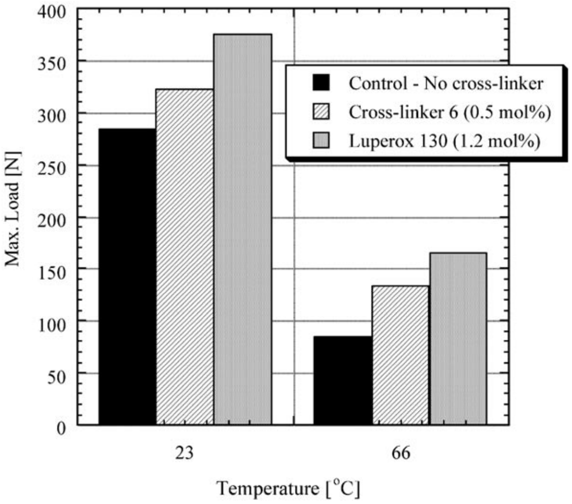


Figure 3. Comparison of bond strength for post-vulcanized EPDM-to-Grit-Blasted Steel using metathesis and peroxide cross-linkers.

Conclusions

Ring-opening metathesis polymerization was used to investigate cross-linking and its affect on adhesion at different temperatures. Surface-initiated ROMP, a grafting-off process where the well-defined catalyst was applied to one substrate surface and the monomer/cross-linker to the other substrate surface, was used to assemble self- and cross-bonded specimens constructed from tire carcass and tread rubber stocks, post-vulcanized EPDM, grit-blasted steel, and polypropylene. Cross-linkers evaluated in this study were based on bis-norbornadienes and were synthesized using cycloaddition reactions and literature syntheses. Cross-linker solubility in the ROMP monomer was found to be a critical variable as too low a concentration did not result in improve performance. Except for self-bonded EPDM, significant improvements in bond strength were observed for bonded specimens at elevated temperatures with little detrimental affect on low temperature strengths even at high cross-linker concentration. No decrease in room temperature bond strength was observed compared with control specimens, which lacked cross-linker. In a second approach, post-vulcanized EPDM was bonded to grit-blasted steel, however here, a peroxide radical initiator was added to the monomer and the bonded assembly cross-linked in a post-cure reaction. This resulted in improved high temperature bond strength. The findings reported herein show that improved bond strength performance can be expected by using either *in-situ* or post-cross-linking chemistries. These approaches demonstrate the latitude available to the formulator for controlling cross-linking chemistry and for matching application/performance criteria for a new product.

Experimental Section

General Experimental Details

^1H and ^{13}C NMR spectra were recorded on a Bruker 250 MHz NMR spectrometer at 250.13 MHz 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' 1st generation catalyst was purchased from Boulder Scientific and used as received. Dicyclopentadiene, ethylidenenorbornene (CaH_2), and methylidenenorbornene 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. Diethyl ether was distilled from sodium benzophenone ketyl. Reduced carbonyl iron powder (R2430) was purchased from ISP Technologies, Inc. Wako azo radical initiator V-65 and Luperox® 130 were obtained from Wako Chemicals USA, Inc. and Elf Atochem North America Inc., respectively. Cyclol Methacrylate® **11** was obtained from Monomer-Polymer & Dajac Labs, Inc.

Cross-linkers **3**,[39] **4**,[39] **9**,[40] and **10**[41] were prepared following published procedures. Combustion analyses were performed by Galbraith Laboratories. EPDM elastomer (BTR 96616) was obtained from British Tyre and Rubber under the designation 96616 and was molded into strips (149.4 mm × 25.4 mm × 3.2 mm) and cured at 154 °C for 9 min. Tire carcass and tread stocks were obtained from B.F. Goodrich. For bonding experiments, the elastomer strips were washed with acetone and allowed to dry for several minutes prior to application of catalyst or monomer. Grit-blasted steel coupons were prepared by blasting 1010 fully hardened cold rolled steel (60.3 mm × 25.4 mm × 1.6 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.

Mechanical Testing of Bonded Assemblies

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 mm × 25.4 mm × 1.6 mm bonded to a strip of elastomer 149.4 mm × 25.4 mm × 3.2 mm. Samples were pulled using a crosshead speed of 50.8 mm/minute. The load-at-maximum load, energy-to-break, and displacement-at-maximum load were measured. Load-at-maximum load correlates to bond strength, energy-to-break (the area under the force-displacement curve) relates to bond toughness, and displacement-at-maximum load correlates to bond elasticity.

Bromination of *p*-Ethyltoluene to give 1-Ethyl-4-methyl-2,3,5,6-tetrabromobenzene

A 250-mL, 3-neck, round-bottom flask was fitted with a rubber septum, thermometer, reflux condenser with gas adapter, and a stirring bar. The apparatus was connected to a dry ice cold-finger and bubbler to trap Br_2 vapor and was charged with 1.40 g (0.025 mol, 0.5 equivs.) of iron powder. The flask was cooled to 0 °C in a 2-propanol/dry-ice bath and then charged with 49 mL (152 g, 0.95 mol, 19 equivs.) of Br_2. To the stirring mixture was added 7.0 mL (6.027 g, 0.050 mol) of *p*-ethyltoluene *via* syringe over a 2 h period. The reaction temperature was not allowed to increase above 6 °C. After addition, the reaction mixture was stirred at 0 °C for 1 h and then slowly brought to room temperature. The rubber septum on the flask was replaced with a glass tube connected to a N_2 tank. Inert gas was then bubbled into the flask to sweep out excess Br_2. The flask was immersed in an oil bath at 35 °C in order to facilitate Br_2 evaporation. After 2 d of gas sweep at elevated temperature, a dark-red to black residue remained. As this residue was stirred and broken-up, Br_2 gas was given off and eventually became a powder, which was washed with deionized distilled H_2O (4 × 50 mL), $NaHCO_3$ (2 × 30 mL), with deionized distilled H_2O (1 × 50 mL), and dried under vacuum to give 23.29 g of gray powder. This was recrystallized from 700 mL of EtOH. The solid was isolated by vacuum filtration, washed with cold EtOH, and dried under vacuum to give the product as give tan, fluffy needles; yield: 22.84 g (56%); mp 104–105 °C; ^{1}H NMR ($CDCl_3$): $\delta = 1.15$ (t, 3H), 2.78 (s, 3H), 3.22 (q, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 12.0$, 28.9, 35.3, 126.9, 127.8, 139.1, 143.9.

Bromination of 1,4-Diethylbenzene to give 1,4-Diethyl-2,3,5,6-tetrabromobenzene

The procedure was equivalent as for the tetrabromotoluene above, except that 7.8 mL (6.72 g, 0.050 mol) of 1,4-diethylbenzene were used. This gave 23.29 g of gray powder after washing. This was recrystallized from 600 mL of EtOH. The solid was isolated by vacuum filtration, washed with cold EtOH, and dried under vacuum to give the product as tan, shiny, needles; yield: 19.46 g (87%); mp 114.5–115.5 °C; ^{1}H NMR ($CDCl_3$): $\delta = 1.15$ (t, 6H), 3.22 (q, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 12.0$, 35.4, 127.3, 144.1.

Synthesis of Cross-Linker 6

A flame-dried, 250-mL, round-bottom flask, which was fitted with a thermometer, rubber septum, reflux condenser with gas adapter, and stirring bar under an argon flow, was charged with 5.00 g (0.011 mol) of diethyltetrabromobenzene and 130 mL of diethyl ether. The clear, light-yellow solution was cooled to −62 °C in a dry-ice bath at which point the bromobenzene precipitated. To the cooled reaction mixture was charged 9.1 mL (7.30 g, 0.110 mol, 9.9 equivs.) of freshly distilled cyclopentadiene. Finally, 9.5 mL (0.0237 mol, 2.1 equivs.) of 2.5 M *n*-BuLi solution in hexanes was charged into the reaction flask drop-wise over a 40 min period using a gas-tight syringe. The reaction mixture was slowly brought to room temperature and stirred overnight. The reaction mixture was quenched with 1.5 mL of MeOH and vacuum filtered to remove undissolved salts. The filtrate was washed with deionized, distilled water (3 × 25 mL) and the organic phase separated and dried with $MgSO_4$ and vacuum filtered. The clear-yellow filtrate was rotovaped at 39 °C under partial vacuum to give a light-yellow, solid residue which was dried under vacuum overnight. The residue was washed with cold MeOH (3 × 5 mL) and then dried under vacuum to give cross-linker **6** as a fluffy, white powder; yield: 2.33 g (80%); mp 139–149 °C; ^{1}H and ^{13}C NMR confirmed that the product had been synthesized in high purity and that it was a mixture of both *syn* and *anti*-isomers. ^{1}H NMR ($CDCl_3$): $\delta =$ 1.19 (6H), 2.30 (4H), 2.78 (4H), 4.02 (4H), 6.88 (4H); ^{13}C NMR ($CDCl_3$): $\delta = 16.5$, 23.1, 47.9, 69.6, 69.7, 129.8, 129.9, 143.3, 143.4, 145.9. Sublimation at 80 °C/0.4 Torr gave shiny, white crystals; anal. calcd. for $C_{20}H_{22}$: C 91.55, H 8.45; found: C 91.15, H 8.50.

Isolation of 6,7-Dibromo-5,8-diethylbenznorbornadiene (8)

During the synthesis of compound **6** on the 50-g scale, a new compound that was later identified as dibromobenzonorbornene **8** (13%) was isolated. Purification either by flash column chromatography (100% hexanes) or by sublimation (75 °C/0.3 Torr) was effective. Recrystallization from

EtOH to give analytically pure shiny, white crystals: mp 70–71 °C; ^{1}H NMR (CDCl$_3$): $\delta = 1.2$ (t, 6H), 2.2 (dd, 2H), 2.8 (q, 4H), 4.0 (s, 2H), 7.8 (s, 2H); anal. calcd. for $C_{15}H_{16}Br_2$: C 50.59, H 4.53; found: C 50.89, H 4.77.

Synthesis of Cross-Linker 7

The procedure was equivalent as for cross-linker **6**, except that 5.00 g (0.0115 mol) of the tetrabromotoluene and 9.5 mL (7.62 g, 0.115 mol, 10.0 equivs.) of cyclopentadiene, and 9.5 mL (0.0237 mol, 2.1 equivs.) of 2.5 M *n*-BuLi in hexanes were used. Work-up as described above gave compound **7** as a cream-colored powder; yield: 1.62 g (57%); mp 139–149 °C; ^{1}H and ^{13}C NMR confirmed that the product had been synthesized in high purity and that the product was a mixture of both *syn* and *anti*-isomers. Recrystallization gave one isomer: mp 84–85 °C; ^{1}H NMR (CDCl$_3$): $\delta = 1.18$ (3H), 2.28 (7H), 2.75 (2H), 3.99 (4H), 6.85 (4H); ^{13}C NMR (CDCl$_3$): $\delta = 14.8$, 16.5, 23.1, 47.9, 48.0, 48.2, 69.8, 123.0, 123.1, 129.6, 129.7, 143.2, 143.4, 145.8, 146.6; anal. calcd. for $C_{19}H_{20}\cdot 0.2\ H_2O$: C 90.57, H 8.28; found: C 90.69 H 8.04.

General Procedure for Preparing Cross-Linker Formulations and Bonding by CMP

Cross-linker and ENB were mixed at a specified concentration or series of concentrations and applied to the substrate surface. Catalyst was applied directly to the other surface to be bonded using the brush procedure[2] which resulted in an average of 5.8 ± 1.8 mg of catalyst per elastomer strip or coupon. The substrates were mated, placed under a 100 g weight and allowed to stand at room temperature for at least 30 min to overnight. The mated assembly was then heated in an oven at a specified temperature (i.e., 70 °C for 30 min) and then subjected to a 180° hand peel while hot. If the assembly could not be pulled apart, it was then pulled on the Instron as described above. At least 3–5 assemblies were bonded for each test.

Cross-Linker Formulation Conditions – Preliminary Bonding Results

Anthraquinone (**1**): No improvement in high temperature strength, as determined by hand peeling the bonded specimens after being placed in an oven at 70 °C for 30 min, was observed at either a 40:1 ENB/catalyst molar ratio (2.5 mole % catalyst) or a 180:1 ENB/catalyst molar ratio (0.55 mole % catalyst).

Polyolefin Bonding

Polypropylene lap shear samples were prepared from 101.6 mm × 25.4 mm × 3.2 mm coupons according to the following procedure. If the polypropylene was sanded, 100-grit sandpaper was used to lightly roughen the bonding area of the lap shear samples. A solution of 200 mg of Grubbs' 1st generation catalyst in 15 mL of dichloromethane was sprayed onto the 645 mm^2 bonding area of 10 polypropylene coupons. After the solvent was dry, about 3.5 to 4.0 mg of catalyst had been delivered to each coupon. About 150 μL of monomer/cross-linker were placed on the conjugate coupon, the catalyst-containing and the monomer/cross-linker-containing coupons were mated, and the adhesive was allowed to cure for 24 h. A set of five lap shear samples were prepared for each monomer/cross-linker test.

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