Adhesion of Fibers to Natural Rubber Elastomer using Ring-Opening Metathesis Polymerization (ROMP)

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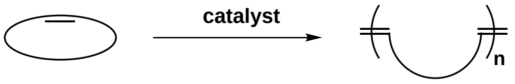
Dedicated Professor Louis D. Quin on the occasion of his 74th birthday.

Abstract: Ring-opening metathesis polymerization is used to investigate adhesion of multifilament fibers (polyester, nylon, Kevlar®) to a natural rubber elastomer through the creation of ROMP polymer coatings on the fiber surfaces followed by encapsulation in pre-cured elastomer. Polymer coated fibers are prepared by 1) physisorption of polynorbornenes which are prepared by solution-phase ROMP and 2) contact metathesis polymerization (CMP) whereby Grubbs' 1st generation catalyst **1** is applied directly to the fiber surface followed by passage of the "activated" fiber through a norbornene monomer bath. Both methods improve adhesion to the elastomer when compared to uncoated control specimens. Catalyst and polymer loading are briefly examined. Although inconclusive, our findings suggest that polymer loading and substrate specificity may affect overall adhesion. ROMP is enabling chemistry for creating an interface to improve fiber adhesion to natural rubber elastomers. Formulated commercial adhesive systems are also included in this study.

Keywords: adhesion; composites; fibers; Grubbs' catalyst; metathesis; ROMP; ruthenium

Introduction

Olefin metathesis provides an excellent methodology for manipulating unsaturated hydrocarbons in a variety of synthetic transformations. For example, cross- and ring-opening metathesis have been used in simple olefin interconversion reactions, ring-closing metathesis has aided in the synthesis of complex natural products, and ring-opening metathesis polymerization [ROMP, Equation (1)] and acyclic diene metathesis polymerization (ADMET) have been used to prepare functional polymers with highly controlled microstructures.[1–5]



(1)

Industrial scale olefin metathesis has been used to prepare chemicals and polymers for use in assorted products from simple detergent-range alkenes to polymers for oil recovery applications. [4,6] Catalyst innovations have been largely responsible for the rise in the use of olefin metathesis as a synthetic methodology. Reactivity and stability are key properties for driving this increased use. Well-defined olefin metathesis catalysts are ideal because many have proven to have high catalytic activity and longevity. The chemistry of these metal alkylidenes is well-understood and has paved the way for designing new robust catalysts that are functional group tolerant and display excellent air- and water-stability.[7] This property is most apparent with the ruthenium-based systems that have appeared in the past ten years. For example, Grubbs' first generation catalyst **1** may be handled in the open atmosphere as a solid and only slowly oxidizes in solution.[8] Recently, Grubbs has quantified the relative stability of several ruthenium alkylidenes to decomposition.[9,10] Their use as polymerization catalysts has led to the synthesis of polymers with controlled architectures, controlled molecular weights, and narrow polydispersities.[7]

Recently researchers have shown interest in using ROMP to modify surfaces. These "grafting from" reactions work by initiation of a polymerization from a surface where the transition metal catalyst is covalently attached to the surface *via* an anchor and tether (Figure 1). Grafting chemistry as applied to the formation of polymer brushes was recently reviewed.[11]

ROMP "grafting from" approaches have been used in a variety of creative ways including self-assembly of polymer brushes,[12] investigation of catalytic activity using gold colloids as substrates,[13] preparation of hybrid gold nanoparticles,[14] covalent attachment of polynorbornenes to vinyl-containing polymer sur-

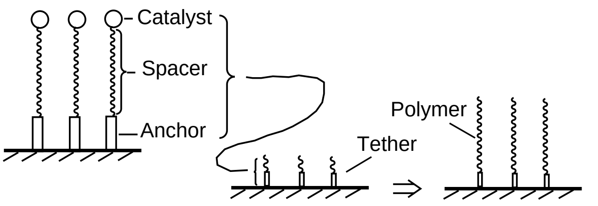


Figure 1. Illustration of ”grafting from” surface attachment of polymers.

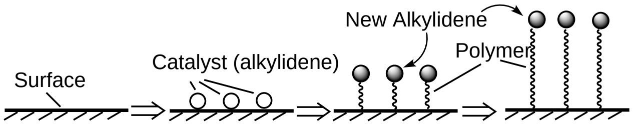


Figure 2. Coating prepared by the CMP process.

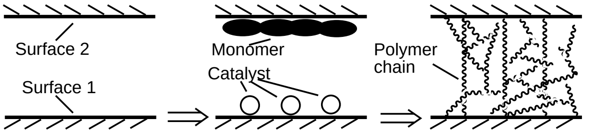


Figure 3. Adhesive bond created by the CMP process.

faces,[15] microcontact printing of a patterned polymer array on silicon,[16] formation of thin films on silicon,[17] preparation of stationary monolith solid supports for chromatographic separations,[18] and preparation of highly loaded polymer supports for combinatorial chemistry[19] and catalysts.[20]

Recently, we used an “initiation off” process where the olefin metathesis catalyst is placed *directly on the surface to be modified and is not attached via a tether.* We call this process contact metathesis polymerization (CMP). The polymerization initiates only when a monomer capable of ROMP comes in contact with the “activated” surface. As new alkylidenes are formed during the polymerization, they serve as sites for further reaction with either the same or another monomer.[21] In this manner, coatings and films of controlled thickness, functionality, and properties can be prepared (Figure 2). This type of approach was used by Grubbs in the preparation of polyacetylene[22] and by Goodall in the preparation of fiber-reinforced molded polynorbornene articles.[23]

Similarly, Figure 3 illustrates how an adhesive bond is created by CMP. One substrate is coated as above with catalyst to give a latent “active” surface and the other coated with a ROMP monomer. When the two surfaces are placed in contact, ROMP ensues, forming an adhesive bond between the substrates.

From the idealized depictions of each process, the generality of CMP is clear. The results of our investigation revealed that ROMP is enabling chemistry for the creation of an excellent primary adhesive bond to low surface energy elastomers, particularly in their post-vulcanized state, at room temperature under ambient conditions in air, in the presence of moisture, and with minimal surface preparation.[8]

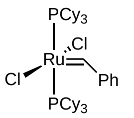
Our interest in surface modification was driven by a desire to understand how olefin metathesis, and ROMP in particular, would work in applications where adhesion was of primary importance. With the excellent self- and cross-adhesion between elastomer and metals that was observed, we wanted to extend this chemistry from flat surfaces to other geometries. The focus of the work reported herein is on adhesion of a natural rubber elastomer to different fiber substrates using ROMP to prepare the interface polymer. One can envision many applications (e.g., composite structures, fiber-reinforced hoses and belts, tires) that could be assembled from these substances. The literature shows that others have used ROMP to affect adhesion. Saunders et al. showed that block copolymers prepared by solution-phase ROMP are useful adhesion promoters for bonding glass-epoxy and copper-epoxy interfaces.[24] Others have used ROMP to promote adhesion to polyolefin substrates[25,26] and at glass-polymer interfaces.[27] Norbornene polymers have been reported to make transparent molding materials with good adhesion to aluminum films[28] and in fiber-reinforced composites.[29]

In the present study, we examined the primary adhesion of several fibers that have been coated with a ROMP polymer created using the CMP approach. The polymer coated fiber was then encapsulated into a rubber matrix to determine overall adhesion of the fiber within the composite structure. Our findings revealed very good adhesion to all three substrates. However, this adhesion was inferior when compared to a commercial formulated adhesive system.

Results and Discussion

Fiber Preparation and Testing

As described above, our surface-initiated polymerization utilizes an “initiation off” approach in which the catalyst is applied directly to the surface and modified by contact with a ROMP monomer (i.e., CMP). In this study, Grubbs’ 1st generation catalyst[30] **1** was used in combination with 5-ethylidene-2-norbornene **2**, dicy-



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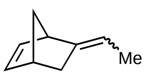

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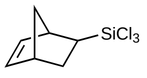

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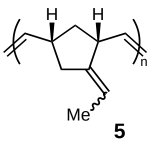

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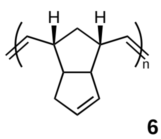

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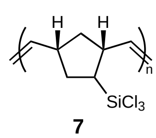

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clopentadiene **3**, and 5-(bicycloheptenyl)trichlorosilane **4**. It is conceivable other functional monomers that might enhance specific interactions between the surfaces and the polymer could be used in this chemistry.

Three types of multifilament fibers (i.e., polyester, nylon, Kevlar®) were evaluated as substrates for testing adhesion with A225P natural rubber elastomer. Adhesion was measured using the American Society for Testing and Materials (ASTM) H-Test, which is a standard method for determining adhesion of tire cords and other reinforcing cords to elastomeric compounds. In this method, a single processed multifilament fiber (*vide infra*) is sandwiched between two elastomer slabs and then cured in a mold. The resulting "H"-shaped specimen is then pulled on an Instron until failure results. Adhesion is determined by the force required to pull the bonded fiber from the encapsulating elastomer.

Polyester, nylon, and Kevlar® fibers were processed using conditions illustrated in Figure 4. Commercially obtained "unprocessed" fibers were washed with hexanes to remove oils that may have been applied to the fiber's surface during processing. Catalyst **1** was loaded onto the surface by soaking the fiber in a dilute catalyst solution followed by air-drying. Coatings to these surfaces were applied in several ways. Using the CMP approach, the alkylidene-coated fibers were dipped into neat monomers **2**, **3**, and **4** to give fibers coated with polymers **5**, **6**, and **7**, respectively. The polymerization reactions were extremely rapid (i.e., the fibers "smoked" on removal from the monomer bath), and the reactions appeared to be finished within seconds as the fibers stiffened considerably. A series of control experiments, which involved subjecting unprocessed, washed/dried, and catalyst-coated fibers to the elastomer encapsulation process, was done to ascertain whether CMP applied coatings had any impact on fiber to elastomer adhesion. Fibers were also coated by physisorption with polymer **5** which had been prepared by normal solution-phase ROMP. This involved dipping the washed/dried fibers into a solution of freshly prepared polymer **5**. Finally, fibers were coated with Chemlok® CH205/233x and CH402, which are two commercial systems formulated to promote fiber-to-elastomer adhesion. As described above, specimens of each fiber type were encapsulated in A225P natural rubber, cured, and analyzed as described for the H-test.

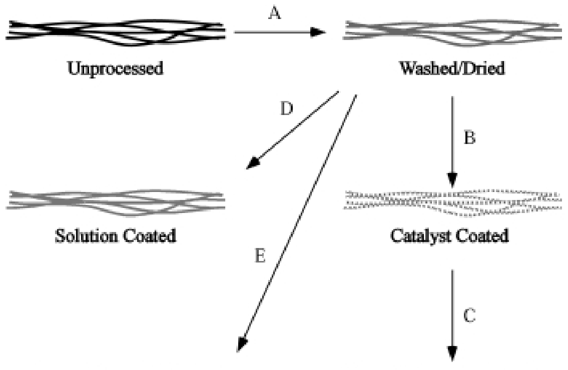

Figure 4. Unprocessed fiber subjected to the following process: A) washed and dried to remove surface oils, B) soaked in solution of catalyst **1** followed by drying in open hood, C) catalyst-coated fibers were dipped in monomer, hung at room temperature, D) fibers were dipped into CH_2Cl_2 solution containing freshly prepared polymer **5**, E) commercial primer and adhesive were brush applied to fiber. See Experimental Section for full details.

Catalyst and polymer loading data for the fibers processed as described above are shown in Table 1. The nature of the catalyst application process leads to variability in the amount of catalyst applied to the fibers. The polyester fiber picked up more catalyst than did the nylon or Kevlar®, which likely reflects fiber swelling by the catalyst processing bath solvent rather than any specific interaction between catalyst **1** and functionality on the fiber surface. In general, catalyst loading is very low but is within two orders of magnitude for all three fibers. Similar variation is seen in the amount of polymer coated or loaded onto the fiber surface. As above, polymer loading is greater for polyester than for nylon or Kevlar® fiber, and loading is greater for CMP *vs.* solution processed fibers for all three fiber types. Distinct differences in molar monomer to catalyst levels are observed for the fiber types. It is anticipated that strict control of catalyst and polymer loading could be accomplished using commercial fiber processing equipment.

Adhesion

Mechanical testing of cured H-test specimens on an Instron provided load-at-maximum load, energy-to-break, and displacement-at-maximum load data (Table 1). Adhesion is determined from the load-at-maximum load data. 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 being pulled apart, the specimens were inspected to determine the mode of failure. While subjective, this analysis provides information about the relative adhesive strength between the various interfaces. The most desirable failure mode is rubber tear, where the rubber elastomer remains on the adhesive-coated fiber 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. Two other failure modes are rubber-adhesive failure (ra) which occurs between the elastomer and adhesive interface and fiber-adhesive failure (fa) which occurs

Table 1. Fiber processing and adhesion to natural rubber elastomer A225P[a]

#	Fiber[b]	Catalyst loading [mmol/mm][c]	Polymer loading [mg/mm][d]	M:C[e]	Load-at-Max. Load [N][f]	Energy-to-Break [J][f]	Displacement-at-Max. Load [mm][f]	Failure Mode[g]
	Polyester							
1	Unprocessed	–	–	–	12 (1)	0.02 (0.01)	1.8 (0.2)	f
2	Washed/Dried	–	–	–	14 (2)	0.04 (0.01)	1.8 (0.3)	f
3	Catalyst **1**	1.34	–	–	18 (3)	0.05 (0.01)	2.0 (0.2)	ra
4	Polymer **5** – solution	–	0.10 (0.010)	3945:1	17 (3)	0.03 (0.01)	2.1 (0.3)	fa
5	Polymer **5** – CMP	1.15	0.46 (0.14)	331:1	58 (5)	0.26 (0.08)	4.2 (0.7)	ra
6	Polymer **6** – CMP	1.08	–[h]	–[h]	33 (5)	0.01 (0.01)	2.8 (0.2)	ra
7	Polymer **7** – CMP	3.13	0.82		37 (7)	0.12 (0.01)	3.4 (0.5)	ra
8	CH205/233X	–	0.14 (0.014)	–	47 (5)	0.10 (0.01)	3.4 (0.3)	fa
9	CH402	–	0.11 (0.015)	–	72 (15)	0.28 (0.09)	5.5 (0.7)	raf
	Nylon							
10	Unprocessed	–	–	–	12 (2)	0.03 (0.01)	2.2 (0.2)	f
11	Washed/Dried	–	–	–	15 (2)	0.05 (0.01)	2.5 (0.2)	f
12	Catalyst **1**	0.38	–	–	15 (3)	0.05 (0.01)	2.6 (0.3)	fa
13	Polymer **5** – solution	–	0.091 (0.011)	3945:1	42 (4)	0.13 (0.02)	4.5 (0.4)	raf
14	Polymer **5** – CMP	0.26	0.27 (0.081)	894:1	48 (11)	0.17 (0.06)	4.6 (1.2)	raf
15	Polymer **6** – CMP	0.13	0.14 (0.010)	822:1	31 (4)	0.08 (0.02)	3.2 (0.3)	fa
16	CH205/233X	–	0.14 (0.010)	–	60 (8)	0.26 (0.04)	5.0 (0.5)	raf
17	CH402	–	0.094 (0.012)	–	66 (11)	0.28 (0.05)	5.8 (0.8)	raf
	Kevlar®							
18	Unprocessed	–	–	–	13 (4)	0.03 (0.01)	2.3 (0.4)	f
19	Washed/Dried	–	–	–	17 (2)	0.04 (0.01)	2.5 (0.2)	f
20	Catalyst **1**	0.063	–	–	15 (1)	0.03 (0.01)	2.4 (0.2)	fa
21	Polymer **5** – solution	–	0.059 (0.0032)	3945:1	30 (6)	0.08 (0.02)	4.1 (0.8)	raf
22	Polymer **5** – CMP	1.08	0.084 (0.0018)	65:1	36 (6)	0.11 (0.03)	4.1 (0.4)	ra
23	Polymer **6** – CMP	0.26	0.11 (0.021)	325:1	21 (6)	0.04 (0.01)	2.6 (0.4)	ra
24	CH205/233X	–	0.15 (0.016)	–	49 (4)	0.16 (0.04)	4.3 (0.3)	fa
25	CH402	–	0.089 (0.020)	–	55 (15)	0.20 (0.06)	5.5 (0.7)	raf

[a] Prepared following ASTM D4776-96.

[b] Fiber and coating application method – e.g., polyester was coated with polymer **5** using solution-phase processing. CH205/233x and CH402 are commercial adhesive systems

[c] All values $\times 10^{-5}$. Standard deviations are on the order of 10^{-9} and not shown. Total weight of catalyst **1** on fiber averaged over total length for 5 fiber specimens, except for #7 where N = 1.

[d] Total weight of ROMP or commercial adhesive polymer coating on total length for 5 fiber specimens, except for #7 where only one fiber was used.

[e] Monomer to catalyst molar ratio determined from final weights of applied catalyst and polymer on fiber.

[f] The mechanical testing data represent the average (standard deviation) of 10 analyses for all fibers, except for #7 where N = 5.

[g] Primary failure mode: f = at fiber surface, ra = at rubber-adhesive or polymer coating interface, fa = at fiber-adhesive or polymer coating interface, raf = mixed mode at all interfaces

[h] Not determined.

between the fiber and adhesive interface. Mixed failure modes were observed in many cases.

For all fibers, only negligible changes in adhesion were observed on progressing from unprocessed to washed/dried to catalyst-coated specimens (Table 1). Slight improvements were observed by washing the unprocessed fibers, whereas application of catalyst **1** to the fibers resulted in variable adhesion. Physisorbed polymer **5** showed little improvement on polyester, but did show a two-to-three-fold increase in adhesion on nylon and Kevlar®. Polymer loading levels (i.e., the amount of polymer coated on the fiber during a processing step) were comparable for all three substrates thus suggesting adhesion substrate specificity (Table 1, #s 4, 13, 21). CMP coated fibers generally showed improved adhesion. This was particularly true for polymer **5** which showed significant increases from the washed/dried control specimens for all fiber types (Table 1, #s 5, 14, 22 *vs.* 2, 11, 19). Catalyst level appears to have little affect on adhesion as loading was low on nylon relative to Kevlar®, but its adhesion to the elastomer was higher. The data suggest polymer **5** levels are important as lower polymer loading resulted in reduced adhesion (#s 5, 14, 22). A similar trend in polymer loading was seen for polymer **6** (Table 1, #s 15, 23). An alternate explanation of these findings is that adhesion is fiber/substrate/polymer specific and not enough data were gathered to make this observation. While the results suggest polymer loading to be the critical parameter for enhancing adhesion, a detailed analysis of catalyst and polymer loading at multiple loading levels on all three substrates is required before such a proposal can be made conclusive. These data support improved fiber adhesion to natural rubber elastomer using ROMP polymers as an adhesive layer and that increased adhesion is attained when using the CMP process.

While the mechanism responsible for adhesion is presently unknown we propose the following to account for these findings. Mechanical interlocking or threading of the multifilament fibers with the ROMP polymer, which forms when the monomer wets each individual catalyst coated fiber surface and polymerizes, is likely of primary importance for adhesion by the CMP process. One can envision that the polymer formed on the surface intertwines with different fibers in the bundle and this in turn with the polymer mass that coats the entire fiber bundle. Support for this is seen by the predominance of rubber-adhesive (ra) failure modes in CMP processed fibers (Table 1). Another aspect of adhesion may result from cross-linking of the curing elastomer with the heavily unsaturated ROMP polymer that is coated on the fiber surface. While little evidence is presented to support these proposals, they do form a basis for follow-up experiments to gain understanding of this method of promoting adhesion.

For comparison to adhesive interfaces prepared by ROMP chemistry, two commercial adhesive systems were also evaluated (Table 1, #s 8, 16, 24, and 9, 17, 25). Not surprisingly, the highest levels of adhesion on all substrates were generally found with the formulated adhesives.

Energy-to-break and displacement-at-maximum load were also determined for each specimen. As expected, these values correlated fairly well with adhesion. All processing conditions caused an increase in both of these measurements. No consistency in failure mode was noted other than on polyester where the CMP processed fibers tended to fail at the elastomer-ROMP polymer interface and not at the fiber-ROMP polymer interface which suggests that adhesion of the ROMP polymer to the polyester was superior than to the elastomer.

Conclusions

Ring-opening metathesis polymerization was used to investigate adhesion of multifilament fibers (polyester, nylon, Kevlar®) to a natural rubber elastomer. The ROMP polymers were prepared using a well-defined metathesis catalyst and applied to the fiber surfaces using two methods: 1) by solution-phase polymerization followed by adsorption of the resulting polymer from a solvent bath and 2) by contact metathesis polymerization (CMP) whereby the catalyst is applied directly to the fiber surface followed by passage of the "activated" fiber through a bath of ROMP monomer. Both methods showed improved adhesion relative to uncoated control specimens. Our findings suggest that for CMP applied coatings, catalyst loading has little affect on adhesion, whereas polymer loading appears to be important, at least for polyester substrates. Because of the limited scope of substrates, we cannot rule out substrate specificity as an important variable affecting adhesion. Further work would clarify these points. The results support the use of ROMP polymers as an interface to improve fiber adhesion to natural rubber elastomers. The highest levels of adhesion on all substrates is found when formulated commercial adhesive systems are used as adhesion promoters. Developing understanding of the mechanism of adhesion in the CMP coated fibers would help in the design of enhanced adhesion promoters for a variety of substrates.

Experimental Section

General Experimental Details

Grubbs' 1st generation catalyst **1** was purchased from Boulder Scientific and was used as received. 5-Ethylidene-2-norbornene **2** (CaH_2), dicyclopentadiene **3**, and 5-(bicycloheptenyl)-trichlorosilane **4** were purchased from Aldrich or Gelest, Inc. and distilled using standard practices for the reagent specified. $CHCl_3$ and CH_2Cl_2 were obtained from Fisher or Pharmco and used as received. Natural rubber (A225P) was obtained from M.A. Hanna Rubber Company, Burton, Ohio, USA, and was molded as described in ASTM method D4776-96 and cured at 325° C for 8 minutes under 552 MPa on a hot press. Polyester (size 693, #97635K83), nylon-6,6 (size 69, #87695K68), and Kevlar® (size 69, #8800K81) multifilament fibers were obtained from McMaster-Carr Supply Company. Fiber and coating thickness were measured using a Fowler Sylvac electronic micrometer. Chemlok® adhesives CH205/233x and CH402 were obtained from Lord Corporation, Erie, Pennsylvania, USA.

Mechanical Testing of Bonded Assemblies

Specimens were prepared and evaluated according to ASTM method D4776-96 entitled "Standard Test Method for Adhesion of Tire Cords and Other Reinforcing Cords to Rubber Compounds by H-Test Procedure". Mechanical testing was performed at room temperature on an Instron Model 4204 Materials Tester equipped with a 5 kN load cell. The H-test specimens were held using clamps, which were built as specified in the ASTM method, and were spaced 1.5 mm apart. Testing was performed at a crosshead speed of 127 mm/min. Load-at-maximum load, energy-to-break, and displacement-at-maximum load were measured. Failure analysis consisted of observing the failed pieces under an optical microscope (× 30 magnification) and noting at which interface failure occurred.

General Process for Fiber Coating

Five 38.1 cm sections of "unprocessed" commercial multifilament fiber (polyester, nylon, Kevlar®) were washed in hexanes for 1 hour and then dried at 40° C in a vacuum oven for 1 hour. The fibers were weighed and their thickness measured with a digital micrometer. The fibers were soaked in a 0.012 M catalyst solution, which had been freshly prepared by dissolving catalyst **1** (0.20 g) in of CH_2Cl_2 (20.0 mL), for five minutes and then hung to dry for 1 hour in a fume hood. The fibers were weighed to determine catalyst level, dipped in monomer (**2**, **3**, or **4**) for 10 seconds, and hung overnight in a fume hood. The coated fibers were weighed and their thickness were measured, and they were subjected to encapsulation with A225P rubber stock.

Fiber Coating with Freshly Prepared Poly(ethylidenenorbornene) 5

Solution-phase polymer **5** coated fibers were prepared by taking fibers that had been washed and dried as described above and adding them to a solution of polymer **5** that had been synthesized by adding a solution of catalyst **1** (0.0062 g, 0.0075 mmol) in CH_2Cl_2 (2.0 mL) to a solution of norbornene **2** (4.0 mL, 29.72 mmol) in CH_2Cl_2 (40 mL) (3945:1 monomer to catalyst molar ratio). The fibers were dipped in the polymer **5** solution for 10 seconds and hung to dry for 1 hour. The coated fibers were weighed, their thickness measured, and they were subjected to the encapsulation procedure with A225P rubber stock.

Application of CH205/233x to Fiber Cords

Fibers coated with formulated commercial two-part Chemlok® 205/233x adhesive were prepared by brush applying the CH205 primer onto the washed/dried fibers and hanging at room temperature. After 30 minutes the CH233x adhesive was brush applied onto the fibers, which were then hung to dry overnight. The coated fibers were weighed, their thickness measured, and they were subjected to the encapsulation procedure with A225P rubber stock.

Application of CH402 to Fiber Cords

Fibers coated with formulated commercial one-part Chemlok® 402 adhesive were prepared by brush applying the CH402 onto the washed/dried fibers and hanging them at room temperature. The coated fibers were weighed, their thickness measured, and they were subjected to the encapsulation procedure with A225P rubber stock.

Rubber Elastomer Encapsulation and Testing Procedure

Following ASTM method D4776-96 fiber specimens were sandwiched between two layers of A225P natural rubber stock, placed in heated mold, and cured at 325° C for 8 minutes under 552 MPa. The fiber sandwiches were then cut to create an H-test specimen consisting of a single multifilament fiber with each end embedded in the center of a tab end of the rubber test block. Excess rubber flashing was carefully removed. The bonded specimens were then analyzed on an Instron (Table 1).

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