Highly Efficient Rubber-to-Stainless Steel Bonding by Nanometer-Thin Cross-linked Polymer Brushes

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ABSTRACT: Stainless steel (SS) surfaces were grafted with poly(glycidyl methacrylate) (PGMA) brushes that were post-modified using allylamine, diallylamine, and propylamine as reagents. Likewise, poly[2-(diethylamino)-ethyl methacrylate] brushes were synthesized. All samples were compression molded with uncured ethylene-propylene-diene M-class rubber and dicumyl peroxide and vulcanized for 12 min at 170 °C. The efficiency of the novel bonding solution was evaluated through peel experiments. Two parameters, the fracture toughness (G) and the cohesive-to-adhesive fracture ratio (Aa), were calculated to evaluate the strength and the performance of the coupling, respectively. For the nanometer-thin PGMA films modified with allylamine, in particular, full cohesive fracture was obtained. The obtained values of G (15.4 ± 1.1 N mm⁻¹) and Aa (1.00 ± 0.01) matched those obtained for a micrometer-thick commercial bonding agent. Cross-linking of polymer brushes by intermolecular reactions by the primary amines proved to have a significant impact on the type of fracture (cohesive/adhesive) and the performance of the adhesives.

1. INTRODUCTION

Over the last decades, the development of components employing surface modifications has become a major research field of both academic and industrial interest. Properties such as cell adhesion, fouling resistance, low friction, and wettability may be designed by chemical adjustment of the first few nanometers of a component surface. Hence, continued development of new and more beneficial ways of surface design is pertinent.

Adhesion of rubber to a metal is important for various purposes, including bridge bearings, mounts in car engines, tires, and so on. What makes rubber particularly efficacious for such applications is its high elasticity and resistance to oxygen, ozone, ultraviolet light, and heat. Unfortunately, most rubbers have a low wettability, and it is hard to create adhesion to metals, rendering interlocking designs the common solution. One interesting approach for handling the adhesion issue is through a chemical modification of either the rubber or the metal. Functionalization of rubber includes halogenation, cyclization, or copolymerization with polar monomers to increase the wettability. Still, pretreatment of the metal is the most extensively used approach to enhance metal–rubber adhesion. Solution-based organic primers and binders are widely employed, and components such as chlorinated polymers and poly(butadiene) are required (among a variety of other additives) to obtain strong adhesion. The challenge with these primers is that they are applied in large amounts (at least a few micrometers in thickness) and are unable to establish covalent bonds all the way from the metal surface to the rubber. For these reasons, development of highly efficient thin-layer primer systems would be desirable.

Several methodologies can be applied for a surface-confined polymerization, that is, free radical polymerization (thermal, photochemical, or radiochemical), controlled radical polymerization, anionic polymerization, or electropolymerization. In this work, we used the controlled radical polymerization approach because the aim was to produce brushes covalently anchored to the substrate with good control of length and with minimal cross-linking of the brushes. Anchoring of polymer brushes to metal surfaces is a versatile approach of making a...
metal compatible with a given coating. Several methods have been designed to ensure both durability and high grafting densities of polymer brushes generating a nanometer-thin primer layer. Specifically, poly(glycidyl methacrylate) (PGMA) and poly[2-(diethyl amino)ethyl methacrylate] (PDEAEMA) polymer brushes may be grown from various surfaces using a controlled radical polymerization. The PGMA brushes can subsequently be modified, exploiting the fact that nucleophiles such as amines, thiols, and azides are able to open the oxirane ring.

In this way, using, for example, allyl- or diallylamine as nucleophile, allylic groups can be introduced to exploit their ability to couple with, for example, an ethylene-propylene-diene M-class (EPDM) rubber during the thermal peroxide free-radical curing process. This would create covalent bonding across the entire interface to ensure strong metal–rubber adhesion. Usually, rubber additives such as triallyl isocyanurate would be introduced to promote effective cross-linking of EPDM rubber by free radical addition and cyclopolymerization reactions. It is also known that polymerization of diallylamine normally yields highly cross-linked polymer networks.

It is worth noting that with allylamine serving as a nucleophile in the ring opening of the oxirane groups in PGMA, it would itself be transformed into a secondary amine. This secondary amine can react further, either intra- or intermolecularly, with another oxirane ring in the PGMA films to give a cross-linked brush structure, even before the curing process. If this kind of cross-linking is unwanted while the introduction of allyl groups is still a goal, the nucleophile to go for would be the secondary diallylamine.

Figure 1 presents an overview of the steps involved in this work. First, PGMA and PDEAEMA polymer brushes are grown from stainless steel (SS) along with PGMA polymer brushes modified using either allylamine, diallylamine, or propylamine as the nucleophile. The brush films are analyzed by ellipsometry, infrared reflectance–absorption spectroscopy (IRRAS), and X-ray photoelectron spectroscopy (XPS). Samples are then installed in a sample holder and compression-molded with EPDM rubber covalently linking rubber and polymer brushes (see Figure S1, Supporting Information). Bonding properties are evaluated by peel testing and subsequent three-dimensional (3D) scanning of the fractured surfaces. The fracture toughness (\(c\)) and cohesive-to-adhesive fracture ratio (\(A_r\)) are used to quantify the adhesive strength and performance of the joints. The different bonding systems are compared in terms of reactivity toward the EPDM rubber, and the impact of the ability of the primary amines to covalently link the polymer films inter- and intramolecularly is discussed. A commercial and traditional bonding agent, Chemosil (see Materials and Methods), is used as the reference system.

2. RESULTS AND DISCUSSION

2.1. Examination of the Reaction Protocol. Scheme 1 outlines the general procedure used for producing polymer brushes.
brushes at the SS surfaces. In brief, the SS samples were electrografted using the diazonium salt approach, specifically 4-(2-hydroxyethyl)benzene diazonium tetrafluoroborate (HEBD), to generate surface-attached primary alcohols (SSOH). These were acylated to afford tertiary bromoalkyl groups (SSBr), that is, the radical initiators. Polymer brushes (SSPGMA) were then grown from SSBr using the surface-initiated activators regenerated by electron transfer atom transfer radical polymerization (SI-ARGET-ATRP) protocol.

Next, the PGMA brushes were post-modified under various conditions using either of the three amines, that is, allylamine, propylamine, or diallylamine, as a reagent to open the oxirane rings (Scheme 2). This produced three kinds of modified samples in terms of (A) SSallyl, (B) SSpropyl, or (C) SSdiallyl. In fact, the SSdiallyl sample came in two versions, that is, SSdiallyl-1, to denote that 0.41 M diallylamine was used in the post-modification step, and SSdiallyl-2 using a higher concentration of 0.81 M.

Figure 2A shows that the dry film thickness (d) of the PGMA brushes on SSPGMA increases proportionally with time, as expected for SI-ARGET-ATRP. Next, the reaction of diallylamine with SSPGMA was investigated. In general, the dry film thickness of the corresponding SSdiallyl samples consistently increases by 10–20 nm. Figure 2B illustrates the trend in the relative thickness increase due to the reaction with the diallylamine in terms of a plot of \( \frac{d_{\text{diallyl-1}}}{d_{\text{PGMA}}} \) versus \( d_{\text{PGMA}} \). It is seen that \( \frac{d_{\text{diallyl-1}}}{d_{\text{PGMA}}} \) decreases from 1.44 ± 0.11 to 1.15 ± 0.06 as \( d_{\text{PGMA}} \) increases, suggesting that the reaction mechanism changes as the brush layer thickness increases. On
the assumption that each oxirane group would react with one diallylamine molecule and that the thickness increase can be calculated directly from the resulting mass increase, one ends up with \( d_{\text{diallyl}}/d_{\text{PGMA}} = 1.68 \). If the concentration of the diallylamine is doubled to 0.81 M (that is, the “diallyl-2” series), the determined value of \( d_{\text{diallyl-2}}/d_{\text{PGMA}} \) becomes as high as 1.78 ± 0.15. This indicates that for short PGMA brushes, essentially, every single oxirane ring re-acts if the availability of diallylamine is high. In contrast, for the thicker films, the concentration of diallylamine decreases with the distance from the top of the brush structure, leaving oxirane rings at the bottom unmodified.

Using allylamine and propylamine as nucleophiles gives \( d_{\text{allyl}}/d_{\text{PGMA}} = 1.31 ± 0.08 \) and \( d_{\text{propyl}}/d_{\text{PGMA}} = 1.45 ± 0.05 \). In the latter case, this is close to the 1.42 expected for a 1:1 amine–oxirane reaction ratio, whereas in the former case, the value is equally close to the 1.2 expected for a 1:2 amine–oxirane reaction ratio. Note that the concentrations used for both of these amines are high (>0.6 M), making their availability throughout the film high. One interesting aspect of the three reactions is that although the secondary diallylamine cannot participate in a cross-linking reaction with two oxirane groups, the primary allylamine and propylamine can. Ultimately, complete cross-linking of the brush structure would result in a 1:2 amine–oxirane ratio, which, thus, seems to be an option for at least the allylamine. In addition, the extent of a potential chain reaction involving the allyl anion from an opened ring with another oxirane seems to be insignificant because this would have resulted in an even smaller mass gain and, accordingly, a smaller film thickness increase.

To support these propositions obtained from the ellipsometry measurements, we resorted to recording the IRRAS spectra of the produced samples (Figure 3). For \( d_{\text{PGMA}} \) bands at 3010 and 2950 cm\(^{-1}\) are assigned to the C–H sp\(^3\) bond stretching, that at 1735 cm\(^{-1}\) to the C=O bond stretch of an unconjugated ester group, those at 1510–1430 cm\(^{-1}\) to C–H deformations, those at 1310–1035 cm\(^{-1}\) to C–O stretching, and that at 909 cm\(^{-1}\) to the oxirane ring deformation.\(^{30}\) For \( SS_{\text{allyl}} \), \( SS_{\text{diallyl-2}} \), and \( SS_{\text{propyl}} \), the IRRAS spectra show a complete disappearance of the oxirane band (using concentrations of 0.67 M allylamine, 0.81 M diallylamine, and 0.61 M propylamine). This is seen most clearly from the spectrum of \( SS_{\text{propyl}} \) whereas in the spectra of \( SS_{\text{allyl}} \) and \( SS_{\text{diallyl-2}} \), a new close-by peak at 930 cm\(^{-1}\), attributed to C–H out-of-plane bending from the introduced olefin moieties, is observed. In comparison, the spectrum of \( SS_{\text{diallyl-1}} \) (based on the lower diallylamine concentration of 0.41 M) shows oxirane groups (Figure S2, Supporting Information) in line with the smaller increase in film thickness noted in this case (vide supra). For \( SS_{\text{PDEAEMA}} \) (see Scheme 1), a peak at 2820 cm\(^{-1}\) is attributed to the C–H sp\(^3\) stretch from an aliphatic component bonded to a tertiary amine, which also appears for the \( SS_{\text{diallyl-2}} \) samples. For all modified PGMA samples, the C=O peak is slightly broadened, most likely because of hydrogen bonding between the C=O ester groups and the hydroxyl groups formed in the ring-opening process.\(^{30}\)

<table>
<thead>
<tr>
<th>sample</th>
<th>C (%) ±</th>
<th>O (%) ±</th>
<th>Cl (%) ±</th>
<th>N (%) ±</th>
<th>N/C ratio ±</th>
<th>( d/d_{\text{PGMA}} ) ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>( SS_{\text{PGMA}} )</td>
<td>72.5 ± 0.7</td>
<td>27.0 ± 0.4</td>
<td>0.2 ± 0.1</td>
<td>0.3 ± 0.2</td>
<td>0.004 ± 0.003</td>
<td>1 ± 0.006</td>
</tr>
<tr>
<td>( SS_{\text{allyl}} )</td>
<td>71.2 ± 0.7</td>
<td>24.3 ± 0.9</td>
<td>0.1 ± 0.0</td>
<td>4.2 ± 0.2</td>
<td>0.059 ± 0.003</td>
<td>1.31 ± 0.08</td>
</tr>
<tr>
<td>( SS_{\text{diallyl-2}} )</td>
<td>71.2 ± 0.1</td>
<td>22.0 ± 0.2</td>
<td>0.1 ± 0.0</td>
<td>4.4 ± 0.1</td>
<td>0.063 ± 0.001</td>
<td>1.78 ± 0.15</td>
</tr>
<tr>
<td>( SS_{\text{propyl}} )</td>
<td>72.9 ± 0.4</td>
<td>22.8 ± 0.3</td>
<td>0.1 ± 0.0</td>
<td>4.2 ± 0.2</td>
<td>0.058 ± 0.003</td>
<td>1.45 ± 0.05</td>
</tr>
</tbody>
</table>

For all investigations, \( d_{\text{PGMA}} \) is in the 30–50 nm range. \(^b\)Traces of sodium, sulfur, phosphorus, and zinc were detected.

Figure 3. IRRAS spectra of various modified SS samples normalized with respect to the C=O absorbance.

Table 1. Atomic Surface Composition of \( SS_{\text{PGMA}} \), \( SS_{\text{allyl}} \), \( SS_{\text{diallyl-2}} \), and \( SS_{\text{propyl}} \) Measured by XPS along with Ratios of Dry Thin Film Thicknesses, \( d/d_{\text{PGMA}} \), Determined by Ellipsometry

For SSPGMA, the major contributions originate from C and O with a C/O ratio = 2.7, which is only slightly larger than the expected 2.3 for a PGMA film. A minor Cl 2p component is found at 200.0 eV from the end-capped PGMA brushes. The small amount of nitrogen detected might originate from residual 2,2‘-bipyridine (BiPy) used in the polymerization protocol. Noticeably, the high-resolution XPS spectra of
SS_PDMA and SS_allyl (Figure S4 and Table S2, Supporting Information) show the large extent by which the characteristic C 1s signal from the oxirane C–O–C group in SS_PDMA is diminished after modification with allylamine. At the same time, the intensity of the aliphatic components (C–C) is increased as expected.31

For the SS_propyl and SS_allyl samples, the N/C ratios are 0.058 and 0.059, respectively, being equal to the expected 0.059 in the case of a 1:2 amine–oxirane reaction (repeating C12H17O3N units; see Schemes 1 and 2). For a 1:1 amine–oxirane reaction, the N/C ratio would be 0.1 (repeating C12H17O3N units, see Schemes 1 and 2). Hence, the results indicate that cross-bonding of polymer segments, either inter- or intramolecularly, takes place when modifying with primary amines. In comparison, SS_diallyl-2 (secondary amine) shows a N/C ratio of 0.063, which is slightly lower than the 0.077 (repeating C12H17O3N units; see Schemes 1 and 2) expected of a 1:1 amine–oxirane ratio. These results are in accordance with the interpretation of the $d/d_{PDMA}$ determinations for diallylamine and allylamine, although the 1.45 for the propylamine seems to be too high considering that the expected value for a cross-bonding situation is 1.2. In a previous study, where PGMA brushes were reacted with propylamine in aqueous medium, a depth profiling XPS study showed an enrichment of nitrogen in the upper layers.16 This indicated that the amine–oxirane stoichiometry presumably changed from 1:1 in the upper brush layer to a smaller value in the lower brush layer. A direct comparison with our investigation is made difficult by the fact that two different solvents are used, that is, N,N-dimethylformamide and water.

2.2. Peel Test of SS_Chemosil and SS_allyl. Figure 4 (left) presents peel curves of three SS_Chemosil reference samples and two SS_allyl samples along with pictures of relevant fracture surfaces. Four stages in response to the applied loading could be identified: (1) loading of the specimen, during which the rubber arm is bent and stretched, (2) stable crack propagation, (3) unstable crack propagation, and (4) loss of load carrying capacity.32 For the SS_Chemosil samples, the peel curves consistently achieved high forces, leaving the exposed surface area ($7.85 \times 7.85 \text{ mm}^2$) completely covered with rubber after fracture (Figure 4, picture 1). The peel curve from the two SS_allyl samples displays about the same high force as that from SS_Chemosil with the characteristic four stages of load response indicating cohesive fracture (Figure 4, picture 2).

Table 2 provides the average $G_c$ and $A_i$ values determined for the peeled samples. For SS_Chemosil they are in good agreement with the literature,33 showing full cohesive fracture ($A_i = 1$). It should be noted that a low $A_i$ may still result in a large $G_c$ if the cohesive fracture area covers the entire width (perpendicular to the crack growth direction) of the exposed sample area. Furthermore, in the case of cohesive fracture, $G_c$ does not quantify the interfacial toughness but the toughness of the rubber. In the case of SS_allyl, the values of $G_c (15.4 \pm 1.1)$ and $A_i (1.00 \pm 0.01)$ are similar to those of the SS_Chemosil reference ($15.2 \pm 0.4$, and $1.00 \pm 0.00$). This is an encouraging result, considering that the thickness of the SS_allyl interface is in the nanometer range and at least 100 times thinner than that of the commercial Chemosil system. The SS_allyl samples were synthesized from initiator-based SS_hBr samples with an atomic percentage of Br $\approx 2.2$ (determined by XPS), which turned out to be an important feature. With low grafting density samples having less than 1% Br (produced according to previous studies),12,34 the peel results showed large variations (Table S3, Supporting Information).

In our previous study,32 we promoted adhesion by activating PGMA brushes with drop-casted benzoyl peroxide (BPO). Some adhesion was found, although a severe problem was encountered in having a rather non-uniform distribution of BPO on the surface along with the “washing” away of BPO from the edges during compression molding, a problem which could be anticipated to be even larger with the injection molding technique. Herein, we exploit the availability of radicals in the interface during the vulcanization to form directly the chemical bonds between the modified PGMA brushes and the EPDM rubber.8,21 Specifically, the allylic and aliphatic radicals formed by H abstraction in the EPDM rubber can react by addition to the double bonds in the allyl- and diallylamine-modified PGMA brushes.

2.3. Peel Test of SS_diallyl-2. With SS_diallyl-2 large adhesively fractured areas are visible (Figure 4, picture 3), indicating that the fracture behavior is less consistent than that of SS_dialyl. The value of $A_i (0.55 \pm 0.37)$ shows a large variation in cohesive fracture and comes with a corresponding lower and fluctuating $G_c (11.9 \pm 3.1)$. The initial expectation was that the SS_diallyl-2 samples would promote a higher degree of covalent linking in the rubber/brush interface because of the higher numbers of allyl groups available. However, the adhesion becomes weaker, which presumably is associated with the inability of the secondary amines to cross-link the brush structure.

2.4. Peel Test of SS_propyl and SS_PDEAEMA. The SS_propyl substrates show reasonably good adhesive properties (Figure 4, picture 4), although the propyl group contains no double bonds ($G_c = 12.0 \pm 1.9$ and $A_i = 0.95 \pm 0.10$). Hence, a lack of unsaturated bonds in itself is not sufficient to prevent the radical chemistry – in terms of addition and/or combination reactions occurring during curing – from establishing covalent bonding between the brushes and the rubber. Both the amine and the secondary alcohol (formed upon ring opening) in SS_propyl facilitate H abstraction and subsequent addition to olefins in the rubber.35 Importantly, the lone pairs on the heteroatoms exert a stabilizing effect on an adjacent radical center once formed.36,37 Surprisingly, the SS_PDEAEMA samples show no adhesive properties, even if the intrinsic reactivity of SS_PDEAEMA would be expected to be similar to that of SS_propyl. Most likely, this can be explained by a somewhat different polymer brush structure of SS_PDEAEMA, considering that it is produced directly in SI-ARGET-ATRP (Scheme 1); the monomer already contains the amine functionality. Finally, it should be noted that the SS_PDMA sample itself shows no adhesion at all to the rubber.

<table>
<thead>
<tr>
<th>sample</th>
<th>$G_c$ (N mm$^{-1}$)</th>
<th>$A_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS_Chemosil</td>
<td>15.2 ± 0.4</td>
<td>1.00 ± 0.00</td>
</tr>
<tr>
<td>SS_allyl</td>
<td>15.4 ± 1.1</td>
<td>1.00 ± 0.01</td>
</tr>
<tr>
<td>SS_diallyl-2</td>
<td>11.9 ± 3.1</td>
<td>0.55 ± 0.37</td>
</tr>
<tr>
<td>SS_propyl</td>
<td>12.0 ± 1.9</td>
<td>0.95 ± 0.10$^a$</td>
</tr>
<tr>
<td>SS_PDEAEMA</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SS_PDMA$^b$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$Two out of seven samples did not yield cohesive fracture and were not included in the result. $^b$From ref 32.
polymer brushes. In contrast, SSdiallyl and SSPDEAEMA are unable to reinforce the brush structure by internal cross-linking, and therefore, the adhesion abilities become poor. For the diallylamine- and propylamine-based PGMA brushes, a PDEAEMA brush modiﬁed with allylamine, diallylamine, and propylamine. In addition, a PDEAEMA brush film containing a tertiary amine was produced in a direct polymerization without the need for the ﬁnal post-modiﬁcation step. All modiﬁed samples were over-molded with EPDM rubber, cured, and peel tested to evaluate the adhesion between the SS and the rubber. The nanometer-thin PGMA brushes modiﬁed with allylamine consistently obtained an adhesion as strong as that provided by a micrometer-thick commercial bonding agent. This holds promise for potential industrial applications of such brushes. For the diallylamine- and propylamine-based PGMA brushes, the adhesion was inconsistent but much better than that of PDEAEMA. The fact that the primary allylamine and propylamine can establish cross-linking of the polymer brushes after fracture.

2.5. Effect of Cross-Linking on Stress Distribution along the Bondline. Until now, we have only paid little attention to the effect that cross-linking in the brush structure exerts on the adhesion properties. Following the analysis of adhesive joints given by Penado et al.,30 the length of the process zone in a peel experiment, that is, the region of tensile stress in front of the crack tip, depends on the stiffness. The stiffness is understood to be a combination of material and geometrical parameters of both the rubber and the adhesive, in particular, the elastic modulus (E) and the thickness. The stress distribution in front of the crack affects the overall fracture process. Increasing the cross-linking density of, for example, rubber increases its E modulus39,40 and consequently the process zone length, thereby, altering the stress distribution.41,42 Distributing the stresses over a larger area means that the peak stress reduces and, thus, makes the structure appear tougher.

As a result, cross-linking the polymer brushes by modiﬁcation with primary amines may increase the process zone length and enhance the adhesive strength of the polymer ﬁlms. The remarkable bonding ability of the SSdallyl samples is thus attributed to the cross-linked polymer structure. Likewise, the enhanced adhesion observed for the propylamine can be assigned to the corresponding cross-linked nature of the polymer brushes. In contrast, SSdallyl and SSPDEAEMA are unable to reinforce the brush structure by internal cross-linking, and therefore, the adhesion abilities become poor.

3. CONCLUSIONS

PGMA brushes were covalently grafted from stainless steel and modiﬁed with allylamine, diallylamine, and propylamine. In addition, a PDEAEMA brush ﬁlm containing a tertiary amine was produced in a direct polymerization without the need for the final post-modiﬁcation step. All modiﬁed samples were over-molded with EPDM rubber, cured, and peel tested to evaluate the adhesion between the SS and the rubber. The nanometer-thin PGMA brushes modiﬁed with allylamine consistently obtained an adhesion as strong as that provided by a micrometer-thick commercial bonding agent. This holds promise for potential industrial applications of such brushes. For the diallylamine- and propylamine-based PGMA brushes, the adhesion was inconsistent but much better than that of PDEAEMA. The fact that the primary allylamine and propylamine can establish cross-linking of the polymer brushes during post-modiﬁcation is suggested to have a signiﬁcantly positive effect on both the fracture toughness and the cohesive-to-adhesive fracture ratio of the adhesives.

4. MATERIALS AND METHODS

4.1. Materials. Acetone (HPLC grade), acetonitrile (MeCN, HPLC grade), methanol (MeOH, HPLC grade), N,N-dimethylformamide (DMF, HPLC grade), dichloromethane (DCM, HPLC grade), glycidyl methacrylate (GMA, 99%), 2-(diethylamino)ethyl methacrylate (DEAEMA, 99%), 2-bromoisobutyryl bromide (BIBB, 98%), 2,2’-bipyridine (BiPy, >99%), triethylamine (TEA, >99%), sodium ascorbate (NaAsc, >99%), allylamine (98%), diallylamine (99%), and propylamine (>99%) were all purchased from Sigma Aldrich, and Cu(NO3)2·3H2O (99%) from Merck. The materials were all used without further puriﬁcation, the exception being GMA and DEAEMA, which were passed through an aluminum oxide column before polymerization to remove the inhibitor. Standard procedures were followed to prepare the supporting electrolyte tetrabutylammonium tetraﬂuoroborate (Bu4NBF4) and 4-(2-hydroxyethyl)benzene diazonium tetraﬂuoroborate (HEBD). Stainless steel (ASTM316) plates were cut into test pieces of 2 × 10 × 10 mm3 size (Jensen Metal A/S, Denmark) (Supporting Information, Figure S1, item 4). They were polished for 1 h using a diamond suspension (Struer, grain size of 9 μm) followed by 10 min sonication in Milli-Q water and in acetone. Noncured EPDM rubber (Shore 70) containing dicumyl peroxide (DCP) (AVK Gummi A/S, was used for spray-painting on the steel surfaces, annealed at 140 °C for 1 h to yield a 30 μm layer, and used as a reference sample (SSChemosil)).

4.2. Preparation of Initiator Layer. Electrochemical grafting was performed on SS substrates using the protocol described elsewhere. In short (see Scheme 1), SS substrates were modiﬁed by potentialostatic electrolysis of 2 mM HEBD in 0.1 M Bu4NBF4/MeCN for 300 s at a potential 0.2 V more negative than the voltammetric peak potential, Epc. The peak potential was determined from an initial cyclic voltammetric sweep carried out at a sweep rate of 0.1 V s−1. Next, the formed hydroxyl terminated SS samples (SSOH) were acylated in 0.46 M BIBB and 0.05 M TEA in DCM at room temperature. This afforded a bromine terminated radical initiator layer ﬁlm (SSBr). The SSOH and SSSBr samples were rinsed in MeCN and DCM, respectively, and sonicated for 10 min in acetone.

Figure 4. Graphs showing peel forces of two SSdallyl (black) and three SSChemosil samples. The pictures are peel pro...
4.3. Polymerization. For the SI-ARGET-ATRP, solutions of 1:1 (v/v) MeOH–Milli-Q water (2 × 4.5 mL) and GMA (1 mL, 0.8 M) were mixed in a Schlenk flask, placed in an ice bath, and purged with Ar for 15 min under stirring. BiPy (12.4 mg, 80.0 mM), NaAsc (7 mg, 3.5 mM), and CuIICl2 · 2H2O (6.8 mg, 4.0 mM) were added, and the solution was purged with Ar for additional 10 min. SSb substrates were immersed into the reaction mixture and polymerized at 0 °C for 0.25–2.0 h under an Ar atmosphere (Scheme 1). To examine the liveliness of the polymerization, the substrates were pulled out of the solution at 15 min intervals and flushed with Ar. The samples produced (SSPGMA) were rinsed with Milli-Q water and MeOH, followed by sonication in acetone. The polymerization of DMEAMA followed the same procedure to obtain corresponding modified samples denoted SSDMEAMA.

4.4. PGMA Modification with Amine Reagents. The amine reactant was added to a three-necked flask containing 19 mL of DMF. The solution was flushed with Ar for 10 min and heated to a given reaction temperature. Samples were immersed in the solution and kept there under an Ar atmosphere for ∼18 h. The modified samples were rinsed with DMF and sonicated for 10 min in acetone. Table 3 lists the specific conditions used in each case.

Table 3. Post-modification Conditions for SS PGMA Samples

<table>
<thead>
<tr>
<th>reactant</th>
<th>bp (°C)</th>
<th>vol (mL)</th>
<th>conc (mol L−1)</th>
<th>temp (°C)</th>
<th>sample name</th>
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<tr>
<td>propylamine</td>
<td>48</td>
<td>1</td>
<td>0.61</td>
<td>48</td>
<td>SS Pprop</td>
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<tr>
<td>allylamine</td>
<td>54</td>
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<td>0.67</td>
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<tr>
<td>diallylamine</td>
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<td>0.41</td>
<td>70</td>
<td>SS Astd-1</td>
</tr>
<tr>
<td>diallylamine</td>
<td>109</td>
<td>2</td>
<td>0.81</td>
<td>70</td>
<td>SS Astd-2</td>
</tr>
</tbody>
</table>

“Notations used are bp: boiling point, vol: volume of amine added, conc: concentration of amine, and temp: reaction temperature.

4.5. Compression Molding. Compression molding was employed to cure the rubber and facilitate bond formation between rubber and the SS samples. Two modified SS samples and one blank SS sample were fitted in a sample holder (Figure S1, item 3) and placed in a heated aluminum mold (PID regulated, Eagle model #1048) in a hydraulic press (Carver model #3912). The aluminum molds (Figure S1, items 1, 6, and 7) were preheated to 170 °C. A sheet of nonvulcanized rubber (Figure S1, item 2), of approx. 80 × 20 × 6 mm² size, was placed on top of the sample holder, and 6 tons of pressure was applied for 12 min at 170 ± 2 °C. Finally, the over-molded samples were post-cured in an oven (Binder E28, Holm og Halby, DK) for 4 h at 150 °C.

4.6. Peel Testing. A full description of the test setup and the data treatment is provided elsewhere. In general, peel tests were conducted on a universal testing machine (Zwick Z005, Zwick GmbH & Co. KG, Ulm-Einsingen, Germany) under a loading rate of 0.5 mm s⁻¹. A custom-made fixture consisting of a sled and a base both fixed to the testing machine was designed. Translating on low-friction brass wheels, the sled ensured a constant peel angle close to 90°. This setup differs from the usual peel experiment where an inextensible tape is peeled along a macroscopically homogeneous growth path. Either two or three specimens separated from each other by an 8.5 mm nonbonded area provided a discontinuous path. Equation 1 was used to calculate the peel energy (P).

\[ P = F/b \]

In this expression, \( F \) is the measured force, and \( b \) is the width of the crack perpendicular to the peel direction, that is, the width of the exposed sample area (\( b = 7.85 \text{ mm} \)). It is assumed that \( P \) equals the fracture toughness \( (G_c) \), once the crack starts to propagate.

4.7. Optical Profilometry. Fracture regions were examined with a 3D macroscopic scanner (VR-3200, Keyence, Japan) with 160× magnification to determine the type of fracture (interfacial/adhesive or cohesive). The fraction of the cohesively failed area relative to the exposed surface area (7.85 × 7.85 mm²), \( A_r = A_{\text{cohesive}}/A_{\text{total}} \), was determined for each sample as a quantitative measure of the bonding quality.

4.8. Ellipsometry. For dry film thickness measurements, a rotating analyzer ellipsometer (Dre, Germany) with a He–Ne laser (632.8 nm) was used. The SS substrates were irradiated at a 75° angle of incident. The parameters \( \Delta \) (phase shift) and \( \psi \) (ratio of amplitude upon reflection) were measured and processed in the Ellips32 software. The software calculated the complex refractive index of the bare surfaces from \( \Delta \) and \( \psi \), whereas for the modified surfaces, a three-layer optical model was used. The refractive index of the organic film was assumed to be 1.55, independent of the thickness. Three measurements per SS sample were performed on three different spots for all substrates, both pre- and post-modification. Film thicknesses reported for brush-modified samples were all subtracted for the initiator layer thickness.

4.9. Infrared Reflectance–Absorption Spectroscopy (IR-RAS). A Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Denmark) equipped with a Varian external experimental module with a narrow band mercury–cadmium–telluride (MCT/A) detector cooled with liquid nitrogen was employed for recording the IRRAS spectra. The spectral resolution and number of scans averaged were 4 cm⁻¹ and 200, respectively. All spectra were recorded at room temperature in a dry atmosphere. The logarithm of the p-polarized reflectivity of the film divided by the reflectivity of the bare substrate was presented as IRRAS absorbance. The substrates were irradiated at an incident angle of 80°. Baseline correction was performed using the OMNIC 8.2 software, and spectra were normalized with respect to the C=O absorbance.

4.10. X-ray Photoelectron Spectroscopy (XPS). A Kratos Axis Ultra-DLD spectrometer (Kratos Analytical Ltd, UK) with a monochromatic Al Kα X-ray source at power = 150 W was used for the XPS analysis. All survey spectra were acquired by accumulation of two sweeps from 0 to 1400 eV at a pass energy of 160 eV and a pass energy of 20 eV for high-resolution spectra. The pressure in the chamber was kept below 5 × 10⁻⁹ mbar during measurements. An electron flood gun was employed as a neutralizer, and the C 1s peak of C=C-C=H components was used as reference for charge correction with binding energy \( \equiv 285.0 \text{ eV} \). Data collections were obtained from three measurement points on one sample. Spectral processing was carried out using CasaXPS v2.3.15 software (Casa Software Ltd, Teignmouth, U.K.).

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02312.
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