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Recyclability of Photoinduced Cross-Linked EPM Rubber with Anthracene-Grafted Groups: Problems and Their Solutions

Alexander T. Zdvizhkov,* Krists Smogorzevskis, Martin van Duin, and Francesco Picchioni



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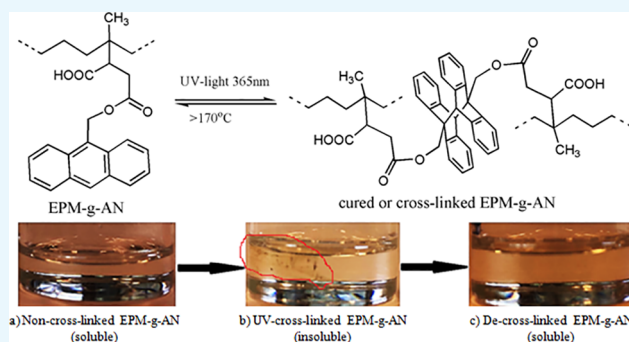
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ABSTRACT: In this paper, we present the formation of reversible covalently cross-linked networks in ethylene propylene rubber with grafted anthracene groups (EPM-g-AN) based on the principles of photoinduced anthracene dimerization. First, an industrial-grade EPM rubber grafted with maleic anhydride functional groups (EPM-g-MA) was modified with 9-anthracenemethanol. By irradiating EPM-g-AN with UV light (365 nm), the anthracene moieties dimerize via [4 + 4] cycloaddition, forming a covalent network. The network cleavage proceeds at high temperatures (>170 °C), even if with considerable (chemical) degradation. Furthermore, one of the degradation routes has been identified by ¹H NMR to occur via the ester bond cleavage releasing 9-anthracenemethanol. Nevertheless, the reversibility of cross-linking has been achieved by performing the reverse reaction in decalin. The UV–vis spectroscopy clearly shows that the de-cross-linking process in these conditions is due to the anthracene dimer cleavage. Although the recovery in mechanical properties upon recycling is yet to be optimized, the disclosed results pave the way toward the use of anthracene chemistry in thermally reversible networks with possible industrial perspective applications.



INTRODUCTION

Cross-linked thermoset resins constitute one of the most significant pillars of the polymer industry. Indeed, these materials cannot be dissolved and do not melt and, as result, show higher strength in comparison with un-cross-linked thermoplastics. Their use is more preferable as compared to thermoplastic if high performance is required, such as in high-temperature applications. For instance, cross-linked materials are applied in aircraft body manufacturing,^{1–3} adhesives,^{4,5} fuel tanks,⁶ and car tires.⁷

However, processing of thermosets is a difficult process, if possible at all after the shaping step, since such procedures are carried out at elevated temperatures, which may result in spontaneous curing of the gear. The fast growth of the polymer industry also entails new regulations on the recyclability of polymer products.⁸ Nowadays, the reactions for thermoset curing are not reversible. The most common processes are free-radical cross-linking with peroxides^{9–11} and difunctional acrylates or styrene,¹² hydrosilylation of polyvinylsiloxanes,^{13–16} and epoxide ring cleavage.^{17–22} As a result, materials based on these curing chemical routes are not able to be recycled and/or reused (as a new polymer) and are usually disposed of as raw waste or ground to a powder (with a significant decrease in economic value) to be used as a filler.

Recently a reversible Diels–Alder (DA) reaction has been applied for thermoreversibly cross-linked rubber²³ and

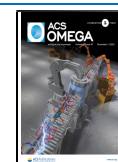
thermosets.²⁴ Nevertheless, some irreversible cross-linking reactions may take place under the same experimental conditions (high temperature) in which the de-cross-linking retro-DA reaction occurs.²⁵ Moreover, for some manufacturing protocols, e.g., three-dimensional (3D) printing,²⁶ photo-induced cross-linking is more preferable.

The photoinduced anthracene coupling reaction ([4 + 4]-cycloaddition) is a common process in material chemistry.²⁷ Anthracene coupling or dimerization proceeds under UV irradiation with the wavelength exceeding 300 nm.²⁸ The reverse reaction might be initiated also by UV radiation (<300 nm)²⁸ or thermally above 170 °C.²⁹ Reversible cross-linked polymers coupled via anthracene moieties were described earlier.^{28–30} However, these works, despite delivering convincing proof-of-principle for the concept, often do not contain any practical investigation of the recyclability of the final product, as well as a systematic comparison of the thermo- and

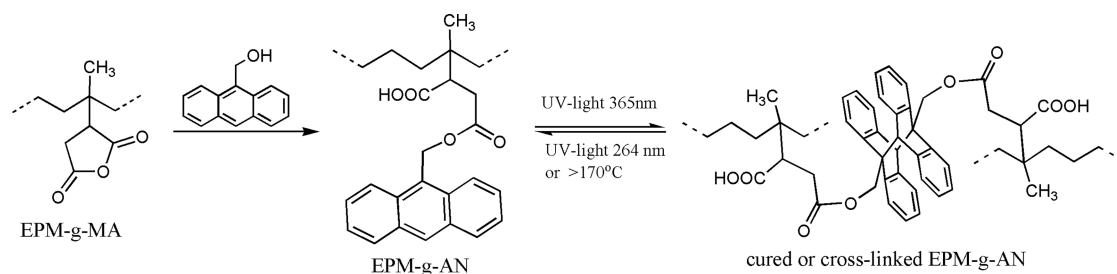
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Scheme 1. Synthesis and Curing of EPM-g-AN



photoinduced routes to dimer cleavage and thus de-cross-linking.

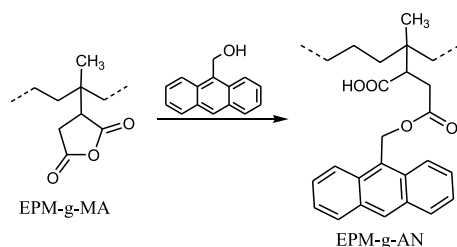
In the present work, we report the results of our research on ethylene propylene rubber with grafted anthracene groups (EPM-g-AN) cured via anthracene moiety dimerization under UV-irradiation exposure and the UV- and thermally induced recyclability of this thermoset material (Scheme 1).

Commercially available EPM-g-MA was treated with 9-anthracenemethanol to yield anthracene-containing EPM rubber (EPM-g-AN). UV irradiation results in polymer cross-linking. The cured rubber might be converted to a de-cross-linked processable form under exposure to either UV irradiation or increased temperature (above 170 °C).

RESULTS AND DISCUSSION

EPM-g-MA Rubber Modification with 9-Anthracenemethanol. To graft the EPM-g-MA rubber with anthracene moieties (Scheme 2), 9-anthracenemethanol was mixed with EPM-g-MA in a Brabender at 170 °C and 50 rpm for 4 min under N₂.

Scheme 2. Anthracene Grafting on EPM-g-MA



Such conditions were chosen to ensure the thorough melting of 9-anthracenemethanol (melting point: 160.0–167.0 °C) and thus optimal mixing with EPM-g-MA. In addition, the reaction was performed under N₂ to avoid oxidation and other side reactions. Two times the stoichiometric amount of 9-anthracenemethanol was used with respect to the MA functional groups of EPM-g-MA to ensure higher conversion. After performing the reaction in Brabender, the resulting polymer was purified by reprecipitation to ensure the removal of the unreacted excess 9-anthracenemethanol. The agreement between the theoretically calculated composition and the experimentally measured values (see Experimental Section) confirms 100% conversion of maleic groups to N-furfurylimide groups. Furthermore, UV-vis and Fourier transform infrared (FTIR) results confirm qualitatively that the grafting was successful to yield EPM-g-AN (Figure 1).

Indeed, a typical anthracene peak between 300 and 400 nm indicates the presence of anthracene groups along the polymer backbone. Also, we can observe a slight shift of carbonyl peaks in the FTIR spectrum (Figure 1b), attributed to the conversion of the anhydride into ester and acid groups. Indeed, the split of the peak at 1710–1720 cm⁻¹ in FTIR confirms the transformation of anhydride group into an ester, 1717 cm⁻¹, and acid groups, 1709 cm⁻¹. These pieces of evidence, together with the very thorough washing of the product by reprecipitation in acetone, clearly suggest the successful grafting of anthracene along the polymer backbone. A more detailed characterization (chemical and/or spectroscopic) is hindered by the polymeric nature of the product, resulting, for example in relevant noise in the FTIR spectrum (vide supra), as well as the relatively low amount of functional groups along the backbone. Nevertheless, it must be stressed here that the

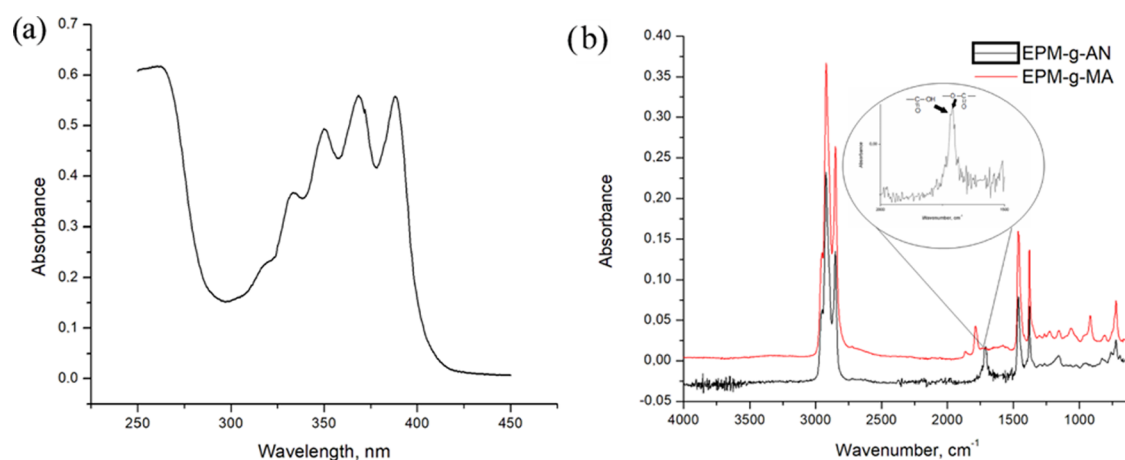
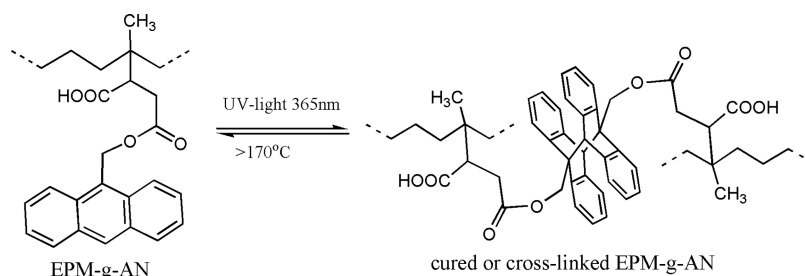


Figure 1. (a) UV absorbance spectrum of EPM-g-AN. (b) FTIR of EPM-g-AN and EPM-g-MA.

Scheme 3. Reversible Cross-Linking of EPM-g-AN Rubber



presented result is in agreement with the previous one obtained in our group on a very similar system.^{23,31,32}

UV-Cross-Linking of EPM-g-AN Rubber. The main idea of this work is based on the ability of anthracene for UV-assisted dimerization. This reaction has several advantages as compared for example to the often used DA reaction between furan and maleimide. In the first instance, the direct and reverse reactions for anthracene are initiated by different sources (irradiation and heat), which allows them to occur independently. Differently from this, the retro-DA reaction is initiated by higher temperatures than the direct DA, thus allowing possible partial cross-linking only while cooling down.

The formation of a reversibly cross-linked network by the principles of UV-induced [4 + 4] cycloaddition between anthracene moieties in EPM-g-AN rubber is attempted (Scheme 3).

From EPM-g-AN, bars are prepared by compression molding at 130 °C, 50 bar for 30 min. To induce cross-linking, the bars are irradiated under a UV lamp ($\lambda = 365$ nm) and consequently characterized by tensile testing.

The stress–strain diagram, shown in Figure 2, illustrates that higher stresses and significantly lower strains at the break, compared to the un-cross-linked counterpart, can be detected.

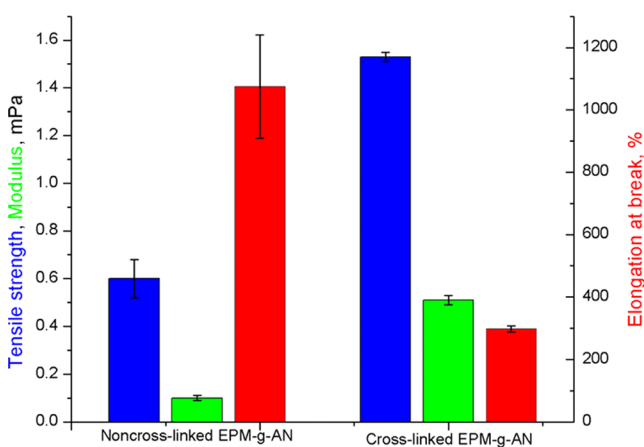


Figure 2. EPM-g-AN Tensile Properties.

The cross-linked bars have notably higher average Young's modulus and ultimate tensile strength values. Furthermore, the average elongation at break is much higher for the un-cross-linked precursor. These observations are in agreement with the expectations, as such changes in the tensile properties upon cross-linking are typical.³³ Furthermore, a similar relationship was established in previous research on EPM-g-furan cross-linked with bismaleimides via the DA route.²³

Recyclability via Compression Molding. As already shown,²⁹ the anthracene dimer can be broken at a temperature above 170 °C. We tried then to investigate whether these conditions would result in a recyclable product (Figure 3).

After grafting the EPM rubber with anthracene moieties and subsequent purification, several samples (bars) were made by compression molding (Figure 3a).

Freshly prepared virgin (un-cross-linked) EPM-g-AN could be successfully processed into a bar (Figure 3a). Furthermore, after performing a tensile test and cutting the un-cross-linked bar in small pieces, a reprocessed EPM-g-AN sample was made (Figure 3c) without noticeable defects to the naked eye. Cross-linking under UV light did not visually affect the samples (Figure 3d). After tensile testing, the UV-cross-linked bars were cut and the attempt of reprocessing failed, resulting in a heterogeneous sample with air bubbles and a clear color change (Figure 3f). Tensile tests on the reprocessed UV-cross-linked bars were not performed due to these defects. Thus, the reprocessing of the UV-cross-linked EPM-g-AN via simple annealing at high temperature (compression molding) was deemed to be unsuccessful at the given conditions. Compression molding at harder conditions (210 °C and 100 mPa for 20 min) did not also give the desired results. It is suspected that due to the presence of oxygen during compression molding, oxidative processes occur³⁴ leading to the degradation processes. Thus, an additional experiment was designed, where the de-cross-linking was performed in a flask under argon at 210 °C. However, also, in this case, a change in the color of the polymer was observed, indicating thermal degradation.³⁴ Furthermore, the formation of yellow crystals on the top of the flask and other parts of the equipment was observed. A UV–vis spectroscopy analysis in tetrahydrofuran (THF) was employed to identify the yellow compound. Figure 4 shows the characteristic peaks (between 325 and 400 nm) of anthracene compounds,³⁵ indicating that the degradation product contains anthracene functional groups.

It is suspected that the yellow compound is 9-anthracenemethanol, hence to further identify the degradation product, ¹H NMR spectra in dimethyl sulfoxide (DMSO)-*d*₆ were recorded for 9-anthracenemethanol and the decomposition product.

Both spectra were compared and all of the characteristic 9-anthracenemethanol peaks (including the alcohol peak) were identified in the spectrum of the degradation product (Figure 5), indicating that 9-anthracenemethanol is present in the degradation product. This proves that the degradation partially occurs via the ester bond cleavage. Numerous unidentified peaks were also observed, indicating other species in the degradation product.

Recyclability via Dissolution. The effects of cross-linking and de-cross-linking have been demonstrated by testing the

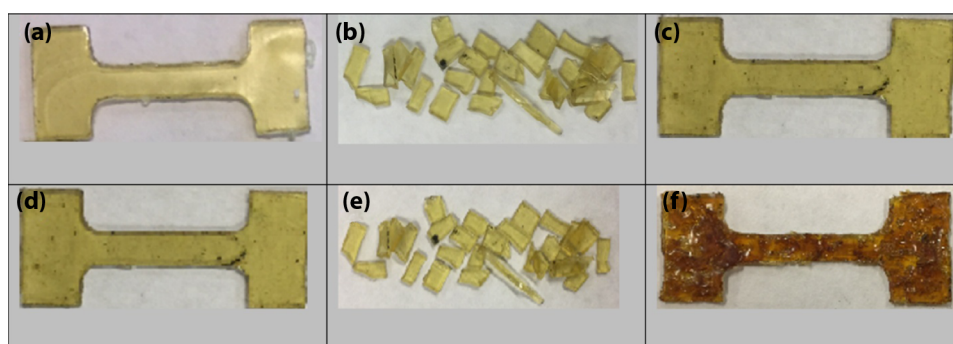


Figure 3. (a) Virgin sample (un-cross-linked), (b) cut virgin sample (un-cross-linked), (c) reprocessed sample (un-cross-linked), (d) UV-cross-linked sample, (e) cut UV-cross-linked sample, and (f) reprocessed UV-cross-linked sample.

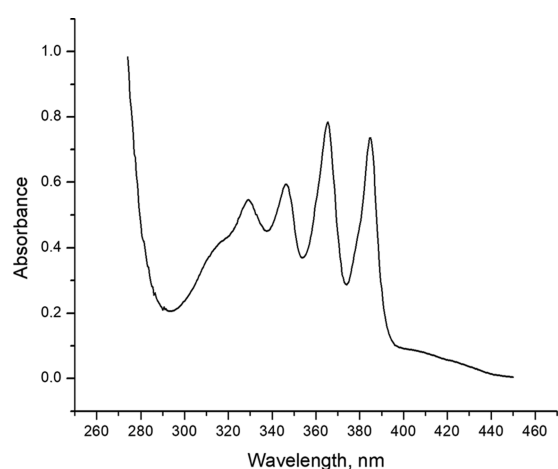


Figure 4. UV-vis absorbance spectrum of the degradation product.

solubility in decalin. This process has some advantages, compared to de-cross-linking by simple annealing in the bulk. First, the solvent “protects” the polymer from oxygen. It also affords to control the process duration more precisely. Since the dissolving process is visible, it can be stopped as soon as complete dissolution has been achieved within about 30 min. This affords to avoid unnecessary exposure to high temperatures, which can cause degradation of the polymer backbone or functional groups. Such control is obviously not possible when compression molding is being applied. Lastly, decalin is a swelling solvent for cross-linked EPM rubbers. This entails then the possibility for the network to be strained in the presence of decalin, thus favoring the breakage of the cross-linking points.

A piece of the bar of un-cross-linked EPM-g-AN easily and fully dissolved in decalin within 30 min at RT (Figure 6a). However, after 6 h of UV irradiation (365 nm) of the same EPM-g-AN bar, the bar segment did not dissolve at all (full insolubility) under the same conditions (Figure 6b). The difference in the solubility of the UV-irradiated (cross-linked) and untreated (un-cross-linked) samples indicates effective cross-linking.³⁶ To examine the reversibility of the cross-links, the same dispersion (insoluble sample) was heated up to 170 °C for 30 min, resulting in a fully soluble mixture (Figure 6c). Thus, the de-cross-linking proceeded effectively, indicating the reversible character of the UV-cross-linked EPM-g-AN.³⁷

However, previous experiments and analysis suggest that ester bond cleavage and degradation occur at 210 °C, leading to the defunctionalization of EPM-g-AN, which also could

cause de-cross-linking of the polymer network. Thus, an additional experiment was designed to examine if the de-cross-linking and the resulting increase in solubility are caused by the dissociation of anthracene dimers in EPM-g-AN or due to the ester moiety cleavage. A piece of cross-linked rubber was heated up to 170 °C in decalin. The obtained solution was reprecipitated in a 10-fold amount of acetone and washed several times with acetone to ensure the purity and the removal of possible impurities. UV-vis spectroscopy clearly showed that the dissociation of anthracene moieties dimers took place (Figure 7).

The presence of the characteristic peaks in anthracene-functionalized compounds indicates that the cleavage of the ester bond did not occur or only occurred partially at 170 °C in decalin (Figure 5).

To confirm the reversibility of the UV-cross-links one more time, the de-cross-linked film was irradiated with UV lamp (365 nm) for 40 min. The disappearance of anthracene peaks confirms effective cross-linking (Figure 7). To reiterate, the polymer was then de-cross-linked in decalin; the presence of anthracene groups was confirmed by UV-vis spectroscopy (film on a quartz substrate), and the cross-linking was again successfully achieved by UV irradiation of the film. Thus, EPM-g-AN can be at least partially reprocessed by de-cross-linking in decalin; however, it is still possible that some defunctionalization occurred.

The de-cross-linking process carried out in decalin and consequent compression molding might be an alternative to the direct compression molding of the UV-cross-linked material. If de-cross-linking in decalin does result in some losses of anthracene functionality, without significant degradation of the polymer backbone, such a method could be used to recover EPM-g-AN. We then proceeded by comparing the recycled rubber to the virgin counterpart in terms of mechanical properties (Figure 8).

After first recycling, we observed a decrease in both tensile strength and elongation at break, which did not cause a change in modulus. Second recycling significantly results in decreased values of tensile strength, while a third one just sets the trend further. Elongation at break values is generally more constant. After dropping in the first recycling step, they remain roughly constant for the next two cycles.

Obviously, we can observe the recycling possibilities but not with high efficiency. This might be due to other reasons such as degradation of weak ester moiety and sequent irreversible cross-linking at the active center and main hydrocarbon polymer chain free-radical irreversible cross-linking processes. Additionally, the oxidation reaction of anthracene under

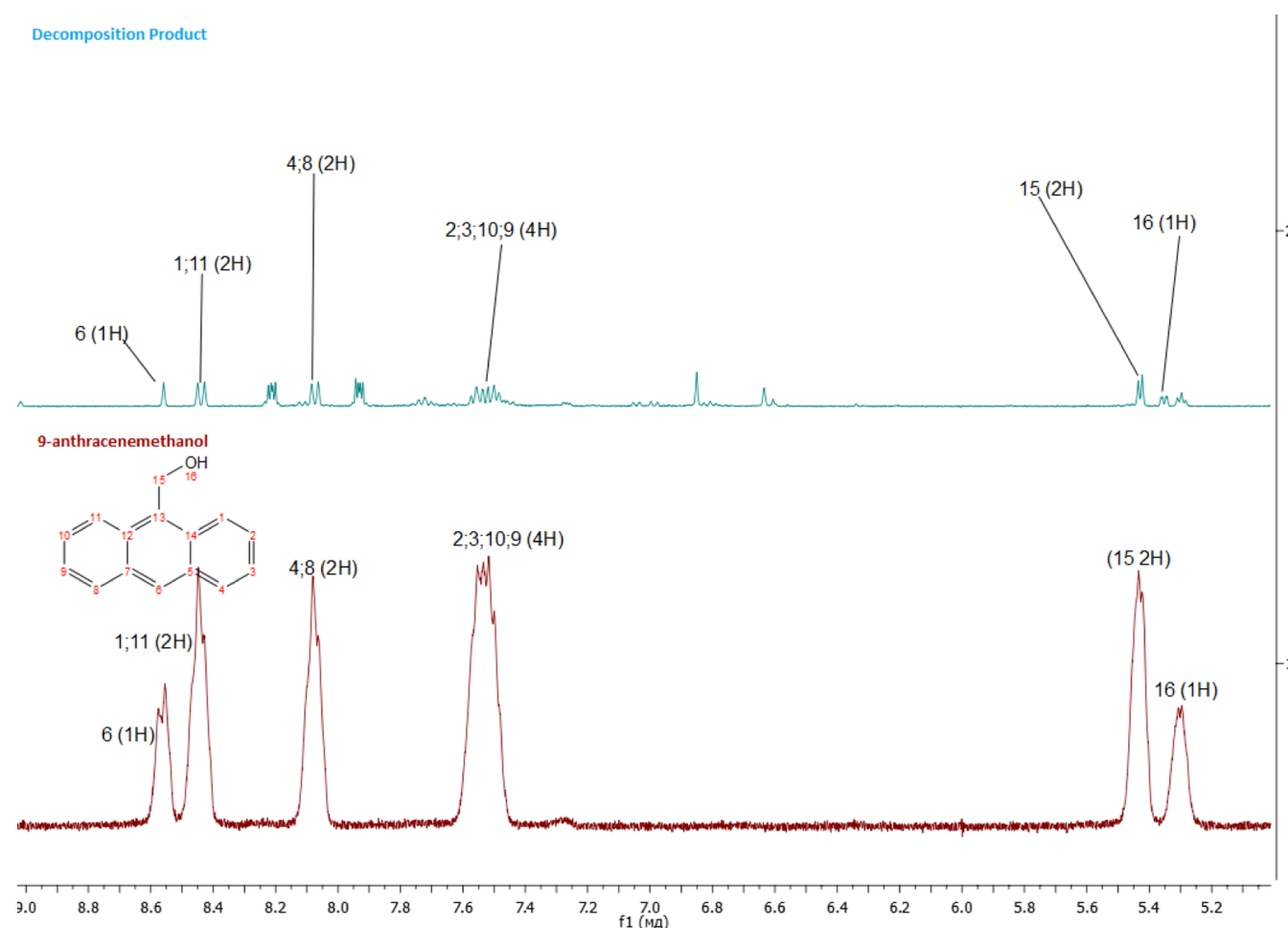


Figure 5. ^1H NMR spectra of the degradation product (on top) and 9-anthracenemethanol (bottom).

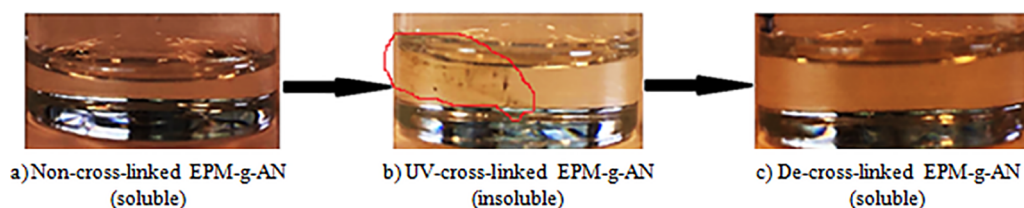


Figure 6. Solubility test of EPM-g-AN.

irradiation with the formation of peroxides is also a possibility.³⁸ This might result in irreversible bonds between the chains and in the beginning in simple chain extension (increase in molecular weight) due to the relatively low amount of anthracene groups along the backbone. Further thermal cycling might then indeed result in cross-linking, and this might be responsible for the deterioration of mechanical behavior. As such, it is fair to say that the observed result merely, although clearly, indicates the possibility for recycling, while additional work should be carried out to fully clarify the chemical reactions that might take place.

CONCLUSIONS

In the present work, the possibility to recycle an EPM rubber containing anthracene pending groups has been investigated. Such a rubber was prepared by the reaction of commercially available materials: EPM-g-MA (Keltan 1519R) and 9-anthracenemethanol. The reaction in the melt showed 100%

conversion of maleic anhydride groups along the polymer backbone.

After cross-linking, simple attempts at recycling the material via heating at high temperatures clearly failed as spectroscopic pieces of evidence, among others, showed the occurrence of a side reaction, namely, the ester breakage with the detachment of the anthracene moieties from the polymer backbone. On the other hand, the use of decalin in the de-cross-linking reaction, first as a swelling agent and later as a solvent for the de-cross-linked rubber, allows recovery of an un-cross-linked rubber sample showing good retention of the mechanical properties upon a second cross-linking reaction. However, upon subsequent de-cross-linking and cross-linking cycles, the mechanical behavior deteriorates very rapidly, thus suggesting once more the presence of chemical degradation mechanisms.

On a more general level, the observed results clearly indicate the possibility of the use of anthracene moieties along a polymeric backbone for UV-cross-linking. The possibility of

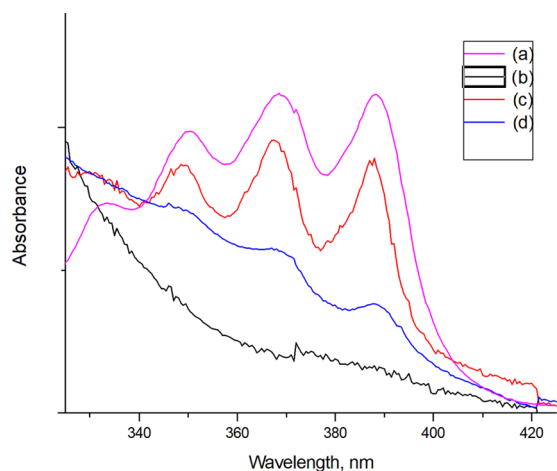


Figure 7. UV absorbance spectra of de-cross-linked and cross-linked EPM-g-AN. (a) Virgin EPM-g-AN rubber; (b) cross-linked EPM-g-AN; (c) heat-treated EPM-g-AN after reprecipitation; and (d) re-cross-linked EPM-g-AN.

	0	1	2	3
σ , MPa	1.53±0.02	1.22±0.15	0.61±0.02	0.51±0.01
ε , %	298±9	258±34	nd	246±75
E, MPa	0.51±0.02	0.45±0.08	nd	0.22±0.07

nd – not detected

Figure 8. Recycling of the UV-cross-linked EPM rubber.

recycling is also clearly shown even if with the help of a swelling agent. This research paves the way toward the use of these functional groups for reversible cross-linking while highlighting that a more robust chemical linkage (for example, amide instead of ester) is actually needed to anchor the anthracene to the polymer backbone. This is the subject of a current project in our research group.

EXPERIMENTAL SECTION

Materials. The EPM-g-MA (2.1 wt % of the anhydride groups) rubber was kindly supplied by Arlanxco (Keltan 1519R) and dried for 30 min at 175 °C, 10 mmHg, before each experiment. 9-Anthracenemethanol was purchased from Sigma-Aldrich and used without purification. Solvents, acetone, chloroform, and decalin, were purchased from Acros-Organics and used without purification.

Functionalization of EPM-g-MA with 9-Anthracenemethanol. Eighteen grams of EPM-g-MA (3.9 mmol of MA) was mixed in Brabender at 170 °C and 50 rpm for 4 min under a nitrogen atmosphere. Consequently, 1.61 g of 9-anthracenemethanol (7.7 mmol, 2.0 molar equivalent based on the amount of MA in EPM-g-MA) was added to EPM-g-MA in the Brabender and mixed for an additional 4 min under the conditions specified above. The obtained product was dissolved in 100 mL of chloroform and reprecipitated in 10-fold excess acetone. Yellow fibers were collected by filtration and dried overnight in a vacuum (10 mmHg) at 60 °C. The yield was 16.95 (90%).

Elemental analysis: calcd %C 84.94; %H 13.77

Found: %C 84.91; %H 13.61

UV-Cross-Linking of EPM-g-AN Rubber. Samples (for both tensile strength test $35 \times 3 \text{ mm}^2$ and films $10 \times 10 \text{ mm}^2$) were exposed to a UV lamp (8W, Spectroline ENB-280C/FE) with a wavelength 365 nm for 3 h on each side (2.4 cm distance from the light source, only for dog-bond bars, films were irradiated on one side at the same distance).

Solubility Test of EPM-g-AN. Un-cross-linked (soluble) and UV-cross-linked (insoluble) EPM-g-AN were put in decalin to dissolve at room temperature. After overnight stirring at ambient temperature, the insoluble cross-linked sample was heated up to 170 °C for 30 min, yielding a clear solution. The un-cross-linked sample yielded a clear solution within 2–3 h at ambient temperature. Then, the de-cross-linked rubber solution in decalin was reprecipitated in ~10-fold excess of acetone and washed several times with acetone to ensure purity.

Recycling of Cross-Linked EPM-g-AN Rubber. Cross-linked samples after tensile testing were cut into $2 \times 2 \text{ mm}^2$ pieces and placed in decalin (sufficient volume to obtain 10 wt % solution of the polymer). The mixture was heated up and stirred until a clear solution was formed (~30 min). De-cross-linked rubber was isolated by reprecipitation in 10-fold excess of acetone and dried at 60 °C, 10 mmHg overnight. The new samples were obtained by compression molding at 130 °C, 50 MPa for 30 min.

Measurements. Ultraviolet–visible (UV–vis) absorbance spectra of thin films on quartz substrates and polymeric chloroform and tetrahydrofuran solutions in quartz cuvettes were recorded on a Helios Aquamate spectrometer (Thermo-Spectronic, England) in the range of 200–450 nm at a scan speed of 600 nm/min and room temperature. The data were processed with VISIONlite Scan software. ^1H NMR spectra for the decomposition product of the UV-cross-linked polymer were recorded on Varian Mercury Plus 400 MHz in DMSO- d_6 . To determine the conversion of the functionalization of EPM-g-MA rubber, after purification and drying, the elemental analysis (EA) of C and H was performed with an Euro EA elemental analyzer. Tensile tests were carried out using an Instron 5565 apparatus. A strain rate of 500 mm/min was selected. For both sets of samples, five samples were tested. The data were processed in Tinius Olsen Horizon software. In calculations for averages, an outlier was excluded.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Notes

The authors declare no competing financial interest.

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