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Oligomeric Curing Activators Enable Conventional Sulfur-Vulcanized Rubbers to Self-Heal

Alan M. Wemyss, Arkadios Marathianos, Ellen L. Heeley, James Ekeocha, Yoshihiro Morishita, Raffaele di Ronza, M. Mar Bernal, David M. Haddleton, and Chaoying Wan*

ABSTRACT: When introducing self-healing properties to elastomers, it is often difficult to balance their ability to recover properties after damage with a good mechanical strength prior to damage. We demonstrate that by replacing the activator system used in conventional accelerated vulcanization (CV) chemistry, from the traditional zinc oxide (ZnO) and stearic acid to a complex formed between ω-propenyl functional oligomers of poly(zinc methacrylate) (pZnMA/ZnO), the self-healing properties of Vulcanized natural rubbers are enhanced while maintaining good tensile strengths. The pZnMA oligomers, as synthesized by catalytic chain transfer polymerization (CCTP), act as an activator for the sulfur curing system, while also forming an ionic network in the rubber. The addition of 20 phr of pZnMA/ZnO to a CV system resulted in a cured natural rubber with a tensile strength of 7.47 ± 0.64 MPa, which recovered 86.7% after self-healing at 80 °C for 2 h. Further addition of 40 phr of carbon black N234 unexpectedly enhanced the self-healing efficiency of these Vulcanized rubbers to 92.2% under the same conditions and also improved the self-healing at room temperature. Finally, dynamic mechanical thermal analysis indicated that the natural rubber formulations containing pZnMA/ZnO showed improved wet traction but with higher rolling resistance to a standard formulation. These results point to an interesting direction for further research into the performance of self-healing composites in vehicle tire applications.

KEYWORDS: vulcanization, rubber, curing agent, self-healing, tire tread materials

INTRODUCTION

Vulcanized commercial elastomers are a key component of transport tires due to their high toughness and durability. There is a huge demand for these products, with around 3 billion tires being manufactured worldwide in 2019. However, while these elastomers provide excellent properties, tires are multilayer thermoset networks that are extremely difficult to reprocess and recycle—a societal problem of increasing concern. While ~80% of waste tire rubbers are reclaimed by mechanical grinding or pyrolysis processes, a large volume still ends up being incinerated or dumped into landfill each year. A feasible and promising alternative approach to reprocessing is extending a tire’s service life through the incorporation of self-healing mechanisms. Not only does this reduce the generation of waste tires, but with each tire requiring in the region of nine gallons of oil to make, extending their service life would significantly reduce global oil usage.

Intrinsically self-healing thermoset elastomers are created by substituting the permanent bonds that would usually cross-link these materials with nonpermanent or dynamic bonds. Cross-linkers containing dynamic covalent bonds, such as Diels–Alder adducts, disulfides, and boronic esters, have been grafted to commercial elastomers to facilitate self-healing, most commonly by either oxirane ring-opening reactions of an epoxidized rubber or by thiol–ene grafting to dienic elastomers. Peroxide curing diene rubbers with monomers containing a carbon–carbon double bond, such as maleic anhydride and methacrylic acid, and zinc oxide have also been shown to give good self-healing efficiencies in these materials due to the formation of an ionic network. However, in these latter systems, shorter curing times and/or lower curing temperatures are typically used to suppress the number of permanent covalent bonds that form during curing, which can result in a lowering of the tensile properties of these materials.

Recently, several publications have emerged that use modified sulfur cure packages to produce self-healing materials. This is an interesting approach, as these compounds could be produced at scale with little or no modification to existing manufacturing facilities. For example, the addition of CuCl₂ to a semifluorinated vulcanization system (semi-EV) catalyzes...
exchange reactions between the disulfide and polysulfide bonds in the network. The rubber chain mobility allowed by this process meant that these compounds were able to recover up to 72% of their original tensile strength of 3.2 MPa after self-healing for 12 h at 110 °C. Transalkylation of C–S bonds has been induced in a conventional vulcanized (CV) rubber network with the addition of sulfonium compounds. In this case, samples recovered 62% of their original tensile strength of 5.8 MPa after just 2 min of self-healing at 165 °C. Interestingly, longer time frames at this temperature resulted in a decrease in their apparent self-healing efficiency due to the thermal aging of these materials. Vulcanized rubber compounds with self-healing ability have also been produced without extrinsic catalysts, but instead by lowering the amount of sulfur that is added as well as their degree of curing. While these have shown good self-healing efficiencies at temperatures as low as 80 °C, these modifications also significantly reduce the mechanical properties of these materials.

In this work, we investigate an alternative approach to enhancing the self-healing properties of vulcanized rubbers by replacing the conventional zinc oxide (ZnO) and stearic acid (SA) activator/coactivator system with ω-propenyl functional oligomers of poly(zinc methacrylate) (pZnMA), synthesized by catalytic chain transfer polymerization (CCTP). In addition to activating vulcanization, the pZnMA/ZnO complex allows the elastomers to be cured to a high degree while retaining their high self-healing efficiencies, as the ω-propenyl functional groups of the oligomers graft to the elastomer during vulcanization, reducing the number of permanent covalent cross-links as well as forming an ionic network throughout the compound. We then investigate the impact that adding carbon black has on the mechanical and self-healing properties of these vulcanized rubbers. Finally, the potential wet traction and rolling resistance properties of these rubbers are examined, which are important performance metrics for tire tread materials.

**EXPERIMENTAL SECTION**

**Materials.** Natural rubber (NR, TSR10, Africa), stearic acid (SA), zinc oxide (ZnO), N-cyclohexyl-2-benzothiazolesulfenamide (CBS), and carbon black N234 (CB) were provided by Bridgestone EU NV/SA. Methacrylic acid (MAA) and zinc dimethacrylate (ZDMA) were purchased from Sigma-Aldrich. 2,2'-Azobis[2-(2-imidazolin-2-yl)-propane] dihydrochloride (VA-044) was obtained from Wako and used as received. Bis(boron difluorodimethylglyoximate)cobalt(II) methanol [(CH3OH)2Co-(dmgBF) or (CoBF)] was synthesized by using a procedure described in the literature. The rubber chain mobility allowed by this process meant that these compounds were able to recover up to 72% of their original tensile strength of 3.2 MPa after self-healing for 12 h at 110 °C. Transalkylation of C–S bonds has been induced in a conventional vulcanized (CV) rubber network with the addition of sulfonium compounds. In this case, samples recovered 62% of their original tensile strength of 5.8 MPa after just 2 min of self-healing at 165 °C. Interestingly, longer time frames at this temperature resulted in a decrease in their apparent self-healing efficiency due to the thermal aging of these materials. Vulcanized rubber compounds with self-healing ability have also been produced without extrinsic catalysts, but instead by lowering the amount of sulfur that is added as well as their degree of curing. While these have shown good self-healing efficiencies at temperatures as low as 80 °C, these modifications also significantly reduce the mechanical properties of these materials.

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**Figure 1.** (a) Catalytic cycle for the CCTP synthesis of pMAA. (b) Illustration of the ionic network formed when using pZnMA/ZnO complex as curing activator for NR vulcanization.
P.3. To evaluate the effect of carbon black, CV-P-CB1/2/3 samples were prepared by adding 10/25/40 phr of CB N234 to CV-P3. A table of these formulations is given in Table S1.

**Analysis and Characterization.** $^1$H NMR spectra were recorded on a Bruker DPX-400 spectrometer in DMSO-$d_6$. Scanning electron microscopy (SEM) was conducted on a Zeiss SUPRA 55-VP scanning electron microscope with a field emission electron gun. An InLens detector was used at a working distance of 3.5 mm, an aperture size of 30 μm, and an acceleration voltage of 3 kV. Rubber samples were attached to aluminum specimen stubs with silver paint and then coated with carbon. A line of silver paint was then used to ground the rubber surface to the aluminum stub.

Tensile tests were on a Shimadzu Autograph AGS-X tester. Dumbbell specimens were cut according to ASTM-D638-14 type V. The tensile rate used was 100 mm/min with a 10 kN load cell, and the tests were performed at 19 °C. Cyclic stress softening tests were performed by elongating specimens to between 0% and 500% for five cycles at a tensile rate of 100 mm/min. A lap-shear test was conducted to evaluate the self-healing performance of the vulcanized NR, as illustrated in Figure S3. To ensure good contact, a force of 20 N was used, and self-healing was assessed at both room temperature and 80 °C. Dynamic mechanical thermal analysis (DMTA) was performed on samples approximately 6 mm × 10 mm × 2 mm in tension mode at a 1% strain and a frequency of 5 Hz, in the temperature range of ~80 and 100 °C.

To measure the total cross-link density of rubbers, $\sim$0.5 g of each sample was first added to 100 mL of toluene and left for 7 days to reach equilibrium swelling. Swollen samples were then weighed before being dried in a vacuum oven at 60 °C for 4 days. The weight of the dried samples was then recorded, and the cross-link densities ($V_c$) were calculated via eq 1:

$$V_c = -\ln(1 - \Phi_i + \Phi_i + \chi \Phi_i^2)$$

$$V_c = \frac{m_1}{m_2/\rho_2 + (m_1 - m_2)/\rho_1}$$

where $\chi$ is the Flory–Huggins polymer–solvent interactions parameter (0.393), $V_0$ is the molar volume of solvent (106.27), and $\Phi_i$ is the volume fraction, which was calculated via eq 2.

RESULTS AND DISCUSSION

**Synthesis of pZnMA/ZnO Activator by CCTP.** Divalent metal oxides, such as Zn(II)O, have been used as a curing activator for rubber vulcanization for over 100 years. Typically, stearic acid is also added as a coactivator, forming a zinc stearate complex that helps to ensure that there is a uniform dispersion of zinc throughout the rubber matrix. In this work, we have substituted the stearic acid component of this activator system with $\omega$-propenyl functional oligomers of methacrylic acid (Figure 1), which complex with ZnO to form a pZnMA/ZnO salt. In this way, the complex acts as a vulcanization activator, while in addition a proportion of the vinyl groups of these oligomers couple to the NR backbone, forming an ionic network that enhances the self-healing properties of the final product. Catalytic chain transfer polymerization (CCTP) is a radical polymerization technique that is ideal for the synthesis of low molecular weight $\omega$-propenyl, $\alpha$-protic oligomers of a range of vinyl monomers, most commonly methacrylates. CCTP uses Co(II) complexes such as CoBF as chain transfer catalysts that abstract a $\beta$-hydrogen from a propagating radical chain, resulting in an oligomeric product and a Co(III)H complex that rapidly reinitiates the polymerization of a further monomer and returns to the Co(II) starting catalyst (Figure 1a). In this system, the molecular weight of the product is determined by the concentration ratio of catalyst to monomer, as described by the Mayo equation, where higher catalyst concentrations result in lower molecular weight products. Because of the high activity of the Co(II) catalysts used in CCTP, the amounts required are in the parts per million (ppm) relative to monomer, which is $\sim$4 orders of magnitude higher than for the conventionally used thiols. This is one of the main reasons that this technique is highly scalable and useful for industrial applications. Recently, oligomers from CCTP have been used as reactive surfactants and emulsion stabilizers, in pigment dispersants, and as oil viscosity modifiers; however, this is the first time they have been applied as additives to a rubber cure package.

To ensure that there were a high number of vinyl groups per unit weight added, and also to help dispersion in the rubber matrix, we aimed to prepare short oligomers of pMAA using a molar ratio of 120 ppm of CoBF relative to monomer. This is higher than would be typically required in the CCTP of methacrylates; however, the acidic conditions occurring in the polymerization of MAA can result in partial degradation of the catalyst, resulting in a lower chain transfer activity in these reactions. Through integration of the $^1$H NMR spectrum (Figure S2a), the DP of the pMAA oligomer was found to be $\sim$8 ($M_n = 430$ g/mol). In addition, from the DSC thermogram (Figure S2b), the $T_g$ of the oligomers equaled 43.4 °C (onset, 55.9 °C endset). This is significantly lower than the literature $T_g$ value for pMAA of 228 °C, as would be expected from the Flory–Fox equation for oligomers of this size. This low thermal transition temperature should improve the mobility of...
these molecules within the rubber matrix during curing at 150 °C.

Mechanical Properties of Rubbers Vulcanized with pZnMA/ZnO Activator. To test the pZnMA/ZnO activator system, we selected a conventional accelerated curing system (CV) used in commercial natural rubber, where the weight ratio of sulfur to CBS accelerator is fixed at 5:1. The amount of sulfur and CBS relative to natural rubber was reduced to a quarter of a standard CV system, as this has been previously shown to facilitate some degree of self-healing due to a combination of reducing the cross-link density and increasing the ratio of disulfide to polysulfide cross-links in the network.

As mentioned above, it was found that the self-healing performance of these materials was enhanced by reducing their degree of curing to 50% ($t_{50}$); however, this came at the expense of reduced mechanical performance. Thus, to ensure optimal tensile properties, all samples in this work were cured to their $t_{90}$. To evaluate the effect of using pZnMA/ZnO as the activator, we also prepared compounds using the conventional stearic acid and ZnO (CV-ZS) as well as ZDMA and ZnO (CV-M) as activators. The curing curves of these samples are given in Figure 2a, and the curing times are given in Table S2.

It is apparent that pZnMA/ZnO activates curing with comparable efficiency to the ZnO/SA system, with $t_{90}$ curing times of 11.1 and 14.75 min, respectively. In contrast, when the ZDMA/ZnO is used as the sole activator, the materials had poor curing properties, with a $t_{90}$ curing time of 102.3 min. One contributing factor to the difference between the monomer and oligomer in these systems may be that the $\omega$-propenyl-terminated oligomers are unable to homopolymerize, and so the structures of their zinc complexes will be less affected by curing when compared with ZDMA, which could polymerize through the radicals generated during vulcanization. This is interesting as ZDMA and zinc monomethacrylate (ZMA) are sold under the brand names Sartomer SR708 and SR709, respectively, as commercial additives for accelerated sulfur vulcanization. However, they are typically used in conjunction with a stearic acid coactivator to provide efficient curing.

The cross-link densities ($V_c$) of the vulcanized rubber products were determined by the equilibrium swelling method (Figure 2b). The total cross-link densities of the rubbers follow the same trend as the maximum torque values in their curing curves, confirming the differences in the number of cross-links formed when changing the activator system. To evaluate the number of ionic cross-links in these networks, we performed equilibrium swelling in a 90:10 mixture of toluene to formic acid for 3 days to break the ionic bonds, before exchanging the solvent for fresh toluene each day for 4 days to remove the residual formic acid. The samples cured with ZDMA/ZnO and pZnMA/ZnO show very high degrees of ionic cross-linking at 85.47 and 87.93% relative to the total, respectively. However, when using the same method with the CV-ZS control sample, an ionic cross-link density of 36.53% was recorded. It would be expected that the cross-links in CV-ZS should be only thioethers, disulfides, and polysulfides, and so some of these covalent bonds appear to be broken during the acid swelling, even when using a weak acid. Consequently, the ionic cross-link density in CV-M and CV-P3 is likely to be lower than was recorded here, but they are clearly higher in these samples than in the CV-ZS control, suggesting that an ionic network has been formed in these compounds.

When examining the effect that substituting stearic acid for $\omega$-propenyl oligomers of MAA has on the mechanical properties of rubbers, we first added pMAA and ZnO separately to the rubber during compounding, as would be performed when using stearic acid. However, this resulted in a relatively low strength material, with a tensile strength of 3.96 ± 0.43 MPa (CV-P1*, Figure S4). This may be due to the pMAA partially agglomerating in the rubber matrix, which would result in weak aggregates distributed throughout the final material. In contrast, when adding these as a preformed salt of pZnMA/ZnO, the materials had a tensile strength of 10.83 ± 0.78 MPa and an elongation at break of 1568 ± 72%.
As shown in the typical stress−strain curves given in Figure 2c, this is slightly stronger than the CV-ZS control sample, which has a tensile strength of 8.61 ± 1.17 MPa and an elongation at break of 1277 ± 58%. The addition of more pZnMA/ZnO resulted in a slight reduction in mechanical properties, with measured tensile strengths of 8.09 ± 0.49 MPa for CV-P2 and 7.47 ± 0.64 MPa for CV-P3. This may be due to the increasing degree of substitution of sulfur cross-links for ionic bonds slightly weakening the material.

Cyclic stress−strain experiments were conducted on the modified rubbers CV-P1/2/3 as well as CV-ZS (Figure S5). As shown in Figure 2d, in all cases we observed a large decrease in the hysteresis loop area after the first cycle, due to the Mullin’s effect. However, the samples with pZnMA/ZnO displayed a larger degree of hysteresis. There is also some correlation between the amount of pZnMA/ZnO added and the decrease in the area of the hysteresis loop, with larger amounts generally exhibiting greater decreases. This is further evidence that when curing in the presence of pZnMA/ZnO the sulfur cross-links in CV-ZS are partially substituted by ionic associations, as these dynamic bonds should rupture more easily during stress cycling, resulting in larger energy dissipation.

An additional cause of hysteresis in vulcanized natural rubber is the energy required to alter its microstructure during strain-induced crystallization (SIC). SIC is an important property in these materials, being the principal reason for their excellent mechanical properties and resistance to crack growth. To examine the SIC properties of the rubbers 2D small- and wide-angle X-ray scattering (SAXS/WAXS) patterns were obtained during the extension of samples to a maximum elongation of 700% at a temperature of −30 °C. The 2D WAXS patterns for CV-ZS and CV-P3 extended to 700% are given in Figures 3a and 3b, respectively. Both samples show that a highly oriented crystalline structure develops, evidenced by the Bragg peaks indexed as (120), (200), and (201), with 2θ positions of 14.4°, 18.0°, and 21.3°, respectively. These can be assigned to the monoclinic unit cell where a = 12.5 Å, b = 8.9 Å, c = 8.1 Å, and β = 92°, as proposed by Bunn for natural rubber.

Figure S6 shows selected 2D WAXS data during the drawing of CV-ZS and CV-P3; here for CV-ZS, at an extension of ~400%, the (120) and (200) peaks start to appear, indicating the onset of SIC. The peaks increase in intensity as the strain is increased to 700%, which has been observed previously in natural rubber systems. Similarly, for CV-P3 the (200) peak, although weak in intensity, is observed at an extension of ~400%, and the SIC develops on further extension. Hence, both samples show SIC readily occurs on elongation at low temperatures. The lower intensity observed in CV-P3 may indicate that pZnMA/ZnO impacts the SIC of this compound, resulting in its slightly lower mechanical strength; however, another contributing factor to this is the greater degree of structural rearrangement occurring in this sample that allows crystallized structures to relax during the measurement.

In the higher angle WAXS patterns, shown on the right of Figures 3a and 3b, Bragg rings indexed as (100), (002), and (101) with 2θ positions of 31.9°, 34.6°, and 36.4°, respectively, from the unoriented ZnO crystals can also be observed in both samples (note that the additional (120) peak from oriented rubber is labeled on both patterns). The greater intensity of the ZnO rings in the CV-P3 WAXS pattern is attributed to the higher concentration of ZnO in this formulation. Another
feature during the SIC of CV-ZS is observed in the SAXS patterns in Figures 3c and 3d, which is the expanded area labeled in Figure 3a. In Figure 3c, the 2D and corresponding 1D SAXS profiles show the stearic acid (SA) (001) and (003) peaks, which form as oriented crystalline platelets during the drawing process. However, these peaks are absent from the CV-P3 trace, given in Figure 3d, as stearic acid was not used in this formulation.

Self-Healing Performance of Vulcanized Natural Rubbers. As previously mentioned, the CV system selected has been previously shown to produce materials with some self-healing ability, in particular when a low degree of curing is used. In this work it was found that samples of CV-ZS that were cured to their 

During tensile testing of the self-healed samples, they typically broke outside of the overlapped region, as illustrated on the right of Figure S3. This suggests that under the self-healing conditions a high degree of chain diffusion occurs at the interface between the two cut dumbbell pieces, which is facilitated by the exchange of bonds in the ionic network. To observe this more closely, SEM images were taken of this interface from specimens that had been self-healed for 2 h at 80 °C. Figure 4c shows the boundary between the self-healed surfaces, where one surface is slightly raised due to imperfect alignment when they were overlapped prior to being subjected to the self-healing conditions. However, it is apparent that there is good contact across this region. At a higher magnification, in Figure 4d, it appears that the surface between these two layers is continuous. This further demonstrates the high degree of chain diffusion that occurs during self-healing, resulting in the restoration of properties observed in Figure 4a.

For tire tread materials, carbon black or silica is often incorporated to improve mechanical performance, increase processing yield, and reduce costs. In particular, carbon black plays an important role due to its excellent reinforcing ability. However, if the formulation includes stearic acid, the mechanical properties of the resulting vulcanizate will be compromised. This is because the stearic acid can act as a fluxing agent, which reduces the curing rate and leads to lower mechanical properties. In this study, the CV system selected has been previously shown to produce materials with some self-healing ability, in particular when a low degree of curing is used. In this work it was found that samples of CV-ZS that were cured to their 

Using pZnMA/ZnO as the activator in these systems resulted in improved self-healing performance, as shown in Figures S8 and 4. In all cases it appears that the strain properties recover faster than mechanical strength in these materials; however, this is due to the nonlinear relationship between stress and strain in rubber compounds, as they become harder to deform at larger strains. The most promising compound we evaluated was CV-P3, which contained 20 phr of the pZnMA/ZnO. As shown in Figure 4, after just 15 min at 80 °C it recovered 43% of its tensile strength, and this increased to 58.7% after 30 min and 86.7% after 2 h. Considering that the tensile strength of CV-P3 is comparable to CV-ZS at 7.47 ± 0.64 MPa, this compound achieved an excellent balance between its mechanical and self-healing performance.

Figure 4. (a) Typical stress–strain curves of pristine CV-P3 as well as CV-P3 after being cut and self-healed for various times at 80 °C; (b) self-healing efficiencies of CV-P3; (c) SEM image of the self-healed area of CV-P3 after 2 h at 80 °C; and (d) a higher magnification in SEM image of the region highlighted in white in (c).
Here we investigated the effect carbon black has on the mechanical properties and self-healing performance of CV-P3. Figure 5a shows typical stress–strain curves of CV-P3 samples containing carbon black N234 at 10, 25, and 40 phr, which are labeled CV-P-CB1, CV-P-CB2, and CV-P-CB3, respectively. Addition of 10 phr of carbon black results in an increase in tensile strength to 9.26 ± 0.56 MPa and a decrease in elongation at break to 872.25 ± 50%. Increasing the amount of carbon black to 25 phr resulted in a further decrease in the elongation at break to 690 ± 25%, along with a reduction in tensile strength to 7.28 ± 0.56 MPa. Further increase in loading to 40 phr resulted in little change, with CV-P-CB3 having a tensile strength of 7.56 ± 0.52 MPa and an elongation at break of 690 ± 9%. The reinforcement index (RI = $M_{300%}$/ $M_{100%}$) of these rubbers shows the same trend as their tensile strength, with values of RI = 2.389, 2.795, and 2.783 for CV-P-CB1, CV-P-CB2, and CV-P-CB3, respectively. The RI gives an indication of the reinforcing effect of the filler at larger deformations and is positively correlated to the amount of bound rubber in the compound. As the RI did not increase when the amount of carbon black was increased from 25 to 40 phr, this suggests that there is a higher proportion of filler–filler interactions in CV-P-CB3 than are present in CV-P-CB2.

Dumbbell specimens were cut and overlapped, as shown in Figure S3 and left for 72 h. From Figure 5, this resulted in a tensile strength recovery of 79.1%. The room temperature self-healing of the unfilled samples was also tested, as shown in Figure S8. Although in these examples it was clear that there was only weak surface adhesion holding them together, whereas CV-P-CB3 was much stronger and even broke outside of the overlapped region during tensile testing. The origin of these low-temperature self-healing properties may be that the carbon black acts as a solid lubricant that increases the mobility of the polymer chains. However, to date, there has been very little research into the effect of carbon black on the self-healing properties of vulcanized natural rubber. The only research paper that was found in the literature showed that self-healing efficiencies decreased with increasing carbon black content. In this work, a dicumyl peroxide cured system was used, a different grade of carbon black (N330), as well as a different cross-linker (zinc thiolate), which could explain the different trends that were observed. Given the importance of carbon black within the tire industry, it is clear that this is an area where significantly more research is needed.

Dynamic Mechanical Analysis of Self-Healing Compounds. The rubbers developed in this current work were found to have an exceptional balance between their mechanical properties and self-healing efficiency. To evaluate their structural properties further, we used DMTA to evaluate the temperature dependence of the loss factor (tan δ). From Figure 6a, we see a small shift in the peak tan δ value with the addition of pZnMA/ZnO, which is at $-53^\circ$C for CV-ZS and shifts slightly to $-50^\circ$C for CV-P3. There is also a significant decrease in the magnitude of the peak tan δ value with the addition of 40 phr of carbon black, which is due to the reinforcing filler having a greater effect on the storage modulus ($G'$, inset of Figure 6a) compared with the loss modulus ($G''$) around this region, as shown in Figure S10.

The region between 0 and 60 °C of the tan δ versus temperature curve can be used as an indicator of key tire tread material performance metrics, such as wet traction and rolling properties. Here we investigated the effect carbon black has on the mechanical properties and self-healing performance of CV-P3.
Interestingly, it was found that the addition of carbon black N234 could simultaneously improve the mechanical properties of the rubber vulcanizates as well as increase their self-healing efficiency at 80 °C. At a carbon black loading of 40 phr, samples were also found to have excellent self-healing ability at room temperature, recovering 79.1% of their tensile strength after 72 h. This property could have a significant impact on the service life of these materials when used in tires. It was also found that both the pZnMA/ZnO curing additive and carbon black increased the tan δ at 0 °C, indicating that these composites would have improved wet traction performance. However, it is noted that more work needs to be done to improve the fuel efficiency of these materials and their overall life cycle effect on the environment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.2c01398.

Experimental procedures, polymer characterization data, and data from our materials testing (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Chaoying Wan — International Institute for Nanocomposites Manufacturing (IINM), WMG, University of Warwick, Coventry CV4 7AL, U.K.; orcid.org/0000-0002-1079-5885; Email: chaoying.wan@warwick.ac.uk

Authors

Alan M. Wemyss — International Institute for Nanocomposites Manufacturing (IINM), WMG, University of Warwick, Coventry CV4 7AL, U.K.; orcid.org/0000-0002-5919-9881

Arkadios Marathianos — Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

Ellen L. Heeley — School of Life, Health and Chemical Sciences, The Open University, Milton Keynes MK7 6AA, U.K.

James Ekeocha — International Institute for Nanocomposites Manufacturing (IINM), WMG, University of Warwick, Coventry CV4 7AL, U.K.

Yoshihiro Morishita — Advanced Materials Division, Bridgestone Corporation, Tokyo 187-8531, Japan

Raffaele di Ronza — Bridgestone EU NV/SA, Italian Branch-Technical Center, 00128 Rome, Italy

M. Mar Bernal — Bridgestone EU NV/SA, Italian Branch-Technical Center, 00128 Rome, Italy

David M. Haddleton — Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.; orcid.org/0000-0002-4965-0827

Complete contact information is available at: https://pubs.acs.org/10.1021/acsapm.2c01398

Notes

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