

Thermal Behavior of Natural Rubber and Chlorinated Rubber Blends

J. W. COOK,¹ S. EDGE,¹ D. E. PACKHAM,¹ A. S. THOMPSON²

¹ School of Materials Science, University of Bath, Bath, BA2 7AY, United Kingdom

² School of Pharmacy and Pharmacology, University of Bath, Bath, BA2 7AY, United Kingdom

Received 2 January 1997; accepted 16 January 1997

ABSTRACT: A solid-state chemical reaction occurs when a solvent cast film of a blend of masticated natural rubber and chlorinated natural rubber is heated in the presence of air at 150°C. The thermal behavior of solvent cast films of chlorinated natural rubber, masticated natural rubber, and a 1 : 1 w/w blend (2% w/v in xylene) of these two polymers has been studied using differential scanning calorimetry, infrared spectroscopy, scanning electron microscopy, and nuclear magnetic spectroscopy. The results suggest that carbonyl groups are incorporated into the blend on heating and that the vinyl functionality of the isoprene units is modified during this apparent oxidation. Heating for 2 h at 150°C results in a material that no longer contains the rubber-like *cis*-1,4-polyisoprene units. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1379–1384, 1997

Key words: natural rubber; chlorinated rubber; adhesion

INTRODUCTION

The bonding of rubber to steel is widely used to produce vibration management systems such as bridge bearings and automobile suspension units.¹ Rubber-to-metal bonding is usually achieved by injection molding rubber onto precoated steel at 150–170°C. The manufacture of rubber-to-metal-bonded components is technologically well understood. However, the scientific basis of rubber-to-metal adhesion is not clear. This is mainly because the adhesive systems work so effectively, which inhibits access to the interfaces which are formed during rubber-to-metal bonding. In addition, another obstacle to gaining an understanding of the bonding processes is the use of proprietary primers and bonding agents. There are reports of the analysis of failure surfaces produced by electrochemical (cathodic)

treatment² and destructive adhesion tests.³ However, those studies do not directly address the actual nature of the interactions occurring during the actual bonding process.

A typical rubber-to-metal-bonded component usually consists of a treated steel substrate, a primer, an adhesive, and rubber. One aspect of the overall bonding process is the interaction between a compounded rubber and the adhesive, in this case, Chemlok 220, during injection molding. The compounded rubber and adhesive are complex formulations; however, our own analysis has confirmed literature reports² that a significant component of the adhesive is chlorinated rubber and the compounded rubber, *cis*-1,4-polyisoprene. Because of the complexity of these proprietary systems, we have undertaken a study of relatively simple model systems in order to try to understand the nature of the interactions that occur during rubber-to-metal bonding. We have therefore studied the interaction between masticated

Correspondence to: D. E. Packham.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/071379-06

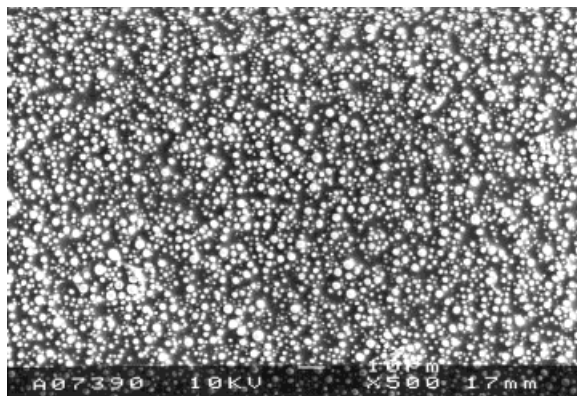


Figure 1 SEM micrograph of a 1 : 1 w/w blend of MNR and CNR. Solvent cast from xylene (2% w/v). Magnification $\times 500$.

natural rubber (MNR) and chlorinated natural rubber (CNR), which serves as a model to complement our more direct work on rubber-to-metal adhesion.

We have reported our preliminary results for the behavior of these polymers at 170°C.⁴ We now report results of a more detailed study of the interactions of CNR and MNR at 150°C.

EXPERIMENTAL

Thin films of the polymers were prepared by casting solutions of MNR (standard Malaysian rubber, grade SMRL), CNR (Pergut S20, Bayer; 59% w/w Cl; M_n 3.9×10^4 g mol⁻¹; polydispersity, 1.8), and a 1 : 1 w/w mixture (2% w/v in xylene) onto glass, allowing the solvent to evaporate, and drying *in vacuo*. In order to simulate the vulcanization process, some of the films were heated at 150°C for up to 2 h.

Electron microscopy, supported by electron probe microanalysis, was performed using a Jeol 6310 equipped with an X-ray analyzer. Transmission infrared spectra were recorded in KBr matrices using a Perkin Elmer 1710 infrared spectrometer. Differential scanning calorimetry (DSC) was studied using a TA Instruments 2910 DSC. Solutions of the samples were placed in DSC aluminum pans, and the solvent was allowed to evaporate. The samples were finally dried *in vacuo* prior to analysis. Isothermal behavior was investigated in open pans at 150°C in air and nitrogen (flow rate, 25 cm³ min⁻¹), and glass transition temperatures were measured in sealed pans at a variety

of thermal cycles (see text). Solid-state ¹³C nuclear magnetic resonance (NMR) spectra were recorded at 75 MHz (cross-polarization) at the University of Durham. All chemical shifts are relative to tetramethylsilane.

RESULTS AND DISCUSSION

The polymer samples, both before and after heating, were studied using scanning electron microscopy (SEM) with electron probe microanalysis, infrared spectroscopy, DSC, and NMR spectroscopy.

SEM

The materials were studied using SEM together with elemental mapping. The surfaces of the homopolymer films were homogeneous, in appearance and elemental distribution, both before and after heating (150°C/2 h). However, films of the blend of the two homopolymers exhibited a two-phase morphology. The micrographs are shown in Figures 1 and 2. Elemental mapping of the surface indicated that the spherelike structures contained a chlorine-rich material. Heating at 150°C for 2 h caused the material to become homogeneous in both morphology and Cl distribution. This behavior is similar to that reported for similar mixtures heated at 170°C.⁴

Infrared Spectroscopy

Solvent cast thin films of the samples were heated on glass at 150°C for 2 h in air. The resulting

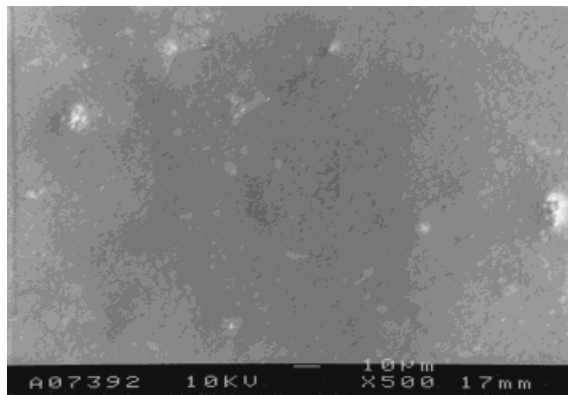


Figure 2 SEM micrograph of a 1 : 1 w/w blend of MNR and CNR. Solvent cast from xylene (2% w/v). After heating at 150°C for 2 h. Magnification $\times 500$.

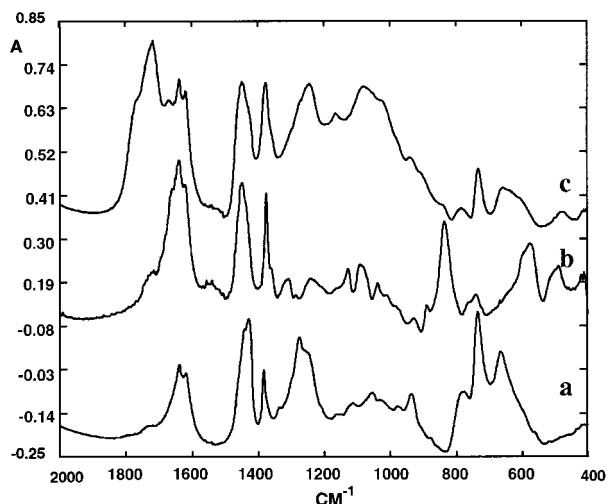


Figure 3 Transmission infrared spectra in KBr matrices of solvent cast polymer films (2% w/v xylene). After heating at 150°C for 2 h on glass. (a) CNR, (b) MNR, and (c) a 1 : 1 w/w blend of MNR and CNR.

materials were dispersed in KBr matrices, and the transmission infrared spectra were recorded. After heating, the blend was distinctly orange in appearance, which suggests the presence of chromophores arising from conjugation or charge transfer. The infrared spectra of the samples heated for 2 h at 150°C are shown in Figure 3. After heating for 2 h at 150°C, the transmission spectra of the component homopolymers were essentially unchanged and contained no significant absorption bands due to C=O. The infrared spectrum of heated MNR exhibited absorption bands at 837 cm^{-1} (assigned to C=CH deformation), 1,480 cm^{-1} (CH_3 and CH_2 deformations), and 1,376 cm^{-1} (CH_3 deformation).⁵ The infrared spectrum of heated CNR exhibited absorption bands at approximately 650–800 cm^{-1} , the maximum absorbance values being at 736 cm^{-1} (assigned to C—Cl stretch), 1,385 cm^{-1} (CH_3 deformation), and 1,275 cm^{-1} (assigned to an activated skeletal vibration).⁵ The spectrum of the unheated blend was essentially a sum of the spectra of the two component homopolymers. This suggests that oxidation of these polymers to form C=O groups does not occur to any great extent under these conditions. However, the spectrum of the 1 : 1 w/w blend, which had been heated for 2 h at 150°C in air, exhibited an absorption band at 1,720 cm^{-1} , which is assigned to C=O functionalities. The absorption band at 737 cm^{-1} , due to C—Cl stretch, is still present, whereas there is

no evidence of the absorption band due to C=CH deformation at 837 cm^{-1} . There are absorption bands present at 1,443 and 1,090 cm^{-1} , which are presumably associated with carbon/oxygen functionalities, possibly esters.

The infrared spectroscopic study of films of CNR, MNR, and a 1 : 1 w/w blend of these two polymers suggests that the homopolymers are relatively stable to oxidation at 150°C, whereas the blend undergoes some form of oxidation. The absence of an absorption band at 837 cm^{-1} in the heated blend suggests that the vinyl functionality is undergoing chemical modification.

NMR Spectroscopy

NMR spectroscopy was used to try to identify the multiplicity of the carbon groups and chemical species present in the oxidized blend. Solution-state (in CDCl_3) was initially used; however, not all of the products from the oxidation studies were soluble in this solvent. Consequently, solid-state ^{13}C -NMR spectroscopy was used to ensure that all of the bulk samples were analyzed.

Solid-State ^{13}C -NMR

The solid-state ^{13}C -NMR spectra of MNR and CNR suggested that these two materials on their own were relatively inert to oxidation after heating at 150°C for 2 h. The spectra of the unheated and heated blends are shown in Figure 4. In Fig-

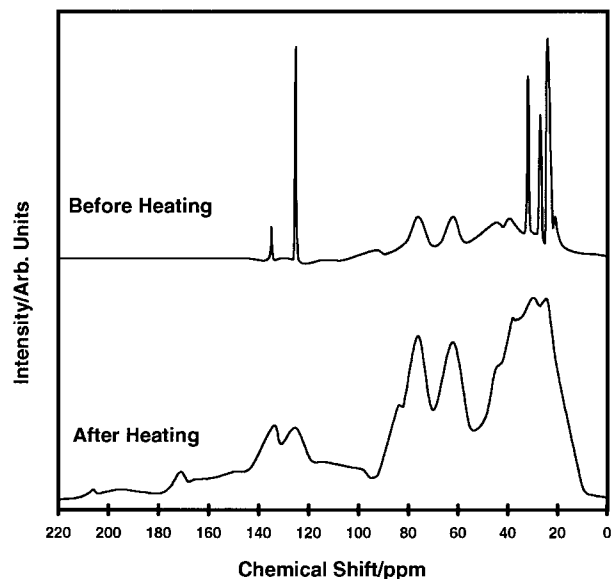


Figure 4 Solid-state ^{13}C -NMR spectra of solvent cast films (2% w/v xylene) of a 1 : 1 w/w blend of MNR and CNR. Before and after heating at 150°C for 2 h.

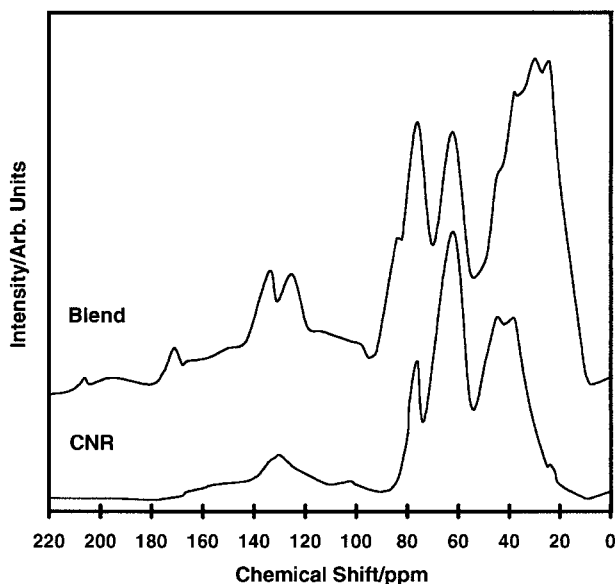


Figure 5 Solid-state ^{13}C -NMR spectra of solvent cast films (2% w/v xylene) of a 1 : 1 w/w blend of MNR and CNR and CNR. Before and after heating at 150°C for 2 h.

ure 5, the spectra of heated CNR and the heated blend are compared. It can be seen from Figure 4 that in the solid-state spectrum of the unheated blend, two distinct types of resonances are observed, that is, sharp and broad. This suggests the presence of a two-component system, a rubber phase and a rigid phase. The sharp peaks are due to polyisoprene at 135.1 [$\underline{\text{C}}(\text{Me})$], 125.6 ($\underline{\text{C}}\text{H}$), 32.7 ($\underline{\text{C}}\text{H}_2$), 27.0 ($\underline{\text{C}}\text{H}_2$), and 23.9 ppm ($\underline{\text{C}}\text{H}_3$). These values are very similar to those obtained from our solution-state ^{13}C -NMR data. The broader resonances arise from the CNR. The resonances were assigned, with references to our own solution and solid-state ^{13}C -NMR data, to 76 ($\underline{\text{C}}\text{R}_3\text{—Cl}$ and $\underline{\text{C}}\text{R}_2\text{Cl}_2$), 62 ($\underline{\text{C}}\text{HCl}$), 44 and 39 ($\underline{\text{C}}\text{H}_2$), and 21 ppm ($\underline{\text{C}}\text{H}_3$). The most striking feature of the spectrum of the heated blend is that heating has caused the disappearance of the sharp resonances due to the polyisoprene component and the spectrum now more closely resembles that of the heated CNR (see Fig. 5). This suggests that a one-phase, that is, rigid, material is now present. However, there are broad resonances which can be assigned to polyisoprene at 134.8 and 125.7 ppm (the vinyl functionality) and in the aliphatic region between 20 and 35 ppm. Additionally, there are resonances above 140 ppm which are probably due to various C/O functional-

ities. The resonance at 171 ppm in particular can be assigned to $\text{C}=\text{O}$.

The ^{13}C -NMR spectra suggest that when MNR and CNR are heated together in the presence of air, a material is produced which is rigid and no longer two phase, that is, the material does not contain a rubberlike component. Solid-state ^{13}C -NMR spectroscopy suggests that $\text{C}=\text{O}$ functionalities are present in the heated blend.

DSC

Samples of the blend and the component homopolymers were studied using DSC isothermally at 150°C in air and nitrogen in order to elucidate the thermal behavior of the two polymers at the molding temperature. The miscibility of the blend was investigated by studying the positions of the glass transition temperatures of the system.

Thermal Oxidation of Blends of MNR and CNR

The thermal behavior of the blend and the component homopolymers was investigated in air and nitrogen at an isothermal temperature of 150°C . In general, no significant thermal events were detected when the samples were heated for up to 60 min at 150°C in flowing nitrogen. The situation for heating in flowing air is very different. The isothermal behavior of the blend and the component homopolymers is shown in Figure 6. It can be seen from Figure 6 that solvent cast films of CNR and MNR are relatively inert at this temperature, whereas the blend exhibits an exothermic thermal event. These results suggests that a solid-state exothermic reaction occurs when solvent

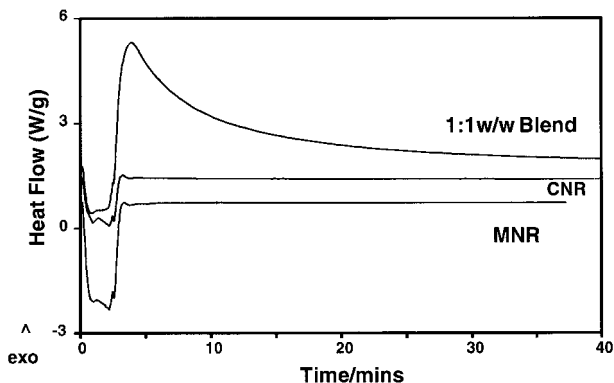


Figure 6 DSC traces of solvent cast polymer films (2% w/v xylene). Isothermal heating in air at 150°C . Open pans. Gas flow, $25\text{ cm}^3\text{ min}^{-1}$.

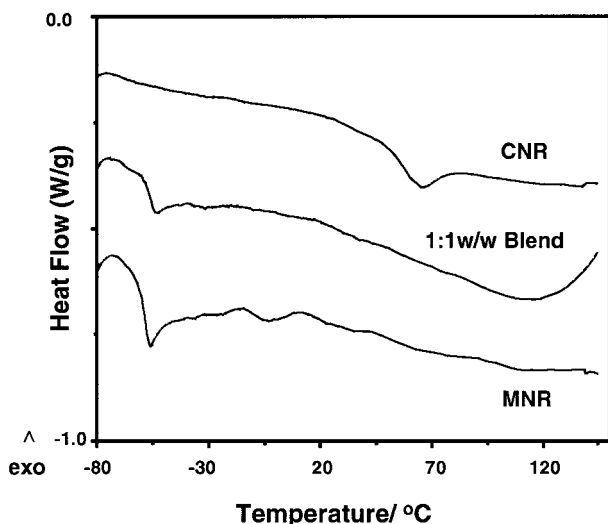


Figure 7 DSC traces of solvent cast polymer films (2% w/v xylene). Heating from -100°C at $20^{\circ}\text{C min}^{-1}$ in nitrogen. Sealed pans. Gas flow, $25\text{ cm}^3\text{ min}^{-1}$.

cast blends of MNR and CNR are heated in the presence of air.

The Miscibility of Rubber and Chlorinated Rubber

The miscibility of polymer systems can be studied using DSC. In general, a two-component polymer blend system will exhibit two T_g values if they are immiscible, one T_g value if they are completely miscible, and three T_g values if they are partially miscible. In a miscible system, the position of the T_g will be dependent on the composition of the blend.

Samples of solvent cast masticated rubber were dried and sealed in aluminium pans, cooled (quenched) to -100°C , held at this temperature for 5 min, and heated at a variety of rates to 150°C in flowing nitrogen. Typically, heating rates of $20^{\circ}\text{C min}^{-1}$ gave a T_g of the MNR of approximately -60°C . As expected, the transition occurred at somewhat higher temperatures when the heating rate was increased. The behavior of the solvent cast CNR was then investigated. No reproducible thermal events which could be assigned to a T_g were found. The thermal behavior of CNR was found to be irreproducible. However, an endothermic thermal event could be detected (on heating) at approximately 60°C (Fig. 7). This thermal event was not observed when the sample was exposed to a second identical thermal study. This probably reflects the complex irregular structure of CNR.

The thermal behavior of MNR/CNR blends was compared with that of the single-component homopolymers in air. The DSC thermograms are shown in Figure 7. On initial heating of the blends from -100°C , the thermal event ascribed to the T_g of the MNR is observed (this transition shifted to slightly higher temperatures as the proportion of CNR in the blend was increased). No thermal event was detected in the 60°C region, in contrast to the behavior of the CNR, but a broad exothermic thermal event was detected from 150 to 220°C .

This behavior was compared with that of films of MNR/CNR blends which had already been subjected to heating in air at 150°C for 2 h. The DSC thermograms are shown in Figure 8. The heated material exhibited no thermal event due to the T_g of the MNR and an exothermic thermal event at $150\text{--}220^{\circ}\text{C}$.

The DSC study suggests that blends of MNR and CNR are initially immiscible but that heating in air causes chemical modification to occur. The disappearance of the polyisoprene T_g suggests that the material no longer contains rubberlike polyisoprene units.

CONCLUSIONS

Results from electron microscopy, thermal analysis, and infrared spectroscopy and NMR spectroscopy

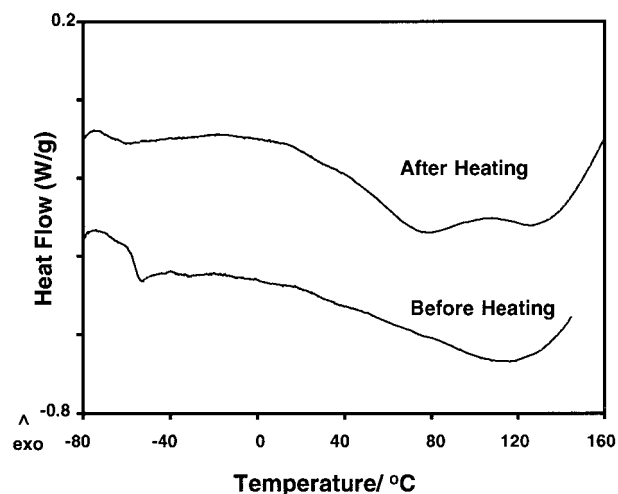


Figure 8 DSC traces of a solvent cast polymer film of a 1 : 1 w/w blend of MNR and CNR (2% w/v xylene). Before and after heating at 150°C for 2 h in air. Heating from -100°C at $20^{\circ}\text{C min}^{-1}$ in nitrogen. Sealed pans. Gas flow, $25\text{ cm}^3\text{ min}^{-1}$.

copy are consistent in supporting the following conclusions. A 1 : 1 w/w mixture of MNR and CNR cast from xylene is essentially immiscible. However, heating at 150°C results in a dramatic change in morphology. There appears to be some type of accelerated chemical oxidation in the blend which does not occur in the component homopolymers. The resulting heated material no longer contains rubberlike polyisoprene units. The implications of this work for a possible mechanism for the adhesion of natural rubber to CNR-containing bonding agents are undergoing further investigation.

The authors thank EPSRC and Avon Rubber for financial support and David Apperley at the University of Durham for recording the solid-state ^{13}C -NMR spectra.

Chlorinated rubber, Pergut S20, was kindly provided by Bayer.

REFERENCES

1. G. J. Lake, in *Handbook of Adhesion*, D. E. Packham, Ed., Longman, Harlow, UK, 1992.
2. F. J. Boerio, S. J. Hudak, M. A. Miller, and S. G. Hong, *J. Adhesion*, **23**, 99 (1987).
3. J. Kurian, G. B. Nando, and S. K. De, *J. Adhesion*, **20**, 293 (1987).
4. J. W. Cook, S. Edge, and D. E. Packham, *J. Mater. Sci. Lett.*, **16**, 445 (1997).
5. F. Scholl and D. O. Hummel, in *Atlas of Polymer and Plastic Analysis*, Hanser Verlag, Munich, 1988, Vol. II, Part a/I.
6. M. V. Eskina, A. S. Khachaturov, L. B. Krentsel, and A. D. Litmanovich, *Eur. Polym. J.*, **26**, 181 (1990).