Curing of a Polysulfide Sealant with Sodium Birnessite

J. D. DONALDSON,[1] S. M. GRIMES,[1] A. D. HOULSON,[1] S. BEHN[2]

[1] Centre for Environmental Research, Department of Materials Engineering, Brunel University, Uxbridge, Middlesex UB83PH, England

[2] Twinstar Chemicals, Cunningham House, Westfield Lane, Kenton, Harrow, Middlesex, England

ABSTRACT: Sodium birnessite ($Na_2Mn_2^{II}Mn_5^{IV}O_{13} \cdot H_2O$), a layered manganese(IV) oxide—based phase, gives a liquid polysulfide cure that is too rapid for normal application when added at 10 pph polysulfide. The curing behavior of sodium birnessite added as 5 pph, 4 pph, and as a 5 : 5 pph mixture with an inert natural manganese dioxide was compared with that of a readily available manganese-based commercial curing agent. The rate of cure at 5 and 4 pph was slower than the commercial agent at 10 pph and led to products with lower tensile strength. The cure with the 5 : 5 pph mixture gave a more rapid reproducible cure than that of the commercial agent, making a product with a higher tensile strength and lower elongation, which indicates better curing and higher crosslinking. The improved performance of sodium birnessite as a curing agent is consistent with the presence of Mn^{2+} in the lattice, creating vacancies in the Mn^{4+}—O^{2-} lattice and increasing the mobility of Mn^{4+} and its transport to the surface of the solid to oxidize the polysulfide. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1177–1181, 2000

Key words: polysulfide polymer; manganese dioxide; sodium birnessite; elastomeric sealant

INTRODUCTION

Polysulfides are used in a range of applications. They adhere to glass, steel, wood, and concrete, resist solvents and chemicals,[1] and are noted for their flexibility and ability to withstand stress and strain. As water-resistant sealants they are used in the construction industry, and cured liquid polysulfides dominate the glass-sealant industry, where they account for 80% of secondary and outer seals in insulating-glass edge sealing.

Liquid polysulfide curing is generally carried out in combination with other additives such as plasticizers, fillers, accelerators, and retardants.[1] A variety of agents can be used to polymerize polysulfides including inorganic curing agents such as metal oxides, organic curing agents such as cumene hydroperoxide, and gases such as oxygen.[2] Manganese dioxide phases are widely used as curing agents via the oxidation reaction shown in eq. (1):

$$2R—SH + MnO_2 \rightarrow R—S—S—R + H_2O + MnO$$

Environmental concerns have made manganese dioxide favored over more toxic curing agents. However, not all manganese dioxide phases are effective curing agents, and some can lead to curing failure and material waste. Naturally occurring manganese dioxide is not effective at curing liquid polysulfide, and commercially available manganese-based curing agents are usually pretreated, for example, under high pressure and alkaline conditions.

The curing of liquid polysulfide results in extension of the prepolymer chains. Eventually the

final Shore A hardness is reached. In insulated glass applications, a Shore A hardness of about 30 is required.[2] Another important property in polysulfide curing is the time needed to reach the gel point, which ensures that the time between applications to a substrate is long enough (between 1 and 4 h) to ensure a good work life of the application but not so long that it remains soft and tacky once the job has been finished.

Using EPR and NMR spectroscopy, Coates et al.[3] studied the mechanism of polysulfide curing with manganese dioxide and suggested that the reaction involves thiol oxidation to the appropriate thiol radical, which dimerizes to make a disulfide:

$$RSH \xrightarrow{MnO_2} RS \quad 2RS \rightarrow RSSR$$

We compared the behavior of a synthetic manganese dioxide phase based on sodium birnessite as a curing agent to that of a standard polysulfide curing agent by looking at the thermal, rheometric, and mechanical properties of the cured polysulfide.

EXPERIMENTAL

The characterization of manganese dioxide–cured polysulfide can be determined in a number of ways, for example, using thermogravimetry and pyrolysis GC[4] rheometry and dynamic mechanical analysis; tensile strength and hardness testing are other important means to study polysulfide curing.[5–6]

The manganese oxide studied in this investigation is a synthetic analogue of the mineral sodium birnessite, which is a layered manganese oxide found naturally in soils. The method of synthesis is similar to that used by Stahli.[7] A 0.5M solution of manganese sulfate in 200 mL of deionized water was added to a 5.5M NaOH solution in 250 mL of deionized water. Oxygen was bubbled through this solution for 4 h, resulting in a precipitate, which was separated from the supernatant and dried at room temperature. The product was identified as sodium birnessite using X-ray diffraction and by thermogravimetric analysis. A particle size fraction of the product for use in this study had a mean of 2 μm and a maximum of 14 μm. The commercial manganese dioxide curing agent used in this study also had the same particle size

range and was supplied by Twinstar Chemicals Ltd (Harrow, England). The pH of an aqueous suspension of the commercial curing agent is 9.65 in comparison with a value of 9.83 for the synthetic sodium birnessite. The analytical composition of the synthetic material (Na 6.1%, Mn 54.7%, H_2O 11.3%) suggests that it is based on the formula $Na_2Mn^{II}_2Mn^{IV}_5 \, O_{13} \cdot 4.5H_2O$, although the water percentage in the final product can vary.

The liquid polysulfide used in this study was a single batch of Morton LP32C, a polymer of 1,2,3-trichloropropane and 1,1′-[methylenebis(oxy)]-bis(2-chloroethane) reduced with sodium sulfide and having the formula HS—$(C_2H_4$—O—CH_2—O—C_2H_4—Sx$)_{23}$—C_2H_4—O—CH_2—O—C_2H_4—SH with an average molecular weight of 4000 and containing 2% terminal —SH groups. At 25°C, LP32C has a viscosity of 46.5 Pa s and a specific gravity of 1.29.

Preliminary curing studies showed that the sodium birnessite as prepared led to a very rapid cure, and for the purposes of this study it was diluted 5:5 with a natural manganese pyrolusite ore, which does not act as a curing agent. A second study used 5 parts and 4 parts sodium birnessite without dilution with natural manganese pyrolusite ore.

Both the commercial and sodium birnessite–pyrolusite curing agents were held in suspension in a phthalate plasticizer, Santicizer 261 (Monsanto, Antwerp, Belgium), to which was added an accelerator, tetramethylthiuramdisulfide (TMTD), supplied by Robinson Brothers (West Bromwich, England). The cure mixture was sealed and stored for 1 week at room temperature to stabilize it. It was then added to the LP32C polysulfide resin and stirred for 10 min at a constant speed using a electric drill stirrer. To 100 parts of the LP32C was added 20.5 parts of the cure paste. The characteristics of the curing process were followed by rheometry, as well as by thermogravimetric analysis, tensile strength measurement, hardness testing, and dynamic mechanical analysis of the cured polysulfide.

The curing profile was followed using a Rheometrics ARES rheometer with 25-mm diameter parallel plates in a dynamic time sweep mode. The plate gap was 1.50 mm, the strain 5%. and the frequency 6.28 rad/s. The glass transition temperatures of the cured polysulfides were measured on molded cylindrical samples using a Rheometrics RSA II instrument in a compression–temperature step mode from −60 to 30°C.

Table I Formulation of Curing System of Liquid Polysulfide

Component A	(i)	(ii)	(iii)	(iv)
Parts polysulfide liquid polymer (LP32 C)	100	100	100	100
Component B				
Curing agent: Commercial agent (pph polysulfide)	10			
or sodium birnessite (pph polysulfide)	—	5	5	4
Curing agent diluent: Natural MnO_2 (pph polysulfide)	—	5	—	—
Accelerator: TMTD (pph polysulfide)	0.5	0.5	0.5	0.5
Plasticizer: Santicizer 261 (pph polysulfide)	10	10	15	16
Total Component B	20.5	20.5	20.5	20.5

Hardness of the cured polysulfides was measured on 7-day-old samples using a Shore A Durometer, and thermal decomposition was studied on 10-day-old samples using a Perkin Elmer TGS-2 thermogravimetric analyzer. Tensile-testing measurements were performed using an Instron 4109 instrument at a strain rate of 50 mm/min on dumbbell-shaped samples cut from a sheet of 1-week-old cured polysulfide.

The sealant formulations for studies using the commercial curing agent, undiluted sodium birnessite at 5 pph and at 4 pph, and diluted sodium birnessite are listed inTable I as (i), (ii), (iii), and (iv), respectively. Fillers, retardants, and adhesion agents that are present in commercial cure pastes have been excluded from the sealant formulation to minimize the variables that affect the curing of the liquid polysulfide.

RESULTS AND DISCUSSION

Curing Profile up to Gel Point

The gel points of the curing polysulfide systems, measured rheometrically at 25°C, were obtained from the intersections of the storage modulus G' and the loss modulus G'' curves (Fig. 1). The results show that the sodium birnessite curing agent at 5 parts, even diluted with 5 parts of
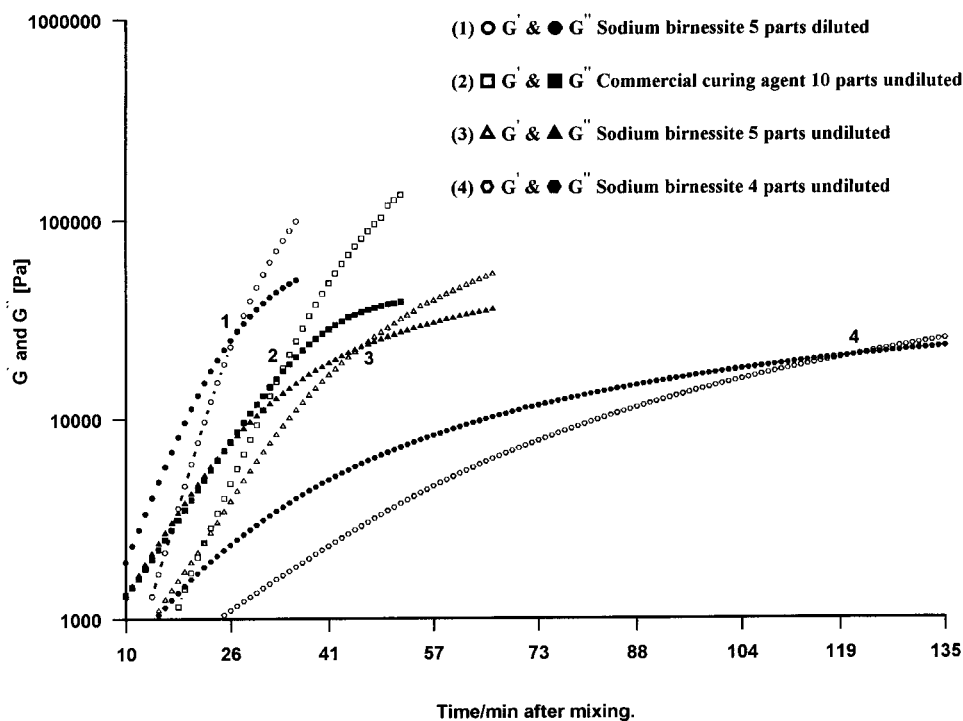
Figure 1 Comparison of the progression to the gel point of storage modulus G' and the loss modulus G' of the diluted and undiluted sodium birnessite and the commercial agent curing of polysulfide at 25°C.
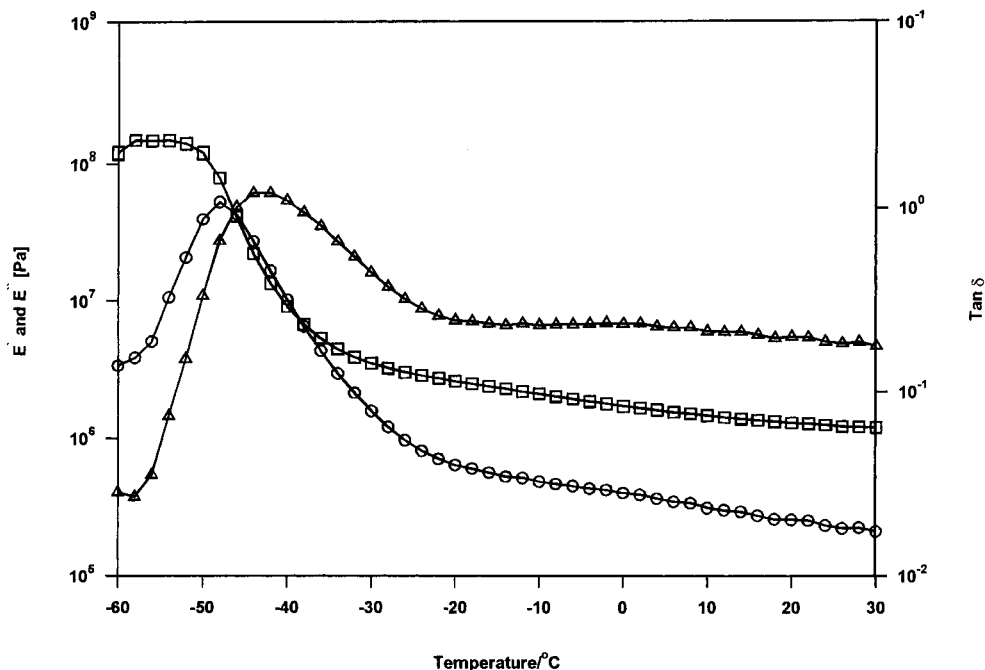
Figure 2 Dynamic mechanical properties of polysulfide sealant cured with 5 parts sodium birnessite diluted with 5 parts natural manganese dioxide ore.

natural manganese dioxide ore, gives a cure that is almost twice as rapid as that for the undiluted commercial agent and that the moduli G' and G'' for the sodium birnessite reaction are greater than those for the commercial agent curing process throughout the reaction period. Undiluted sodium birnessite used at 5 and 4 pph polysulfide gives a slower rate of curing. The times taken to reach the gel point are 38 min for the commercial agent, 32 min for the diluted sodium birnessite, and 51 and 126 min for the undiluted material used at 5 and 4 pph, respectively. The cures give measured 7-day Shore A hardness values of 31 for the commercial agent cured polysulfide, 31 for the diluted sodium birnessite, and 30 and 25 for undiluted sodium birnessite used at 5 and 4 pph, respectively. These data indicate that the diluted

sodium birnessite cured polysulfide has at least the same degree of crosslinking as that achieved by the commercial curing agent.

Glass Transition Temperatures and Thermal Stability

The glass transition temperatures of the cured polysulfides were obtained by measuring the elastic moduli E', E'', and the damping parameter, tan δ as functions of temperature. The glass transition temperatures, the maximum temperature in the damping curve tan δ of 3-week-old cured polysulfides from all sodium birnessite formulations is $-42°C$, the same as that for the commercial curing, showing that all the cure conditions studied led to products with a similar energy-absorb-

Table II   Effect of Curing Agent on Thermal Stability of Polysulfide Sealant

	Temperature of Weight Losses (°C)						
Polysulfide curing agent:	10%	20%	30%	40%	50%	60%	T_{max} (°C)
10 parts commercial agent undiluted	263	280	290	297	302	306	307
5 parts sodium birnessite diluted with 5 parts manganese dioxide	265	282	293	300	305	309	308
5 parts undiluted sodium birnessite	258	280	292	300	305	309	309
4 parts undiluted sodium birnessite	257	281	292	298	302	307	307

ing capacity. The data for the diluted sodium birnessite are in Figure 2.

The thermal stabilities of the cured polysulfides determined by TGA (Table II) confirm that the sodium birnessite product has at least the same degree of crosslinking as that achieved by the commercial agent

Tensile Properties

The tensile strengths of the cured polysulfide polymers obtained in this study are low because they contain no filler material and the crosslink density using LP32C polysulfide is low.[5] The results show that liquid polysulfide cured with sodium birnessite has a higher tensile strength but lower elongation at peak than the polysulfide cured with the commercial agent. The values for the strain at peak are 326%, 234%, 220%, and 275% for products obtained using the commercial curing agent, the diluted sodium birnessite, and the undiluted sodium birnessite at 5 pph and 4 pph, respectively. The corresponding stress at peak values are 0.42, 0.58, 0.24, and 0.15 MPa, respectively.

CONCLUSIONS

The properties of polysulfide sealant cured with sodium birnessite diluted with manganese dioxide ore, show, when compared with the corresponding data for a commercial agent, that the sodium birnessite formulation gives a more rapid cure and leads to similar properties for the cured material, except that it has a higher tensile strength and lower elongation at break. The speed of the cure with sodium birnessite provides an opportunity to reduce active material consumption by diluting the active agent with inert manganese dioxide or any other suitable inert diluent. This possibly means economic and environmental savings can occur in the usage stage of the polysulfide sodium birnessite life cycle if sodium birnessite is used instead of the commercial agent as a polysulfide curing agent.

All manganese-containing curing agents are based on manganese(IV) oxide, but not all manganese dioxide phases are effective curing catalysts. The results of a study of more than 20 manganese(IV) oxide materials[8] showed that curing activity ranged from zero for pure stoichiometric MnO_2, which has the rutile structure, to rapidly curing phases that contain other components such as alkali metals or water. It seems likely that the activity of the catalyst depends on the mobility of Mn^{4+} in the lattice,[9] which allows easy migration of this ion to the surface to take part in the oxidation-reduction reactions involved in the curing that result in the oxidation of thiol groups and the formation of manganese(II) oxide. Mobility of the Mn^{4+} in an oxide lattice can be increased by deliberately creating defects in the lattice by changing the oxidation state of the manganese, by incorporating hydroxide ions and water in the structure, and by forming nonstoichiometric alkali metal manganates(IV). The analytical composition of sodium birnessite is not consistent with all the manganese being present in the IV+ oxidation state. The composition is consistent with two Mn atoms in every seven being in the II+ oxidation state and with the presence of one sodium atom per three manganese atoms. The best formulation for the sodium birnessite would thus be $Na_2Mn_2^{II}Mn_5^{IV}O_{13} \cdot xH_2O$ ($x = 4-5$). Since Mn^{2+} has a Mn^{4+} d^5 and a d^3 outer electronic configuration, Mn^{4+} will have a preference for an octahedral site because of the value of its crystal field stabilization energy, while Mn^{2+} will have a zero octahedral site preference. The Mn^{2+} ions are therefore likely to occupy tetrahedral sites, leaving vacancies in the $Mn^{4+}—O^{2-}$ sublattice, which will favor Mn^{4+} migration to the surface and improve the rate of the curing reaction. The results of this work are therefore consistent with the idea that the presence of mobile Mn^{4+} in the $Mn^{4+}—O^{2-}$ lattice is required in order to achieve optimum polysulfide curing.

REFERENCES

1. Ghatge, N. D.; Vernekar, S.P.; Lonikar, S. V. Rubber Chem Technol 1980, 54, 197.
2. Lucke H. Aliphatic Polysulfides Monograph of an Elastomer; Huthig and Wepf: Basel, Germany, 1994.
3. Coates, R. J.; Gilbert, B.C.; Lee, T. C. P. Perkin Trans 1992, 1387.
4. Radhakrishnan, T. S.; Rama Rao, M. J Appl Polym Sci 1987, 34, 1985.
5. Usmani, A. E. Polym-Plast Technol 1982, 19, 165.
6. Krishnan, K.; Ninan, K. N. J of Thermal Analysis 1986, 35, 1223.
7. Stahli, E. Ph.D. Thesis, University of Bern, Switzerland, 1968.
8. Goldblatt, N. Z. Ph.D. Thesis, Brunel University, Uxbridge, Middlesex, 1999.
9. Minkin, W. S.; Sukhanov, P. P.; Averko-Antonovich, L. A.; Dzhanbekova, L. R. International Polymer Science and Technology 1994, 5, 21.