Journal of Thermal Analysis, Vol. 35 (1989) 1223–1228

THERMAL AND MECHANICAL STUDIES ON THE CURE TIME OPTIMISATION OF POLYSULPHIDE RESIN

K. Krishnan and *K. N. Ninan*

ANALYTICAL AND SPECTROSCOPY DIVISION, SPPC
VIKRAM SARABHAI SPACE CENTRE, TRIVANDRUM-695 022, INDIA

The effect of two commercially available metal oxide curing agents, PbO_2 and MnO_2, on the cure time, kinetic parameters and ultimate tensile strength of the polysulphide polymer was investigated. The kinetic parameters for the thermal decomposition of the two systems were evaluated from their TG data. Both the energy of activation and pre-exponential factor showed a systematic increase with increase in cure and levelled off after the reaction. The cure time was also followed by determining the mechanical properties of the samples at regular intervals. The ultimate tensile strength values and the kinetic parameters follow similar trend with respect to the cure time. The kinetic parameters and the ultimate tensile strength for the PbO_2 cured polysulphide system were on the higher side.

Polysulphide polymers are widely used in the preparation of adhesives and sealants [1]. The major advantages of polysulphide polymers are their excellent adhesion to a variety of substrates when compounded with specific additives, maintenance of integrity in the seal under extension and compression by relieving the stress under fixed strain through interchange of disulphide linkages, outstanding fuel resistance because of the sulphur linkages in the chain, very low gas and vapour permeability and very high resistance to ozone, sunlight and weathering because of the oxygen saturated backbones [2]. Polysulphide adhesives and sealants find extensive application in aircraft industry, ship-building, gas main sealings, corrosion and abrasion resistant industrial coatings, building construction, etc. The chemistry, mechanism of cure, reinforcement and various applications of liquid polysulphide polymers have been discussed in detail by Berenbaum et al. [3].

A wide variety of curing agents such as *p*-benzoquinone dioxime, methyl ethyl ketone peroxide, metal oxides like lead dioxide (PbO_2), manganese dioxide (MnO_2) and ammonium dichromate [$(NH_4)_2Cr_2O_7$] have been used to convert the liquid polymer to an elastomer [4]. In the present work, it is attempted to study the effect of two commercial curing agents, viz., PbO_2 and MnO_2 on the cure time of the

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

polysulphide resin. It is also attempted to evaluate the kinetics of the thermal decomposition of the samples cured at different intervals and correlate the kinetic parameters with the tensile strength of the samples.

Experimental

Sample

The polysulphide resin used in this study is the mercaptan terminated liquid polymer having the formula:

$$HS\text{–}C_2H_4\text{–}O\text{–}CH_2\text{–}O\text{–}C_2H_4\text{–}(\text{–}S\text{–}S\text{–}C_2H_4\text{–}O\text{–}C_2H_4\text{–})_n\text{–}SH$$

prepared as per reported procedure [2]. The main features of the resin are: (i) viscosity: 35,000 cps at 25°. (ii) Specific gravity: 1.303 at 25°. (iii) Molecular weight: 3100. (iv)–SH content 1.7% and (v) Trichloropropane cross-linking agent (2%). The curing agents were commercial grade PbO_2 and MnO_2.

Instruments

The TG experiments were done using a DuPont 951 thermogravimetric analyser under identical conditions of heating rate 10 deg min^{-1}, sample mass 10 ± 0.5 mg and atmosphere: nitrogen at a rate of 50 cm^3 min^{-1}. The mechanical properties of the cured samples were evaluated using an Instron Universal Testing Machine, Model No. 4202. Kinetic calculations were done with a CDC computer using a FORTRAN IV Program.

Procedure

The polysulphide resin and the curing agents, PbO_2 or MnO_2, were mixed separately in the optimum ratios (8 phr PbO_2 and 4 phr MnO_2) and cured at room temperature. The TG experiments were carried out immediately after mixing and at regular intervals for several days. The ultimate tensile strength of the cured polysulphide samples was determined by using dumb-bell shaped specimens conforming to ASTM–D412 after 48 h and at regular intervals.

Results and discussion

The kinetic parameters, viz., activation energy E and pre-exponential factor A for the thermal decomposition of the samples, cured with two curing agents, were calculated from their TG curves using the Coats–Redfern equation [5]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\varphi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

(where α = degree of conversion, n = order parameter, A = pre-exponential factor, E = activation energy, R = gas constant and ϕ = heating rate).

Using computer, linear plots of the left-hand side of the above equation versus $1/T$ were drawn for different values of n in the range of 0 to 2 and the order parameter was chosen from value of n which gave the best fit straight line [6]. The best fit value of n was found to be zero for both samples. Inserting this value of n into the Coats–Redfern equation, the energy of activation and pre-exponential factor were calculated for the two types of samples drawn at different intervals. The results along with the correlation coefficients (r) of the corresponding linear plots are given in Tables 1 and 2 respectively for PbO_2 and MnO_2 cured samples.

From these tables it is also evident that before the onset of the cure reaction the kinetic parameters are not much affected by the two curators. The values of E and A

Table 1 Kinetic parameters for the thermal decomposition of polysulphide–PbO_2 system

Cure time, h	E, kJ mol^{-1}	A, s^{-1}	r
0	56.27	2.543×10^2	0.9974
24	65.89	3.137×10^3	0.9965
48	70.54	5.369×10^3	0.9968
96	76.27	1.466×10^4	0.9965
144	79.62	2.307×10^4	0.9975
192	79.91	2.512×10^4	0.9965
240	80.08	2.554×10^4	0.9966
288	79.91	3.153×10^4	0.9977
336	80.12	3.158×10^4	0.9965

Table 2 Kinetic parameters for the thermal decomposition of polysulphide–MnO_2 system

Cure time, h	E, kJ mol^{-1}	A, s^{-1}	r
0	55.98	2.234×10^2	0.9920
24	60.24	6.005×10^2	0.9900
48	63.01	9.604×10^2	0.9925
96	67.94	3.512×10^3	0.9945
144	70.29	3.881×10^3	0.9965
192	70.70	1.420×10^4	0.9945
240	71.33	1.810×10^4	0.9940
288	71.54	2.010×10^4	0.9955
336	71.54	2.020×10^4	0.9965

Table 3 Ultimate tensile strength for the polysulphide resin cured with PbO_2 and MnO_2

Cure time, h	$PS+PbO_2$ UTS, kg/cm^2	$PS+MnO_2$ UTS, kg/cm^2
48	3.4	2.3
72	3.8	2.6
96	4.5	3.3
120	4.6	3.5
144	4.6	3.6
168	4.6	3.7
240	4.5	3.8
336	4.6	3.8

are nearly the same (E = 56.1 kJ mol^{-1} (13.4 kcal mol^{-1}) and $A = 2\times 10^2\ s^{-1}$) for both samples mixed with the two different curators and these values are in agreement with the values reported for polysulphide resin [7]. From Tables 1 and 2 it can also be seen that the E and A values show a systematic increase with the increase in cure and level off after a certain time which depends on the curator used.

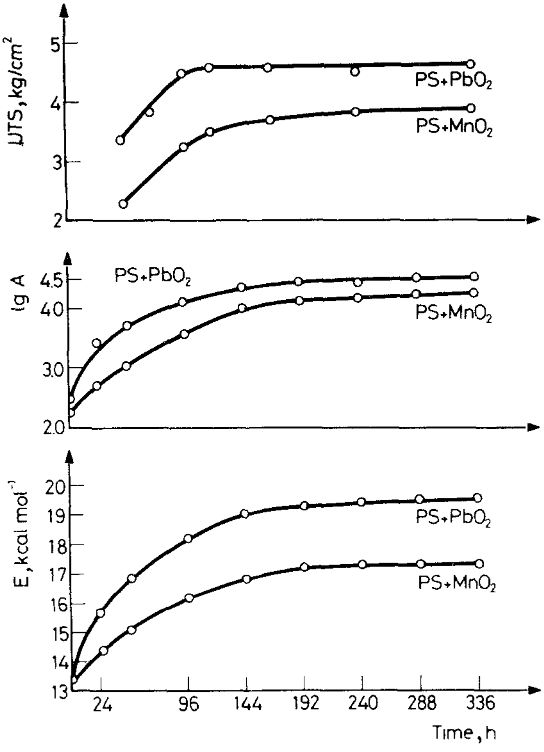

Fig. 1 Effect of cure time on kinetic parameters and UTS

Thus the PbO_2 cured samples attained the maximum values after 120 h whereas the MnO_2 cured samples required more than 240 h. The maximum values attained are not identical; they are higher for the PbO_2 cured samples than for the MnO_2 cured samples.

The ultimate tensile strengths (UTS) of the PbO_2 and MnO_2 cured polysulphide samples are given in Table 3. For the PbO_2 cured samples, the initial value after 48 h of curing is 3.4 kg/cm^2. It gradually increased to a maximum of 4.6 kg/cm^2 after 120 h of curing and then levelled off. In the case of MnO_2 cured samples the UTS values showed an increase from 2.3 kg/cm^2 to 3.8 kg/cm^2 from 48 h of curing to 240 h and then they levelled off. Similar trend was reported by earlier workers also [8].

The trend of kinetic parameters is similar to that of the UTS which is the usual index of cure, and hence the former method may offer a possibility of following the cure especially where the sample quantities are very small. The kinetic parameters and the UTS are plotted against cure time in Fig. 1 from which it can be noted that the similarity in the trend with respect to cure time is followed by E and log A. This can be explained on the basis of the kinetic compensation effect [9].

Conclusions

Based on the experimental results obtained it has been shown that the curing agents influence the thermal and mechanical properties of the cured polymer. The values of E, A and ultimate tensile strength increased with increase in cure. The cure time estimated from the thermal decomposition kinetics agrees well with the optimum cure obtained from UTS measurements. Similarly, the samples with higher strength give higher values of E and A, which can be attributed to the higher degree of crosslinking in them. The correlation between extent of cure, thermal decomposition kinetics and ultimate tensile strength has thus been established for the polysulphide polymer.

* * *

We thank Dr. R. Ramaswamy for supplying the resin and Dr. K. V. C. Rao and Director, VSSC for the kind permission to publish this work.

References

1 T. C. Lee, Eur. Rub. J., 165 (1983) 26.

2 A. V. Tobolsky and W. J. Macknight, Polymeric sulphur and related polymers. Polymer Reviews Vol. 13, Interscience Publishers, New York, 1965, p. 39.

3 M. B. Berenbaum and J. R. Panek, Polyethers, Part III, Polyalkylene sulphides and other Polythioethers, N. G. Gaylord, Ed. Interscience Publishers, New York, 1962, p. 43.

4 J. R. Panek, in Ref. 3, p. 165.

5 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.

6 K. N. Ninan and K. Krishnan, J. Spacecraft and Rockets, 19 (1982) 92.

7 M. Braden, J. Dent. Rs., 45 (1966) 1065.

8 R. Ramaswamy and P. S. Achari, J. Adhesives, 11 (1981) 305.

9 P. D. Garn, J. Thermal Anal., 10 (1976) 99.

Zusammenfassung — Es wurde der Einfluß von zwei im Handel erhältlichen Metalloxidhärtemitteln. PbO_2 und MnO_2, auf die Aushärtungszeit, die kinetischen Parameter und die Zugfestigkeit von Polysulfidpolymeren untersucht. Die kinetischen Parameter für die thermische Zersetzung der zwei Systeme wurden aus deren TG-Daten ermittelt. Sowohl die Aktivierungsenergie als auch der präexponentielle Faktor wachsen mit fortschreitender Aushärtung ständig an und erreichen nach Verlauf der Reaktion einen konstanten Wert. In gleichmäßigen Zeitabschnitten wurde die Aushärtungszeit auch durch Bestimmen der mechanischen Eigenschaften der Proben verfolgt. In Bezug auf die Aushärtungszeit zeigen die Zugfestigkeit und die kinetischen Parameter einen ähnlichen Verlauf. Die kinetischen Parameter und die Zugfestigkeit von mit PbO_2 gehärteten Polysulfidsystemen zeigen bessere Werte.

Резюме — Изучено влияние продажных двуокисей свинца и марганца, как вулканизирующих средств, на период вулканизации, кинетические параметры реакции вулканизации и максимальный предел прочности на растяжение полисульфидного полимера. Исходя из ТГ данных для двух вышеуказанных систем, были определены кинетические параметры их термического разложения. Величины энергии активации и предэкспоненциальный фактор показали систематическое увеличение при вулканизировании и выравнивались после завершения вулканизации. Путем определения механических свойств образцов взятых в строго определенных интервалах времени, был прослежен период вулканизации. Максимальный предел прочности и кинетические параметры подчиняются такой же зависимости, как и период вулканизации. В случае полисульфидной системы, завулканизированной двуокисью свинца, кинетические параметры к максимальный предел прочности на растяжение были более высокими.