Pergamon

0039-9140(93)E0041-B

Talanta, Vol. 41, No. 5, pp. 755–759, 1994

0039-9140/94 $7.00 + 0.00

INVESTIGATION OF THE THERMAL OXIDATION OF A POLYBUTADIENE BY HEADSPACE SAMPLING–GAS CHROMATOGRAPHY

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(*Received* 10 *September* 1993. *Revised* 22 *November* 1993. *Accepted* 23 *November* 1993)

Summary—A novel method was developed, utilizing headspace sampling in conjunction with gas chromatography, to quantitatively follow the thermal oxidation in air of a low molecular weight, hydroxy-terminated polybutadiene. This method was found to offer an efficient and simple technique by which to analyze both the rate and the extent of oxidation of the polymer. Rate studies of the oxidation revealed an induction period followed by self-catalyzed oxidation, the rate of which quickly becomes controlled by diffusion of oxygen into the polymer. By determining the rate of oxygen consumption at various temperatures, an Arrhenius-type plot was derived and an activation energy value of 13 kcal/mol was calculated. The relative effects on oxidation of a number of common antioxidants and organometallic cure catalysts were also determined by this technique.

Hydroxy-terminated polybutadienes are widely used as precursors in the production of polyurethanes, particularly in binders for solid rocket fuel propellant. Due to unsaturation along the backbone of the polybutadiene, and on pendant functionalities, both the polymer and the resulting polyurethane are susceptible to attack by atmospheric oxygen. Such oxidation results in a number of undesirable changes in the properties of the prepolymer and the polyurethane, including changes in molecular weight distribution, functionality and cross-link density.[1] For this reason, most polyurethane formulations include one or more antioxidants which act to prevent substantial oxidation of the polymer by combining with reactive intermediate species, such as free radicals.

To date, the rates of oxidation of polymers have been determined largely by following the rate of oxygen depletion upon heating in a controlled environment.[2,3] This test is performed using a fairly complex apparatus consisting of glassware, including a manometer, as well as an oven for sample heating. Other techniques include measuring the rate of carbonyl group formation by infrared spectroscopy and following the depletion of antioxidants.[4,5] The gross effects of oxidation are also used as a measure of the extent of oxidation, including changes in polymer viscosity and the cross-link density of polyurethanes.[1,6] These techniques, however, are labour-intensive and do not lend themselves to automation. More recently, Venema utilized dynamic headspace analysis–gas chromatography to qualitatively determine the thermal stability of a polymer blend with and without antioxidant.[7]

Our aim in conducting this research was, firstly, to utilize modern analytical instrumentataion to provide an efficient and precise method for the quantitative determination of polymeric oxidation and secondly to study the characteristic oxidation of a specific polymer, that being the R45M brand of hydroxy-terminated polybutadiene manufactured by Atochem, Inc. R45M is a low molecular weight compound, with an average molecular weight in the range of 3000. The polymer chain consists of approximately 60% *trans*-1,4 unsaturation and 20% each of *cis*-1,4 and vinyl-1,2 groups.

In order to develop such a method, a headspace sampling instrument equipped with an autosampler was interfaced to a gas chromatograph (GC). The headspace sampler was capable of holding sealed sample vials at temperatures from slightly above ambient to 200° for periods of up to 1000 min, thus allowing a wide array of temperatures and exposure times to be examined. Heated transfer lines allowed aliquots of a vial's headspace to be sampled and sent to the GC, which was equipped to separate and detect permanent gases, including oxygen and nitrogen. By determining the concentration of oxygen in a given vial, the rate of oxygen depletion, equivalent to the oxidation rate, could be calculated.

Samples of R45M were allowed to oxidize at various temperatures in contact with air in order to determine the temperature dependency of the oxidation rate. Since cured polyurethanes are often heated to high temperatures to simulate aging, knowledge of the relationship between oxidation rate and temperature may play an important role in determining the parameters for such aging experiments. The oxidation of the polymer at a single temperature was also followed over time in order to determine the stages in which oxidation occurs.

The efficiencies of various antioxidants in preventing oxidation of R45M were also studied in this same manner. The antioxidants in question were those commonly used in industry and were either aromatic amines or substituted phenols. There were listed in Table 1.

Previous research has shown that the addition of metallic species to polymers may result in a catalytic acceleration of oxidation.[3,8] This is of special interest in the production of polyurethanes, since organometallics are often added to formulations in order to increase the rate of polymerization. Two cure catalysts were examined during this research to determine whether or not they markedly catalyzed the oxidation process; these being ferric acetylacetonate (FeAA) and dibutyl tin dilaurate (DBTDL).

EXPERIMENTAL

Flexzone 6H was purchased from Uniroyal Chemical Ltd, Cyanox 2246 from American Cyanamid Co., DPA (A.C.S. grade) from Anachemia Canada Ltd, PBNA from Anchor Chemical Ltd., and BHT (99 + %) from Aldrich Chemical Co., Ltd. All were used as received without further purification. FeAA was purchased from Aspex, Inc. and DBTDL (98%) from Aldrich. Both were used as received.

Table 1. Compounds investigated as antioxidants for R45M polymer

Common/brand name	Systematic name
Flexzone 6H	*N*-phenyl-*N*′-cyclohexyl-*p*-phenylene diamine
Cyanox 2246	2,2′-methylene-bis(4-methyl-6-terbutyl phenol)
DPA	diphenylamine
PBNA	2-naphthylphenylamine
BHT	2,6-diterbutyl-4-methyl phenol

Sample preparation

The R45M (hydroxy-terminated polybutadiene) samples analyzed were taken from two lots of pure R45M purchased from Atochem North America, Inc. in 1991 and 1992. Polymer samples were degassed under vacuum for 1 hr prior to analysis to remove any dissolved gases.

Solutions of antioxidants in R45M were prepared by adding the required amount of antioxidant to the polymer and stirring at room temperature or with mild heating until the antioxidant dissolved completely. All antioxidants were added at a concentration of 1% by weight, except for a mixture of 0.5% Flexzone 6H and 0.5% Cyanox 2246. Ferric acetylacetonate was added as a solution in methylene chloride and dibutyl tin dilaurate was added neat. Both were added at a concentration of 0.01% by weight. All samples were again degassed following these additions to remove any dissolved air or solvent.

Headspace–GC analysis

A Tekmar 7000 Headspace Autosampler was interfaced to an HP 5890 series II gas chromatograph fitted with two PLOT (porous layer open tubular) columns in series; a PoraPlot Q fused silica column (25 m × 0.53 mm ID) followed by a 5 Å Molsieve fused silica column (25 m × 0.53 mm ID). Both columns were purchased from Hewlett-Packard. A column switching valve was preprogrammed to switch the Molsieve column off at 2.7 min after injection and on at 4.8 min, in order to allow CO_2 to elute. Helium was the carrier gas at a total flow of 22 ml/min. The inlet operated in the split mode with the column flow regulated at 5 ml/min. The columns were maintained at 40°C throughout the chromatographic runs. A thermal conductivity detector was utilized in the low sensitivity mode. On this system, oxygen eluted at 5.3 min and nitrogen at 5.8 min with baseline resolution between the two. Data was collected and analyzed using an HP Vectra PC with HP Chemstation software.

Samples were weighed into 20 ml gas vials in air and sealed with Teflon faced rubber septa and crimp cap seals. The amount added to each vial was 2.0 ± 0.1 g. Since preliminary tests showed that the surface area of the polymer exposed to air greatly affected the rate of oxygen depletion, care was taken to add the polymer directly to the bottom of the vials such that the exposed surface area was always equal to the cross-sectional area of the vials. This area was 6.3 cm^2. All samples were sealed under an ambient atmosphere which was assumed to contain the standard 20.95% proportion of oxygen.

Samples were heated in the platen area of the headspace sampler at preprogrammed temperatures for various lengths of time. The platen was found to adhere to the setpoint temperature within ±0.2°C.

RESULTS AND DISCUSSION

Basic oxidation rates and kinetics

The combination of analytical instrumentation described above functioned well to separate and quantify oxygen and nitrogen in samples of vial headspaces. Oxygen and nitrogen were baseline resolved in the resulting chromatograms and were readily integrated to provide arbitrary area counts which were used for calculations of oxidation rates. The amount of oxygen in a vial was taken as being proportional to the area count of the oxygen peak, which was normalized according to the area of the nitrogen peak. The absolute amount of oxygen consumed by a polymer sample was calculated by simply taking the ratio of its oxygen peak area over the oxygen peak area of a 'blank' (empty) vial and multiplying this by the amount of oxygen in the volume of the vial.

Initial experimentation consisted of heating samples of R45M at 110°C for periods of time ranging from half an hour to 4 hr. The resulting decrease in oxygen content for the various samples is shown graphically in Fig. 1. Note that the oxidation appears to occur in three distinct phases. This is a phenomenon seen in the literature previously for unsaturated polymers.[9] The initial phase, lasting approximately 30 min, is referred to as an induction period. During this stage both the polymer and molecular oxygen are reacting to form radicals and other reactive centres which will lead to further oxidation. Following this stage, the rate increases substantially. This is an autocatalytic period, during which reactive centres already formed go on to cause further reactions and so an ever increasing number of reactive species is formed. Soon after the catalytic increase, the rate begins to slow down considerably. This is likely due to the decreasing concentration of oxygen in the vial's headspace, as well as control by the rate at which oxygen can diffuse below the exposed surface of the polymer. It is important to note here that pure R45M may contain

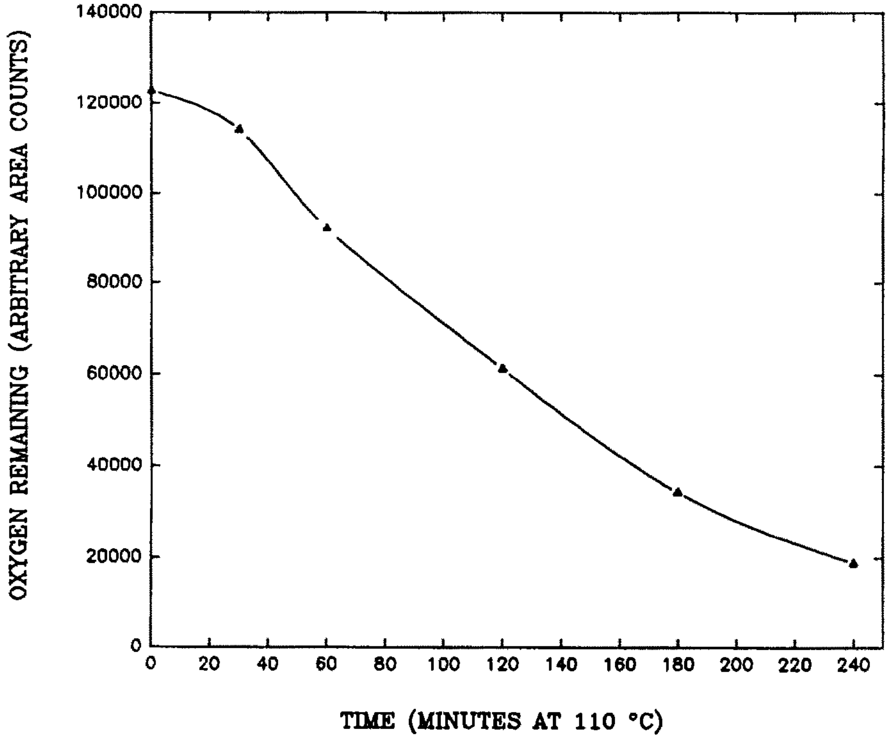

Fig. 1. Oxygen depletion over R45M polymer upon heating at 110°C.

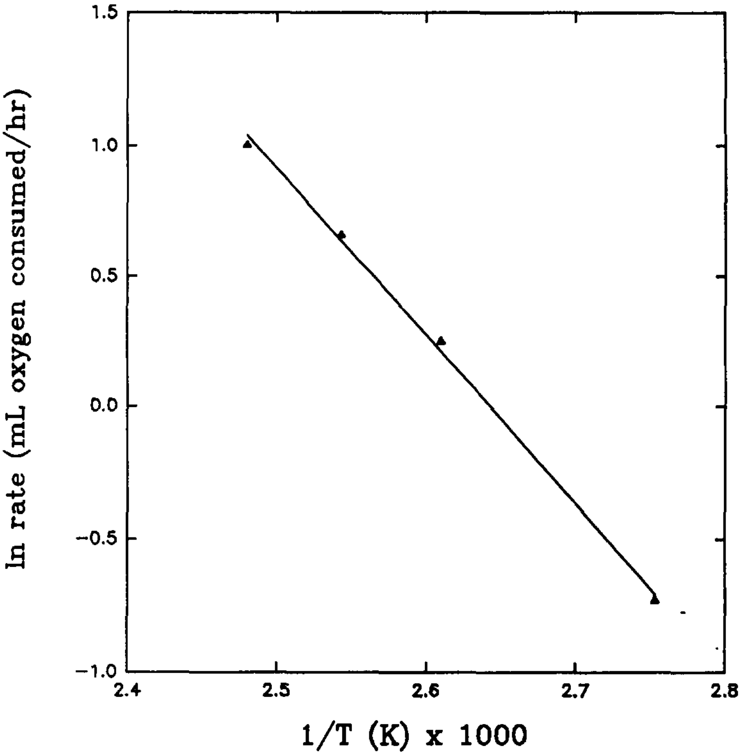

Fig. 2. An Arrhenius-type plot for R45M polymer oxidation.

some active oxygen species when it is initially received. These will decompose to induce oxidation of the polymer and thus may partly account for the relatively short induction period observed.

Further experimentation involved heating the R45M samples for periods of 1 hr at varying temperatures. By assuming the rate of oxidation over this period to be representative of the maximum rate, it was possible to construct Arrhenius-type plots for the oxidative reactions of this polymer. Figure 2 shows such a plot for temperatures spanning 80–120°C. The linearity of this plot supports our contention that this method is suitable for measuring kinetics of polymer oxidation. From this graph we may derive a value for the slope of -6399 K, which is equal to $-E_a/R$, where E_a is the activation energy for polymeric oxidation and R is the gas constant. E_a is thus calculated to be 13 kcal/mol, which is reasonably close to the value of 21 kcal/mol derived by Cunliffe *et al.* for the oxidative cross-linking of polyurethane-based solid propellant.[10]

Antioxidants and organometallics

An analysis of the effects of antioxidant addition was undertaken by heating solutions of the antioxidants in R45M at 120°C for 12 hr. The percentage of oxygen remaining in the vials was taken as a direct measure of the extent to which the solutions had resisted oxidation. Table 2 compares the oxygen depletion rate of pure R45M with solutions of antioxidants in R45M. The extent to which the antioxidants function to prevent oxidation is readily apparent. Table 3 illustrates the relative efficiencies of all the antioxidant solutions. With the exception of DPA, the differences between the various antioxidants are minor and may be due to a

Table 2. Oxygen depletion rates over R45M polymer with and without antioxidants at 120°C

Antioxidant	Rate (*ml* O_2 *hr*$^{-1}$ *g*$^{-1}$)
None	1.930
PBNA	0.036
Cyanox 2246/Flexzone 6H	0.069
Cyanox 2246	0.074

Table 3. Percentage oxygen remaining over R45M polymer/antioxidant solutions following 12 hr at 120°C

Antioxidant	% O_2 remaining
Cyanox 2246	84.1
Flexzone 6H	83.2
Cyanox 2246/Flexzone 6H	83.8
DPA	51.3
BHT	82.8
PBNA	92.4

number of factors, including purity of the antioxidants and homogeneity of the solutions.

A solution of 0.01% FeAA in R45M was found to have a greatly accelerated oxidation rate when heated at 110°C for 1 hr. The measured rate of 1.29 ml O_2 consumed hr^{-1} g^{-1} was approximately twice that of pure R45M. A solution of DBTDL showed no increase in the oxidation rate. These results concur with findings by other researchers in which iron was found to catalyze the oxidation of butadiene rubber to a greater extent than tin.[3]

CONCLUSIONS

Headspace sampling–gas chromatography has been shown to be a viable instrumental technique for the quantitative analysis of polymeric oxidation. A number of aspects of oxidation, including kinetics, may be measured quickly and efficiently with no sample preparation.

The R45M brand of low molecular weight polybutadiene will oxidize rapidly under air upon heating and this oxidation is autocatalytic, quickly becoming a diffusion-controlled process. The activation energy of this oxidation is on the order of 13 kcal/mol. A number of common antioxidants greatly reduce the rate of R45M oxidation at concentrations of one per cent, while low levels of an iron organometallic compound catalyze the oxidation process. A tin organometallic species was found not to catalyze oxidation.

Acknowledgements—The majority of the instruments utilized during this research were purchased with the aid of funding from Industry, Science and Technology Canada.

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