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A viscometric method for the determination of induction period for polymer thermal oxidation

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Summary

On the basis of viscometry technique a novel method was developed to determine the induction period for polymer thermal oxidation (τ_i). Natural rubber films from *Manihot glaziovii* degradated at 90°C were used as a model. $\bar{M}_v$ values were calculated by using the equation: $[\eta] = 1.9 \times 10^{-4} \bar{M}_v^{0.745}$ in toluene at 30°C. A random chain scission process was applied. A plot of lnN (N is the number of broken bonds , C=C in case of rubber) versus time of heating shows two lines. The first indicates no degradation ($\ln N = \ln N_o$, to $t \leq \tau_i$) while the second represents the real kinetics of the process ($\ln N = \ln N_o - k(t - \tau_i)$, to $t \geq \tau_i$). The intersection of these lines is the induction period of thermal oxidation. The effect of a protective agent, carnauba wax, was tested. The resolution of the method is comparable to that of chemiluminescence and is superior to that of IR and DSC.

Introduction

The thermal oxidation of polyolefins and unsaturated elastomers is an autocatalytic, free radical chain reaction whose mechanism can be summarized as (1) :

Ketones
Aldehydes
$RH \longrightarrow RO_2 \longrightarrow RO_2H \longrightarrow$ Epoxides
macromolecules Carboxylic acids, etc

The kinetics of the early stage is very different from that of later stage of this oxidation (2). Low rates and degrees of oxidation characterize the early stage making difficult the collection of the kinetics data. It is believed that a minimum of hydroperoxide accumulation is necessary to initiate the later stage, the autocatalysis reaction. Recently, Livanova (3) proposed that the early stage is also due to the structure-related and chemical localization (in the case of inhibited oxidation) at primary initiation sites on catalytic impurities. The end of this stage is indicated by the expansion of the oxidation reaction from the initiation sites and its propagation over the entire polymer.

The time necessary to initiate autocatalysis or to finish the early stage is defined as the induction period (4) . This parameter has been used to evaluate the purification (5), vulcanization (5) , epoxidation (6) and molar mass effects (7) in the oxidation of natural rubber .This parameter was also used for the comparison between isotropic and oriented polypropylene films (3,8) , as well as various antioxidants in butadiene rubber (9). The effects of oxygen pressure, polymer structural anomalies and level of stabilizer protection during processing on the induction period of thermal oxidation of polyethylene and polypropylene were discussed by Iring and Tudos (10).

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The induction period for polypropylene, natural rubber and derivatives, and butadiene rubber has been determined by oxygen uptake (3,8), chemiluminescence (6),DSC (5) and IR spectroscopy (6,7,9,11). Comparisons among the values obtained by these techniques are very difficult, since each method is related to specific and different features of the thermal oxidative processes. In DSC and IR techniques an overall effect is measured. Small structural changes are diluted in the bulk unmodified form until the changes become sufficient to be detected. A delay of detection is verified. In the chemiluminescence method an intermediate product of oxidation is directly measured and as soon as it appears, this technique is promptly able to detect it. There is no method based on viscometry available.

In this work, we evaluate $\bar{M}v$ for the determination of the thermal oxidative induction period of natural rubber from *Manihot glaziovii*, a poly-cis-isoprene of $\bar{M}v$ ranging between 1.0×10^6 and 1.5×10^6 (12). The response of the method has been evaluated by using NR in the absence and presence of a protective agent, carnauba wax. Carnauba wax is the highest melting of commercial vegetable waxes (82 - 86 °C) and it is composed of substances with average chain lengths of 50 carbons (13): esters (ca. 80%), alcohols (10 - 15 %), free acids (3 - 5 %) and hydrocarbons (2 - 3 %) (14).

Experimental

Materials

The sample of rubber from *Manihot glaziovii*, a plant popularly known as maniçoba, was collected in Pacatuba County, State of Ceará, northeast of Brazil. About 5.0g of this polymer was dissolved in 500 mL of $CHCl_3$ under N_2 atmosphere at 18°C in darkness and then filtered. The coagulation was performed with methanol (3 L) and the remaining solvent was evaporated in a desiccator under vacuum to constant weight. The purified rubber was stored at -10°C in darkness.

Carnauba wax, a natural wax produced by the leaves of *Copernicia cerífera* palm tree, was supplied by Johnson & Johnson (extracted in Ceara, northeast of Brazil in 1990). The pale yellow material (B-065) was used without further purification.

Thermal oxidation

Natural rubber films of thickness 100 ± 10 μm and 2.5 cm x 6.0 cm dimensions were prepared by successive casting and solvent evaporation from 1.5 % (w/v) polymer solution in $CHCl_3$ on polytetrafluoroethylene films (PTFE, 0.1 mm). The rubber samples on PTFE were stored in darkness at -10°C before thermal treatment.

NR films in presence of carnauba wax were obtained as described to NR. The solution was prepared by mixing 0.5 mL of 1.5% (w/v) of wax to 50 mL of 1.5% (w/v) of polymer solutions, both in $CHCl_3$.

The thermal oxidation experiments were performed in a Thelco (model 19) oven from GCA/Precision Scientific Company at 90°C under air.

Viscosity measurements

Prior to viscosity measurements of the oxidized material, the wax and any gels or insoluble materials eventually formed during the oxidation were eliminated. The heated samples were dissolved in $CHCl_3$ at 18°C in darkness and filtered. The solvent was removed by low pressure evaporation. No significant loss of mass occured.

Ubbelohde viscometer with to of 190 s at 30.0°C for toluene was used for the determination of the flow time. Temperature control was made by using a water bath with 0.1°C accuracy. All flow times are averages of at least three replicates. Rubber concentration was in the range of 0.1 and 0.4 g/dL in toluene. Six different concentrations were employed on the determination of intrinsic viscosities of each sample. Kinetic energy and shear corrections were negligible. Intrinsic viscosities were determined by extrapolation based on the Huggins equation. Least square analyses were performed for all linear relationships.

Results and Discussion

Chain scission

Thermal oxidative degradation of polymers can lead to chain scission and changes in molar masses. The data in Table I show that the intrinsic viscosity of oxidized rubber initially stays constant and as the heating time increases it decreases. Similar behavior has been observed with photodegradation (15) and with chain-scission during epoxidation (16) of NR.

Viscosity-average molar masses were determined by the Mark - Houwink - Sakurada equation: $[\eta] = 1.90 \times 10^{-4} \overline{M}_v^{0.745}$ in toluene at 30 °C and in dL/g (17) . In the present conditions of oxidation the structural changes (main chain modifications) are considered irrelevant. Inspection of the IR spectrum of the degradated material did not reveal any new bands. The Huggins constant falls as the $\overline{M}_v$ is reduced. No abnormal value was found. The important fact is that thermal oxidation causes scission of the double bond.

The degradation of rubber was verified by the decrease of $\overline{M}_v$ with time of heating (Fig. 1). An initial period where no degradation occurs is observed. Unfortunately the limit between this initial period and the beginning of degradation (induction period) cannot be established precisely.

Table I. Intrinsic viscosities of rubber films oxidized at 90°C as function of heating time. Solutions in toluene at 30 °C

heating time (min)	$[\eta]$ (dL/g)
0	6.44
15	6.44
30	6.36
60	5.90
120	5.23
150	5.01
210	4.48

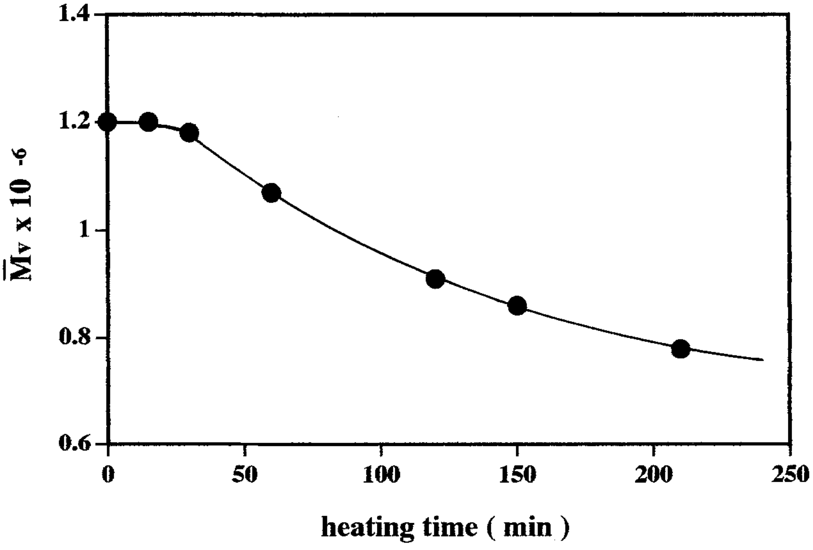

Figure 1. The dependence of the viscosity-average molar mass of NR from maniçoba on the heating time at 90°C.

Random chain scission has been applied as the model of thermal oxidative degradation of rubber (18 -20). It has been interpreted in terms of a first-order process that could be reduced to a pseudo-zero-order kinetics for relatively short time of reaction (19). Sawada (21) has proposed that in a random degradation the number of chain cleavages is proportional to the number of linkages. If a linear polymer is subject to this kind of degradation, the variations of the number of bonds N as a function of time t is proportional to the number of bonds present at time t:

$$- dN/dt = kN \qquad (1)$$

where k is the rate constant. Integrating equation 1, when at the start of reaction $t = 0$ and $N = N_o$, give at time t: $N = N_o e^{-kt}$

or

$$\ln N = \ln N_o - kt \qquad (2)$$

Equation 2 represents the first-order kinetics followed by the rate of disappearance of chain linkages. In the case of natural rubber the C=C bond is involved in chain breaking, and so $N = \bar{M}_v / 68$, where 68 is the molar mass of the isoprene unit.
Values of N at various heating times (t) are calculated and ln N *vs* t plotted (Fig. 2). The first line (A) indicates that no chain rupture occurs. The second one (line B), obtained by exclusion of initial points using the best linear correlation coefficient, is the true kinetics of degradation. The linearity of this kinetics suggests a first-order reaction. The intersection of the lines A and B shows the beginning of degradation and the corresponding time of heating is the induction period (τ_i) . Line B equation to NR is: $\ln N = 9.823 - 2.57 \times 10^{-3}\, t$ with a linear correlation coefficient of 0.996. Using $\ln N_o = 9.778$, relative to the initial value of $\bar{M}_v$ (1.2×10^6), the time of heating and so the induction periods for thermal oxidation of natural rubber will be 18 min.
The situation could be summarized as:

$$\ln N = \ln N_o \qquad \text{when } t \le \tau_i$$

and

$$\ln N = \ln N_o - k(t - \tau_i) \qquad \text{when } t \ge \tau_i \qquad (3)$$

Equation 3 represents a more suitable form of the conventional equation 2. For NR it will be: $\ln N = 9.778 - 2.57 \times 10^{-3} (t - 18)$

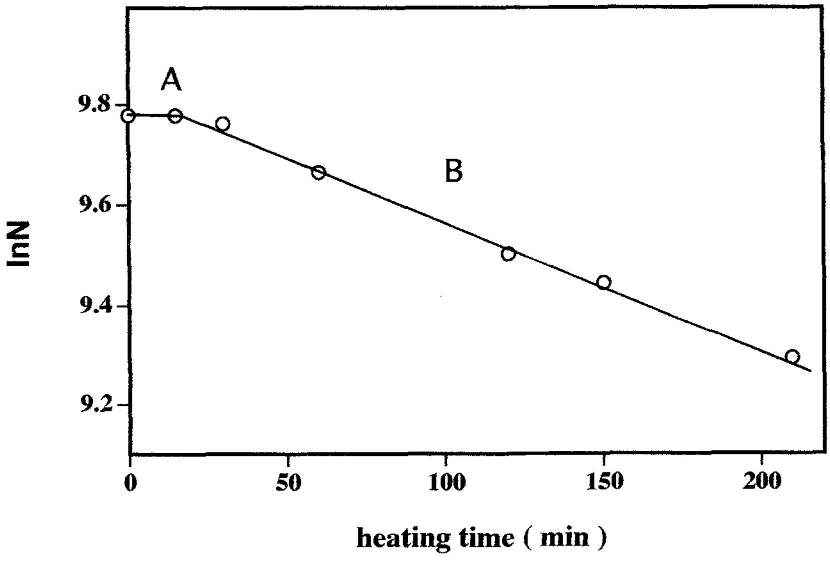

Figure 2. Logarithmic transformation of the number of C=C bonds in NR from maniçoba during heating at 90 °C.

Effect of carnauba wax

The response to oxidation was evaluated by using NR in the presence of 1% carnauba wax. It is generally agreed that waxes compounded into rubber are capable of migrating to the surface, thereby providing protection against ozone attack by formation of an impervious barrier (22 - 24). Figure 3 shows a plot of lnN *vs* time of heating for NR in presence of wax. In this case the intersection of the two lines is well defined. The line B equation (when $t \geq \tau_i$) is :

$$\ln N = 9.894 - 2.34 \times 10^{-3}\, t$$

The induction period of 50 min was determined by using the proposed steps . The equation 3 applied to this system is :

$$\ln N = 9.778 - 2.34 \times 10^{-3}\,(t - 50)$$

A protective action of carnauba wax against thermal oxidation of rubber is verified since its induction period is longer than that of pure NR (18 min). The method was shown to be capable to distinguish among different oxidation conditions.

Comparison with other methods

Some methods of induction period determination are presented in Table II . Most of all use infrared spectroscopy by following the carboxyl group at 1720 cm^{-1}. The resolution of the DSC method seems lower than those of IR and luminescence. The resolution of the proposed method is comparable to that of luminescence and higher than those based on DSC and IR. According Arnaud and De Monte (5) the induction period increases as temperature decreases ($\log \tau_i = K/T$) . Superior values of 1,600 min (DSC)(5) and 340 min (IR)(6), both determined at 100°C , would be expected to oxidation of NR at 90°C. Therefore the induction period of 18min calculated by viscometry for NR is comparable to that of luminescence (>8min)(6) and much lower than those determined by DSC and IR. Viscosity is very sensitive to small structural and molar mass changes and it is well suited for the measurement of the induction period for thermal oxidation of polymers.

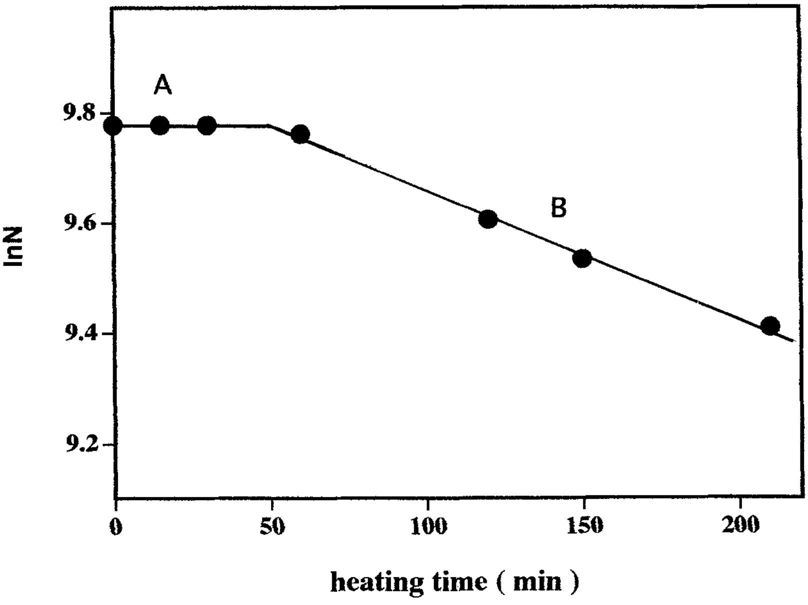

Figure 3. Logarithmic transformation of the number of C=C bonds in NR from maniçoba in presence of 1% carnauba wax during heating at 90°C.

Table II. Methods of induction period determination

Method	Description	Polymer	Ref.
oxygen uptake	time of consumption of 0.07 mol of oxygen/kg of polymer	PP	3
oxygen uptake	extrapolating the linear representation of kinetics curve in parabolic coordinates	PP	8
DSC	time necessary to the appearing of oxidation peak at constant temperature	NR	5
chemiluminescence	determination of hydroperoxy group	NR , ENR	6
IR	variation of absorbance of characteristic band vs. time of heating:		
	- double bonds at 580 and 840 cm^{-1}	NR , DNR	16
	- carbonyl at 1720 cm^{-1}	NR, DNR	6,7,16
	- carboxyl at 1760 cm^{-1}	NR, DNR	16
	- hydroperoxide at 3400 cm^{-1}	BR	9

PP - polypropylene ENR - epoxidized natural rubber
DNR - natural rubber derivatives BR - butadiene rubber

Conclusions

The proposed method to determine the induction period for thermal oxidation of polymers is simple and reliable and it uses an accessible technique , viscometry. The steps of method could be summarized as :

a) determination of intrinsic viscosity of polymer oxidized at various time of heating (t);
b) calculation of M_v ;
c) plot of lnN versus t , where $N = M_v / M_m$ (N is the number of bonds to be broken and M_m = molar mass of monomeric unit);
d) determination of τ_i as the intersection of the line A ($\ln N = \ln N_o$) and line B ($\ln N = \ln N_o - k (t - \tau_i))$.

Comparison with other methods indicates that the order of increasing resolution in induction period determination for thermal oxidation of polymers is :

DSC < IR < chemiluminescence ~ viscometry

Carnauba wax protects natural rubber against thermal oxidation at 90°C. A delay in the beginning of degradation was verified.The induction periods for NR in the absence and presence of carnauba wax are, respectively, 18 and 50 min.

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References

1. Barnard D, Lewis PM (1988) Oxidative ageing. In: Roberts AD (ed) Natural Rubber Science and Technology. Oxford University Press, New York
2. Rapoport NYa, Goniashvili ASh, Akutin MS, Miller VB (1979) Vysokomol Soed **21A** : 2071
3. Livanova MM (1994) Polym Sci USSR, Serie A **36** : 32
4. Henman TJ (1985) Characterisation of oxidised polyolefines by reaction with sulphur dioxide. In: Grassie N (ed), Elsevier, England (Developments in Polymer Degradation, vol. 6, pp 109)
5. Arnaud R, De Monte P (1991) Caoutch et plast **708** : 95
6. Ivan G, Giurginca M, Jipa S, Tavaru E, Setnescu T, Setnescu R (1993) J nat Rubb Res **8** : 31
7. Hhivíková J, Blazková A, Lapcik L (1980) J Appl Polym Sci **25** : 761
8. Rapoport NYa, Zaikov GE (1985) Kinetics and mechanism of the oxidation of stressed polymer. In: Grassie N (ed), Elsevier, England (Developments in Polymer Degradation, vol.6, pp 235-240)
9. Paoli MA, Schultz GW, Furlan LT (1984) J Appl Polym Sci **29** : 2493
10. Iring M, Tudos F (1990) Prog Polym Sci **15** : 217
11. Bac NV, Terlemezyan L, Mihailov M (1990) Eur Polym J **26** : 1055
12. Rodrigues JF, Rodrigues AS, Cardoso ALH (1991) J nat Rubb Res **6** : 134
13. Basson I, Reynhardt EC (1988) J Phys D. Appl Phys **21** : 1429
14. Lawrence JF, Iyengar JR, Page BD, Conacher HBS (1982) J Chromatogr **236** : 403
15. Kok CM (1985) Eur Polym J **21** : 37
16. Bac NV, Terlemezyan L, Mihailov M (1993) J Appl Polym Sci **50** : 845
17. Chirico A (1964) Chim Ind **46** : 53
18. Sambhi MS (1988) J nat Rubb Res **3** : 107
19. Chee KK (1990) J Appl Polym Sci **41** : 985
20. Gan LH, Ng SC, Chee KK (1992) Rubber Chem Technol **65** : 1
21. Sawada H (1987) Depolymerization. In Encyclopedia of Polymer Science and Engineering, John Wiley & Sons, Inc., New York, vol. 4, pp. 719
22. Dimauro PJ, Paris HL, Fath MA (1979) Rubber Chem Technol **52** : 973
23. Muriandy K, Southern E, Thomas AG (1988) Diffusion of liquids and solids in rubber. In Roberts AD (ed) Natural Rubber Science and Technology. Oxford University Press, New York
24. Lavebratt H, Ostman E, Persson S, Stenberg B (1992) J Appl Polym Sci **44** : 83