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THERMOANALYTICAL STUDY ON THE INHIBITION OF METALLIC ION CATALYZED OXIDATION OF NATURAL RUBBER WITH 1,4,8,11-TETRA-AZACYCLOTETRADECANE

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ABSTRACT

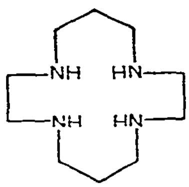
The effect of a macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (cyclam) on the metallic ion catalyzed oxidation of natural rubber was studied by differential scanning calorimetry. Cyclam showed antioxidant activity and was able to suppress oxidation catalyzed by copper, cobalt, iron and manganese ions. The effect of cyclam against copper ion was particularly good.

INTRODUCTION

The catalytic effect of metallic ion on the oxidation of rubber is well known. The metallic ion exerts its catalytic effect by first forming unstable complexes with hydroperoxides followed by electron transfer reactions to give chain propagating peroxy radicals[1]. To protect rubber against oxidation catalyzed by metallic ions, suitable chelating agents are used to deactivate the ion by forming inactive complexes.

Recently, considerable interest has been shown in macrocyclic ligands and their complexes[2, 3]. If the cavity of the macrocyclic ligand is of the same size as the metallic ion, the ion can be complexed and held firmly within the cavity. Moreover, the macrocyclic complex shows an enhanced stability as compared with the similar non-macrocyclic complex[4–6]. It is therefore envisaged that macrocyclic ligands could provide protection for rubber against metallic ion catalyzed oxidation. The use of a macrocyclic polyether as heat stabilizer for polyester fibers was recently reported[7].

Recent studies[8–13] showed that thermal analysis provided a simple and reliable means to evaluate the effectiveness of antioxidants and the catalytic activities of metallic ions. This technique is most suitable for the preliminary study on a new compound as a small amount of material is needed. This paper reports the thermo-analytical evaluation of the effectiveness of a macrocyclic ligand, 1,4,8,11-tetraaza-cyclotetradecane (cyclam), in the inhibition of metallic ion catalyzed oxidation of natural rubber.



Cyclam

EXPERIMENTAL

Natural rubber of pale crepe grade was used. It was extracted with acetone for 24 h and then purified by solution in benzene, followed by precipitation in methanol. The naphthenates of cobalt, copper, iron and manganese were obtained from K & K Laboratories Inc. The naphthenates were used as received. Cyclam was prepared according to the method of Barefield et al.[14].

A Perkin-Elmer DSC-1B differential scanning calorimeter was used. The details of the experimental method and sample preparation have been described earlier[13]. It suffices to mention that the sample was prepared by dissolving appropriate amounts of rubber, cyclam and metallic naphthenate separately in benzene. The solutions were mixed and a droplet of the solution was placed in the sample pan and allowed to dry. For isothermal study, the sample was brought to 400 K with the fastest heating rate 64 K min^{-1}.

The activation energy of oxidation was evaluated by using Kissinger's method[15] as previously described[13]. For isothermal study, the time required for the appearance of the oxidation exotherm peak was taken as the induction period.

RESULTS AND DISCUSSION

The DSC curves of natural rubber containing 0.2 p.h.r. (parts per hundred parts of rubber) of copper naphthenate and various amounts of cyclam scanned with a heating rate of 16 K min^{-1} are shown in Fig. 1. The catalytic effect of copper ion is evidenced from the DSC curves. The addition of copper ion produced a broader oxidation exotherm, and the temperature at which oxidation began as well as the oxidation peak temperature were both lowered. Upon the addition of cyclam, the initial oxidation temperature and the oxidation peak temperature were increased. The oxidation exotherm became sharp and narrow. Similar observation was also noted for samples containing the naphthenates of cobalt, iron and manganese.

The activation energy and induction period values of samples containing 0.2 p.h.r. of metallic naphthenate and various amounts of cyclam are given in Tables 1 and 2, respectively.

In the absence of metallic ion, the addition of cyclam to natural rubber increased the activation energy and prolonged the induction period. The activation energy values are of the same order of magnitude as natural rubber containing amine type antioxidants such as *N*-phenyl-*β*-naphthylamine and *N*-isopropyl-*N'*-phenyl-*p*-

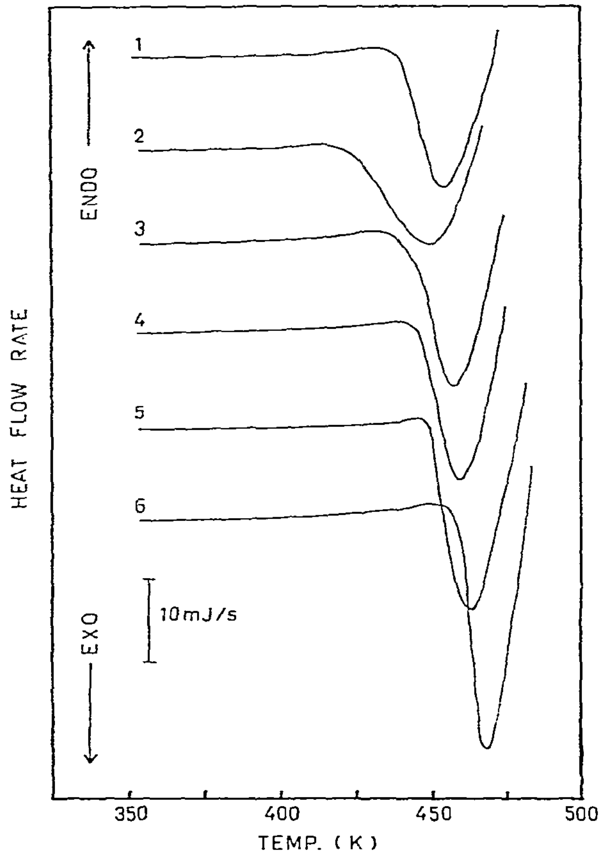


Fig. 1. DSC curves of various natural rubber samples. 1, without additives (sample weight: 0.50 mg); 2, with 0.2 p.h.r. copper naphthenate (sample weight: 0.43 mg); 3, with 0.2 p.h.r. copper naphthenate and 0.1 p.h.r. cyclam (sample weight: 0.51 mg); 4, with 0.2 p.h.r. copper naphthenate and 0.2 p.h.r. cyclam (sample weight: 0.57 mg); 5, with 0.2 p.h.r. copper naphthenate and 0.3 p.h.r. cyclam (sample weight: 0.56 mg); 6, with 0.2 p.h.r. copper naphthenate and 0.5 p.h.r. cyclam (sample weight: 0.50 mg).

TABLE 1

ACTIVATION ENERGY OF OXIDATION OF NATURAL RUBBER CONTAINING 0.2 P.H.R. OF METALLIC NAPHTHENATE AND VARIOUS AMOUNTS OF CYCLAM

Metallic naphthenate	*Activation energy (kJ mole⁻¹)*				
	Amount of cyclam (p.h.r.)				
	0	*0.1*	*0.2*	*0.3*	*0.5*
Copper	61	79	82	83	91
Iron	62	69	76	77	82
Cobalt	53	70	74	78	83
Manganese	51	53	77	77	78
Blank	73	83	84	87	97

TABLE 2

INDUCTION PERIOD OF NATURAL RUBBER CONTAINING 0.2 P.H.R. OF METALLIC NAPHTHENATE AND VARIOUS AMOUNTS OF CYCLAM

Metallic naphthenate	*Induction period (min)*				
	Amount of cyclam (p.h.r.)				
	0	*0.1*	*0.2*	*0.3*	*0.5*
Copper	8	26	30	43	66
Iron	8	12	21	29	43
Cobalt	3	11	17	19	26
Manganese	3	5	29	30	38
Blank	24	35	50	65	101

phenylenediamine[12]. These results indicate that cyclam possesses antioxidant activity. The common amine type antioxidants are arylamines and derivatives of *p*-phenylenediamine. These compounds act as chain breaking antioxidants by intercepting the chain propagating peroxy radicals

$$ROO\cdot + AH \rightarrow A\cdot + ROOH$$

The amine will be an effective antioxidant if there is a high electron-donating tendency on the nitrogen atom to facilitate the electron transfer to the peroxy radicals, and there is an effective delocalization of the unpaired electron of the radical A·. The radical A· will then couple or disproportionate to form non-radical products. Cyclam being an aliphatic secondary amine does not meet these two conditions. Apparently, the inhibition mechanism of cyclam is quite different from that of arylamines. The antioxidant activity of cyclam is probably due to the formation of nitroxide radicals during oxidation. Dialkyl nitroxide radical was reported to be an excellent antioxidant because of its ability to react rapidly with alkyl radicals[16].

The activation energy values for natural rubber samples containing 0.2 p.h.r. of metallic naphthenates are in good agreement with values reported previously[13]. The activation energy and induction period values of these samples are lower than that of the blank rubber sample, demonstrating the catalytic effects of these ions.

Cyclam appears to be highly effective in deactivating copper ion. The addition of 0.1 p.h.r. of cyclam restored the activation energy and induction period similar to the blank rubber sample. Further addition of cyclam increased the activation energy and prolonged the induction period. The catalytic effects of cobalt, iron and manganese ions were also suppressed by cyclam, but a larger amount of cyclam was required.

The effectiveness of a chelating agent to inhibit metallic ion catalyzed oxidation depends on the ability of the chelating agent to complex the metallic ion as well as on the coordination number of the metallic ion. Copper[6,17,18], iron[19], cobalt[20-22] and manganese[23] ions all form stable complexes with cyclam. It appears that the difference in the effectiveness of cyclam to inhibit the oxidation catalyzed by these four ions is more likely to be due to the coordination number of the ions. In the study of metallic ion catalyzed oxidation of petroleum, Pederson[24] showed that while all the tetradentate chelating agents were effective against copper, they were not uniformly effective against other ions having coordination number greater than four. In some instances, the chelating agents even promoted oxidation. Copper has a co-ordination number of four and usually forms square planar complexes. Cyclam, being a tetradentate ligand, can block all four coordinating sites of the copper ion, making it unable to catalyze oxidation. The usual coordination number of iron, cobalt and manganese is six. When cyclam forms complexes with these ions, there are still two coordinating sites available. As a result, cyclam is not that effective in deactivating these three ions as compared with the copper ion. Nonetheless, the present work indicates the possibility that other suitable macrocyclic ligands could be excellent antioxidants and metallic ion deactivators for rubbers and plastics.

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