

Accelerated Aging of Natural Rubber

INTRODUCTION

Natural Rubber (NR) aging in air affects not only its physical properties but also its dynamical-mechanical properties. Due to the high level of unsaturation of NR, it can be easily attacked by oxygen. It was found that the oxidation of NR is further accelerated by heat, light, impurities, and mechanical strains.

Björk and Stenberg¹ studied the aging of NR vulcanized with TMTD and S/CBS. Their samples were heated for more than 2000 h in air oven at 100°C. They found that an oxidized layer was formed on the surface of their samples which was hard and brittle and attributed these properties to thermooxidative crosslinking. They found also that the samples can be cracked easier after aging.

Colclough, Cuneen, and Higgins² suggested that NR oxidation occurs either through main chain or crosslink scission. This claim has been questioned by several scientists^{3,4} and recently was confirmed by many others.^{2,5}

For this article we used photoacoustic spectroscopy (PAS) for the study of accelerated aging of NR. The samples were studied as they were delivered by the supplier. No sample cleaning was performed. This makes our study more realistic and similar to the actual aging of NR than the studies carried out by other scientists for obvious reasons. No other technique we know of can carry out such study using NR delivered by the supplier without transforming the samples into thin films, pellets, etc., which could perturb NR physical and mechanical properties.

EXPERIMENTAL

Natural Rubber samples were obtained from Firestone Co. (U.S.). The samples were used as they were delivered by the supplier. No sample cleaning was performed. The samples were heated in air in a temperature-controlled oven for different periods. The accelerated weathering was accomplished by subjecting the samples every day to 12 h of UV light at 60°C followed by 12 h condensation at 35°C. The accelerated weathering was performed at Kuwait Institute for Scientific Research.

The photoacoustic spectrometer used in this experiment was discussed in detail in earlier publications.⁶⁻⁹ The PAS spectrum of a fresh (nonirradiated) sample was first recorded as a blank (*B*) and stored on floppy disk. (*B*) was then subtracted from the spectrum of each irradiated sample (*S*) to yield the net changes (*S-B*) that might take place as a result of any degradation. The microprocessor was then automatically normalized (*S-B*) against the carbon black reference spectrum (*R*) to give (*S-B*)/*R* signal. The same reference carbon black (*R*) and the same blank sample (*B*) were used for all irradiated samples of the same kind. This is to ensure that all spectra are taken under the same conditions and that any possibility of spectrum variation, from one sample after certain irradiation time to the same kind of sample after a different irradiation time, is eliminated. This was accomplished by first storing (*R*) and (*B*) for a certain kind of sample. Then every time we turned the spectrometer on, we checked to be sure that the spectrometer is working well by using carbon black as both blank and sample. In this way, if we record *S/R*, a straight line should be obtained with a PAS signal equal to unity. Once this is accomplished, we call from the memory of the computer the old (*R*) and (*B*) and use them with our sample.

RESULTS AND DISCUSSION

Figure 1 shows the net degradation changes in PAS spectra for NR heated at 150°C for different periods together with PAS spectrum of unheated sample (*B*). The PAS of the unheated NR sample shows two main absorption bands at approximately 220 and 280 nm. The 280 nm

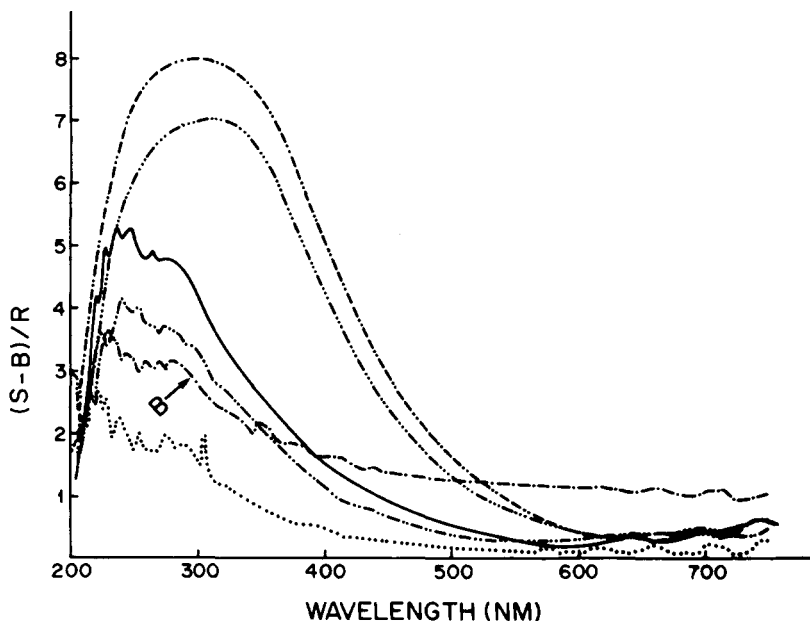
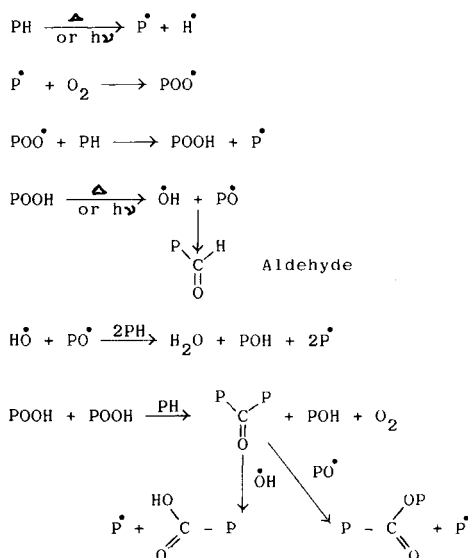
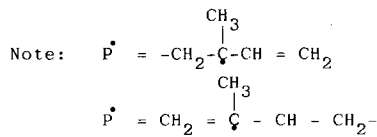


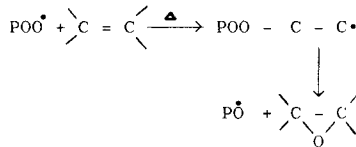
Fig. 1. PAS spectra of NR heated at 150°C for the periods (min): (....) 5; (-----) 15; (—) 30; (— · — · —) 45; (— · — · — · —) 60. Curve B, (— · — · —), is the PAS spectrum of the blank sample.

band was extended with a long tail that reaches 700 nm. These bands are attributed to π - π^* transition characteristic of all unconjugated unsaturated compounds such as NR. From Figure 1 it was noticed that on exposing NR to heat at different periods, the 220 nm band decreases with a simultaneous build up of new bands at ~ 250 and ~ 290 nm. These new bands drastically increase for exposure periods of 45 and 50 min, where all the peaks appear to be amalgamated in a single band peaking at ~ 300 nm with extended tail to around 600 nm. The two bands at 250 and 290 nm are assigned to the formation of conjugated ketone and aldehyde resulting from the decomposition of hydroperoxide which was produced from the reaction of the secondary and tertiary allylic radicals according to Scheme¹⁰ 1:





Furthermore it was suggested by Gemmar and Golb¹¹ that epoxides are formed during thermal degradation of NR. They suggested attack on the double bond by peroxy radical according to Scheme 2:



Epoxides absorb¹² between 300 and 320 nm, which is located adjacent to the above-mentioned bands. As a result a broad structureless PAS band observed at higher exposure time in thermal degradation of NR.

In the case of accelerated weathering study of NR, however, carbonyl is more likely to be produced at the middle of the chain due the UV irradiation.¹³ Such carbonyls react with hydroxy radicals forming carboxylic acid or with alkoxy radicals forming esters (Scheme 1). These species gave rise to PAS absorption bands at ~330 and ~380 nm as evidence from Figure 2. The nature of the free radicals leading to the formation of these two species is questionable, although there are enough experimental data indicating the formation of carboxylic acid and esters as a result of photodegradation.¹⁴

As was mentioned before the undergraded NR shows two strong absorption bands at a wavelength < 300 nm. However, NR PAS shows also an extended long tail beyond 300 nm, which could be due to the probable existence of either impurities or structure defects. These impurities are mainly responsible for the initiation of photodegradation of NR.

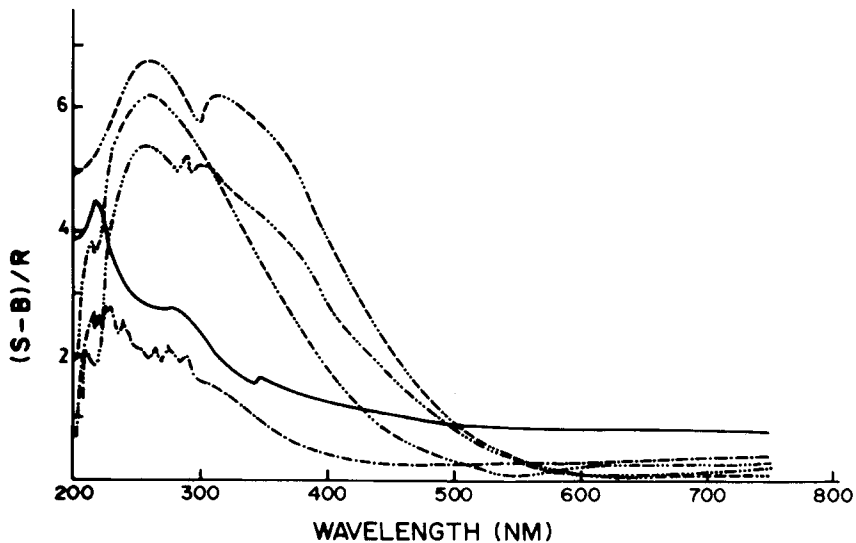


Fig. 2. PAS spectra of NR exposed to accelerated weathering for the periods (days): (—) 10; (---) 20; (-·-·-) 37; (·····) 92. The solid line curve is the PAS spectrum of the blank sample.

CONCLUSION

Thermal aging of NR shows two distinct PAS absorption bands at 250 and 290 nm. These two bands amalgamated, giving rise to a broad band peaking at ~ 300 nm. These bands are due to the formation of ketone and aldehyde. However, accelerated weathering of NR shows PAS absorption bands between 330 and 380 nm due to the formation of carboxylic acid and esters.

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