

ENHANCEMENT OF RESISTANCE TO OXIDATIVE DEGRADATION OF NATURAL RUBBER THROUGH LATEX DEGRADATION

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Abstract A fully characterised natural rubber latex was subjected to mechanical degradation by stirring at intervals. The resistance to oxidative degradation of the different samples were studied by measuring the Plasticity retention indices (PRI).

The results show that there is an enhancement of the PRI from 57% for the undegraded rubber to 79% for the one-hour degraded sample. Further degradation resulted in decrease of PRI as time of degradation increased. Therefore, the one-hour degraded sample is a special rubber with high oxidation resistance which is of great importance in engineering.

Keywords Plasticity; Rubber; Degradation; Oxidation; Resistance

INTRODUCTION

Plasticity retention index (PRI) tests are designed to provide a rapid assessment of the susceptibility of raw natural rubber to thermal oxidative degradation^[1~3]. High PRI values are generally associated with rubbers that possess good resistance to thermal oxidative breakdown^[3,4]. The PRI values are also useful because they can be correlated with certain performance aspects of the rubbers during mastication and compounding as well as ageing performance for the derived vulcanisates.

Oxidative breakdown of natural rubber takes place as a result of the reaction between the unsaturation and oxygen in the presence of heat, as well as hydrogen abstraction which ultimately leads to chain scission. Plasticity retention tests are normally carried out on a raw rubber before it is subjected to mastication and compounding. As a result, these tests do not represent the rubber performance during service having been subjected to degradative forces. Hence it has become necessary

to produce rubbers with high resistance to oxidative breakdown during degradation. In this work natural rubber samples with varying degrees of degradation and resistances to oxidative breakdown have been produced and their PRI's investigated.

EXPERIMENTAL

Materials and equipment

Fresh field natural rubber latex obtained from the Imo Rubber Estates, Ltd., Obitti, Ohaji, Nigeria. Isooctylphenoxyethanol (Triton X-100), a non-ionic surfactant (BDH).

Brookfield viscosimeter; Ubbelohde viscosimeter. Instron Universal Testing Machine, Model 1122; Two-roll Mill (UNIEK Ban Tech., Singapore); Wallace Plastimeter, punch, steam generator, and thickness gauge (Wallace, England).

Procedure

All chemicals were analytical grades and used as received. The fresh latex was collected in a stoppered bottle and stabilised by adding 25 cm³ concentrated ammonia solution to 2.5 dm³ of the latex (1.0% v/v). The latex characteristics are determined^[5] as shown in Table 1^(b).

Table 1 Characteristics of the natural rubber latex

Dry rubber content (DRC) (%)	41.30
Plasticity retension index (PRI) (%)	56.82
Ash content (%)	0.21
Nitrogen content (%)	0.60
Volatile matter (%)	0.62
Dirt content (%)	0.02
Viscosity average molecular weight ($\overline{M}_v$)	1.31×10^6

Degradation

The method of degradation involved the following steps

Construction of the mechanical stirrer A shaft 45 cm long and 2.5 cm in diameter carrying three baffles (3.0 cm × 6.0 cm each) was welded to the shaft of an electric motor (50 Hz; 4.0 KW; 380 V; 8.9 A) having a constant speed of 1440 rpm. A hole was created through the lid of a stainless bucket (which served as the reactor) through which the stirrer shaft was passed. The stirrer was mounted on a tripod stand.

Preparation of the latex Fresh natural rubber latex was diluted to approximately 15.0% by adding 3.5 dm³ of distilled water to 2.0 kg of the latex. Then 60.0 g of Triton X-100 surfactant (3.0% w/w on the latex) was added and the mixture was

gently stirred for 1 h with a stirring rod to attain maximum stabilisation before the degradation stage.

Mechanical degradation The prepared latex was stirred with the mechanical stirrer at ordinary temperatures and pressure. Samples were collected at intervals and filtered under pressure to exclude gelled lumps of rubber. The viscosity of the filtrate was measured with a Brookfield Viscometer. The latex was later coagulated with methanol. The coagulum was rolled into sheets of about 3.00 mm, washed extensively in running water, and dried in an oven at 50°C for 48 h to a constant weight.

Plasticity retention index (PRI) The plasticity retention indices were determined according to standard methods^[1] using the following procedure.

Calibration The plastimeter was first calibrated with a Standard CV Rubber to ensure that the loading spring and timing unit were in order.

Homogenization of the rubber The rubber samples were homogenized by passing each six times through the gap between the rolls of a 150 mm × 300 mm laboratory mill. The rolls were cooled with running water at room temperature while the gap was set at 1.65 mm.

Preparation of the test pieces About 20.0 g of the homogenized rubber was passed twice through the rolls of the cool mill while doubling the sheet between passes. The nip of the rolls was adjusted in such a way that the final sheet thickness was 1.6 to 1.8 mm. It was doubled immediately and the two halves were lightly pressed together by hand. Six test pieces (pellets) were cut from the doubled sheet with the Wallace Punch. The test pieces were divided into two sets of three, one set each for plasticity determination before and after ageing in the oven.

Ageing of the test pieces One set of the test pieces was inserted into the oven that had been set and stabilized for ten minutes at 140°C. After thirty minutes they were removed and allowed to cool to room temperature.

Plasticity tests The rapid plasticity of the test pieces were determined by sandwiching each test piece between two pieces of cigarette paper and compressing between two parallel platens of the plastimeter to a fixed thickness of 1.00 mm. It was held in this position for fifteen seconds to reach approximate equilibrium with the platen temperature (the platen was heated to a constant temperature by passing steam through it). Then it was subjected to a constant compressive force of 10.0 kgf for thirty seconds. Its thickness (mm) at the end of this period was taken as the measure of rapid plasticity. The plasticity retention index in percent, was calculated as follows:

$$\text{PRI}(\%) = \frac{\text{Mean of aged plasticity}}{\text{Mean of unaged plasticity}} \times 100\%$$

RESULTS AND DISCUSSION

Fig. 1 shows the variation of PRI with time of degradation.

The PRI of the undegraded natural rubber is low (57%). The PRI increased after thirty minutes to 70%. A further increase up to 79% occurred after the first 1 h of degradation, thereafter there were reductions in PRI as time of degradation increased.

Plasticity retention index measure the resistance fo rubber to oxidative degradation when heated. A high value denotes high resistance to oxidative breakdown. Raw undergraded natural rubber consists of rubber molecules of varying chain lengths including other non-rubber molecules, e.g. proteins which act as stabilisers. Some of these molecules are heat labile and on heating exhibit very easy oxidative breakdown. As a result of this, raw undegraded natural rubber shows a low PRI. During the mechanical degradation the non-rubber molecules were first degraded since proteins are easily denatured by agitation. Subsequently, the rubber molecules are broken down and this results in the generation of rubber macro-radicals, which in the absence of radical acceptors initiate various competing processes in the presence of oxygen^[7,8], viz:

(a) The macro-radicals react with oxygen to form hydrocarbon peroxy radicals and subsequently hydroperoxides.

(b) Recombination of the rubber macro-radicals in random manners to form rubber molecules of varying sizes with some degrees of branching.

(c) Reaction between the rubber molecules and oxygen either by hydrogen abstraction or addition to the double bonds to form rubber peroxy chains. Here the chain lengths remain unchanged.

Before the onset of mechano-degradation, reaction (c) exists and is accelerated on heating or on stirring. As a result, the oxygen uptake of raw natural rubber is high especially when heated, thus leading to easy oxidative breakdown. Thus the PRI of undegraded natural rubber is low. Once mechano-degradation sets in, the reactive sites created by molecular fracture encourages recombination of the rubber radicals to an extent that the recombination is much faster than the reaction between oxygen and the rubber molecules. By this, there are more hydrocarbon chains than there are hydrocarbon peroxy chains. The recombination process enhances the resistance

to oxidative breakdown, hence the high PRI value observed within the first 1 hr of degradation.

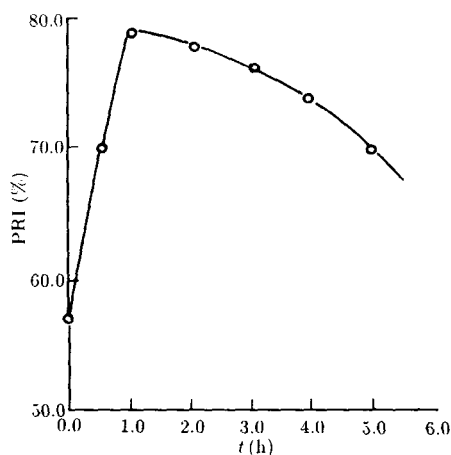


Fig. 1 Graph showing variation of PRI with Time of degradation

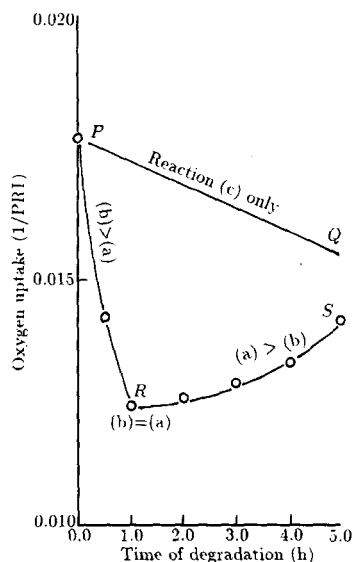


Fig. 2 Variation of oxygen uptake (as inverse PRI) with Time of degradation

Continued degradation increases breakdown of the rubber molecules thus reducing the size of chains and this increases the number of molecules. This increase in the number of molecules also increases oxygen uptake and leads to increase in oxidative breakdown. This in effect means a lowering of PRI as observed after the first 1 h of degradation. The breakdown into smaller molecules continues with degradation and reaches maximum at the 5 h. The more the number of molecules the greater the amount of oxygen that takes part in the reaction; hence the lower the PRI. In any case, the PRI of undegraded rubber is always lower than that of any of the degraded rubber samples because in the undegraded rubber there are no competing reactions for oxygen. This is in agreement with the finding that the diffusion constant for oxygen in undegraded natural rubber is very high when compared with other common polymers^[9].

The above envisaged processes which account for the changes in PRI in degraded natural rubber are illustrated in Fig. 2 in which oxygen uptake is plotted against the time of degradation of the rubber; from this the following can be derived:

P - Q: The only reaction taking place is between the rubber molecules and oxygen to give peroxy radicals. No degradation takes place, so no smaller molecules are produced within the time of observation. However, at very long periods of observation these peroxy radicals can break up to form aldehydes and ketones.

P - R: The mechanical shearing process breaks up the molecules to give rubber

macro-radicals. Here two processes compete, i.e. the reaction between two rubber free radicals to form natural rubber molecules, and the reaction of the rubber free radicals with oxygen to form rubber peroxy radicals or hydroperoxides. Within this section, the reactions between any two rubber radicals outweigh those between the rubber radicals and oxygen. Thus within the system there are more neutral rubber molecules of varying chain lengths than there are peroxy chains. This accounts for the increase in PRI at this period of degradation.

R: At *R*, the maximum rubber radical-radical reaction takes place. The competing reaction between oxygen and rubber radicals reaches its minimum, thus representing the maximum PRI at this point.

R-S: Within this period, both the rubber molecules and rubber hydroperoxides are broken down into smaller radicals. Within the system, the number of smaller neutral molecules increases as time of degradation increases. Each smaller unit then takes up oxygen in the process. Thus the reaction with oxygen outweighs the recombination of rubber radicals. This leads to reduced PRI as time of degradation increases.

The oxygen uptake of raw undegraded natural rubber is always higher than that of the degraded rubber samples at any given time; thus $Q > S$. Therefore the PRI of undegraded natural rubber is the lowest among the various grades of rubber.

In conclusion therefore, mechanical degradation of natural rubber by stirring the latex for 1 h produces a very high quality rubber with high plasticity and oxidation resistance. This sample can be regarded as a special rubber grade that may be adapted for engineering use.

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