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Kinetics of Peroxide Vulcanization of Natural Rubber

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Introduction

The crosslinking of elastomers with peroxide has been known for more than 90 years[1]. Peroxide curing was introduced to overcome the deficiencies of well known sulphur vulcanization[2.] The peroxide crosslinked vulcanizates have very good heat resistance and hence the technique is important in automotive applications. Selection of a curing system for a particular application requires better understanding of crosslinking mechanism and also about factors controlling rate of reaction (kinetics).

Hummel[3] studied the decomposition of dicumyl peroxide in natural rubber. The compression set (high temperature) and the vulcanization time of natural rubber - peroxide cure system were investigated by Bristow [4, 5.] Ogunniyi[6] studied the generalised mechanism of crosslinking reaction and the elastomers where only peroxide system is suitable. Dluzneski[7] reviewed the competing chemical reactions involved, polymer selection, cure temperature and the effect of other compounding additives in the peroxide vulcanizates. Though peroxide vulcanization of natural rubber has been widely explored, details of parameters like optimum peroxide required, effect of other ingredients, vulcanization time etc. till remain unanswered. Due to the marching cure behaviour of peroxide, the reported cure time for a particular system is often inconsistent. The physical properties of peroxide cured natural rubber were investigated, but the influence of residual peroxide on mechanical properties is not yet reported. Hence this study was proposed to optimize the vulcanization conditions and also to explore the effect of residual peroxide in the peroxide vulcanization of natural rubber. The study was followed through the kinetics of peroxide vulcanization at different temperatures. Assessment of mechanical properties was also performed to evaluate the cure level in the vulcanizates.

Experimental

Materials

NR used for the study was ISNR 5 grade obtained form the Pilot Crumb Rubber Factory, Rubber Board, Kottayam, Kerala, India. DCP (40%) was supplied by Arkema Peroxides India Private limited, Cuddalore, A.P, India.

Preparation of compounds

The compounds were prepared in a two-roll mixing mill (ASTM D 3182-07) as per the formulation given in Table 1.

Table 1 : Formulation of mixes

Ingredients	A	B	C	D	E	F
NR, phr	100	100	100	100	100	100
DCP, phr	2.35	3.4	5.0	6.0	7.0	8.5

Cure characteristics were measured using a Monsanto Rheometer and the cure kinetic data was recorded in the temperature range 150 to 165^{0}C. The compounds were moulded based on their respective t_{90}, t_{95} and t_{100} values as obtained from the Rheometer.

Physical Testing

Tensile tests were carried out as per ASTM D 412 using dumb bell- shaped samples at a crosshead speed of 50 cm/min with a universal testing machine (UTM) Zwick model 1474 .Compression set was determined at 70 and 100^{0}C (ASTM D-395).

Swelling studies

Cured test piece were swollen in toluene for equilibrium swelling. The crosslink density was measured using Flory- Rehner equation.

Results and Discussion`

1. Cure characteristics

The rheographs (Figure1) showed that as the temperature increases, the rate of cure increases which leads to high torque. All the curves converge to a point which gives a constant value of t_{100} except at 165^{0}C. At 165^{0}C, rate of decomposition of peroxides is high and all the peroxide is consumed in a limited time. The t_{90} and t_{95} was found to decrease with increase in cure temperature. There exists an empirical relation between cure temperatures and maximum time of cure. For every 5^{0}C increase in cure temperature, optimum cure time t_{90} decreases by 8 unit and the t_{95} decreases by 10^{0}C. The scorch time ts_2 is remain more or less constant except at 150^{0}C.

2. Vulcanization kinetics

The general equation for the kinetics of a first order chemical reaction is

$$\ln(a-x) = -kt + \ln A$$

(a = initial peroxide concentration, x = reacted quantity at time't', k = first order reaction rate constant, A = Arrhenius frequency factor). A first order reaction is identified by linearity in the plot of log (a-x) against time. The advantage of first order kinetics is that the value of rate constant can be derived from a relative measure of the concentration of reactant with time. The absolute concentration of reactant is not required.

3. Temperature dependence of rate constant

The temperature dependence of rate constant is described by Arrhenius equation. The rate of a reaction increases with increase in temperature. The larger the activation energy the greater is the sensitivity of the reaction to changes in temperature. For every 10 K rise in temperature the rate constant doubles. The half-life decreases with increase in temperature. In the first half-life, 50 per cent of the peroxide decomposes and the process continues and theoretically never reaches 100 per cent decomposition/consumption. Essentially for maximum decomposition of peroxide during vulcanization, requires the cure time to be at least five half-lives at the cure temperature, giving 97 per cent decomposition, or preferably 10 half-lives, which accounts for 99.9 per cent decomposition.

4. Residual peroxide

At optimum cure time t_{90}, peroxide decomposition accommodated three half-lives and the percentage of residual peroxide is approximately 12 per cent. At t_{95}, vulcanizates contain approximately 6 per cent residual peroxide since it includes more than four half-lives. At 150^0C, the half-life is 12.2 minutes. It accommodates 4.9 half-lives at t_{100} and about 97 per cent of the peroxide is expected to be reacted at this temperature. At 155^0C, the half-life is 9.33 minutes it completed 6.04 half-lives and here 98.5 per cent peroxide consumed. At 160^0C, 99.6 per cent decomposition occurs as the cure time is equal to 8.34 half-lives. At 165^0C, the completed half-lives and peroxide consumption are 10 and 99.9 per cent respectively. Hence the cure temperature (t_{90}, t_{95} or t_{100}) is to be calculated from a fully decomposed peroxide cure curve. For this the peroxide vulcanization reaction (rheographs) is to be run for a minimum of 60 minutes.

6. Concentration of peroxide on cure time

Since the cure time and residual peroxide influences the mechanical properties, the studies have extended to vulcanizates with different loading of DCP. As the concentration of peroxide increases the torque increases regularly. This is due to the fact that more radicals are formed and crosslinking efficiency will be higher.

7. Mechanical properties

The mechanical properties are measured at different cure times t_{90}, t_{95} and t_{100}. At higher peroxide level there is an increase in the amount of residual peroxide and a decrease in almost all mechanical properties. Irrespective of the concentration of peroxide the maximum value of tensile strength is observed at t_{90} and as the cure time increases tensile strength decreases and is minimum at t_{100} (Figure1). This is because crosslink density is maximum at t_{100} and as the number of crosslinks increases the shorter C - C crosslinks restrict the orientation of the macromolecular chains of NR when stretched. Moreover, the formed bonds cause increased stiffness and as a result chains are less mobile and consequently lower the mechanical properties.

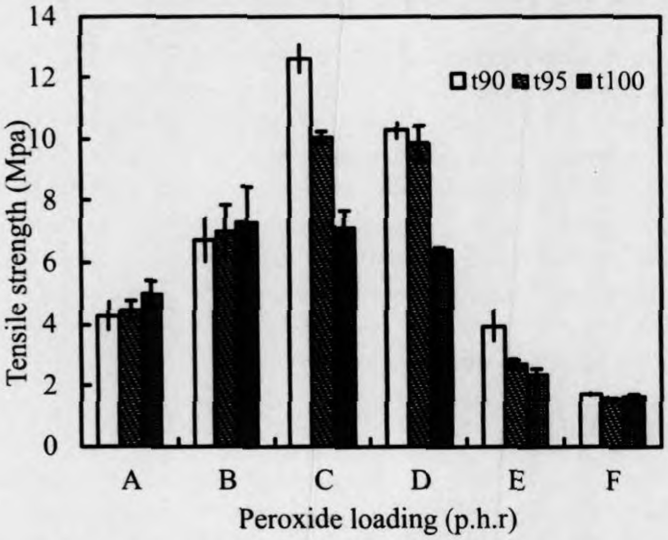

Figure 1 : Variation of tensile strength with peroxide loading at 160°C.

The elongation decreases with increasing concentration of peroxide. Higher the level of peroxide greater will be the crosslink density and hence lower elongation at break. At t_{90} modulus increases with increase in concentration of peroxide and do not show much increase at higher cure time (t_{95} and t_{100}). Modulus depends upon the extent of crosslinking also.

8. Compression set

It is found that at 70^0C larger set values are observed with smaller peroxide concentrations at t_{90}. This is because an under- cured specimen shows excessive set due to the formation of extra crosslinks in the compressed state, which prevent recovery. The minimum set value is for sample C containing 5 phr DCP. Again the set value increases due to the presence of excess residual peroxide. At t_{95} and at t_{100} compression set values follow the same trend as that of t_{90}. At elevated temperature (100^0C), set values are higher than that at 70^0C. The maximum set is observed at t_{90} and the value decrease at t_{95} and the minimum value is observed with t_{100}.

9. Crosslink density

The increase in torque during rubber curing is a measure of the amount of crosslinks formed. The maximum torque increases with temperature and also with the concentration of peroxide. An explanation of this phenomenon could be that, as the concentration of peroxide increases more radicals are generated and the radicals react with NR by abstraction or by addition. At high temperature and high DCP loading, abstraction and addition take place. The addition reaction requires a favorable orientation of the double bond in order to be attacked by the radical and this reaction is predominated at the temperature.

Summary

The kinetics and cure characteristics of peroxide vulcanization of natural rubber with dicumyl peroxide have been studied. The ideal temperature for the peroxide vulcanization of NR is 160°C and the optimum level is 5 phr (40 % DCP). Residual peroxide has no significant effect on tensile strength, elongation at break, modulus and low temperature compression set. However, high temperature set increases with residual peroxide in the vulcanizate. The crosslinking efficiency of peroxide depends on the number of completed half-lives which in turn depends upon the initial concentration of peroxide. The peroxide concentration is the dominant factor which controls the final crosslink density and properties of the vulcanizates.

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