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A new method to control scorch time in peroxide vulcanisation

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Introduction

R*ubbers and plastics belong to a class of* materials known as polymers characterized by their long chain molecules and very high molecular weight of the order of hundred thousand to more than a million. Rubber is flexible while plastics are hard at room temperature. The long chain molecules of plastics remain "frozen" at room temperature ensuring dimensional stability which makes them hard at room temperature. However, the molecules of rubber or to be precise the segments of the long rubber molecules could move with respect to other segments at room temperature making it flexible. In fact rubber *could be considered as "highly viscous liquid"* and could flow under stress or gravity. This is why raw rubbers as such could not find many applications. This was the case until Charles Goodyear accidentally discovered the process called vulcanization in 1839. In vulcanization, the sulphur molecules mixed and heated with rubber could arrest the flow of highly viscous rubber by linking the flexible rubber molecules, thereby transforming the viscous rubber into an elastic material.

Vulcanisation of rubbers

In a sulphur vulcanized rubber, the long chain rubber molecules are inter linked or cross- linked by sulphur atoms through C-Sx-C (carbon-sulphur-carbon) bonds where x can be 1, 2, 3 *or more. However, the* reaction between rubber and sulphur are extremely slow even at very high temperatures. It took almost a century after the discovery of vulcanization to develop and fine- tune new organic accelerators and activator systems currently used in sulphur vulcanization of various rubbers to produce innumerable number of rubber products which have become indispensable for modern life.

1920s and 30s have also seen lot of activities *for alternative chemicals for vulcanization of* rubber other than sulphur. These efforts have led to the development of peroxide vulcanization in

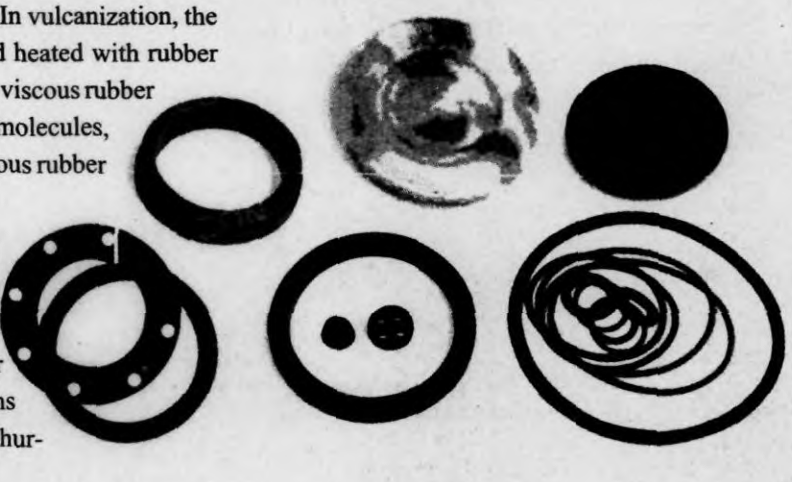

Fig1. Rubber gaskets and seals

which the rubber molecules are cross-linked by carbon- carbon (C – C) bonds initiated by the thermal decomposition of organic peroxides. Industrial use of peroxide vulcanization started during 1950s with the development of Dicumyl peroxide (DCP). Presently a large number of rubber products, especially EPDM rubber based products are manufactured by peroxide vulcanization using DCP/ co-agent combination. Both sulphur and peroxide vulcanization have advantages and disadvantages. Sulphur vulcanization imparts high strength properties and excellent dynamic properties to the vulcanisate while it imparts inferior ageing resistance and set properties. Peroxide vulcanization, though leads to poor dynamic properties, can impart excellent resistance to ageing and leads to low compression set. It also allows the co-vulcanization of saturated and unsaturated rubber blends.

Issues in peroxide vulcanisation

For a product manufacturer, the final properties of the product alone cannot be important, but the ease with which the vulcanization process could be carried out is also extremely important. For manufacturing various rubber products, moulds with complicated designs are used and it is absolutely important that the vulcanization process could be arrested for a few minutes initially in order to allow the rubber compound to flow and fill into all parts of the mould. This induction time, indicating the process safety, which is known as the "scorch time" is extremely important for the manufacture of thick, large and complicated rubber articles. If the scorch time is very low, the compound will start to vulcanize before it could flow and fill the entire mould resulting in products with dimensional irregularity and will have to be rejected. The chemistry of sulphur vulcanization is so well developed that scorch time could be controlled to any required level depending on the type of products to be moulded. This is not the case with peroxide vulcanization and therefore its use is restricted to the manufacture of comparatively thinner products like rubber gaskets and rubber seals (Fig1). If scorch control or process safety can be significantly improved the range of industrial application of peroxide vulcanization can be broadened.

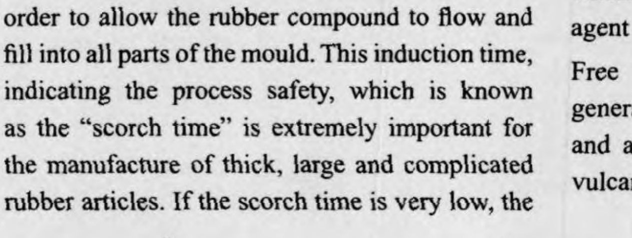

Fig.2. Typical cure curves for sulphur (a) and peroxide (b) vulcanization of rubbers

New finding

Fig.2a and Fig.2b show typical cure curves for sulphur and peroxide vulcanization. The breadth of the trough area in Fig. 2a shows the scorch time which is well developed in sulphur vulcanization while it is very small in peroxide vulcanization (Fig.2b). Achieving sulphur cure like scorch or process safety control in peroxide vulcanization has been an outstanding problem for more than half a century in rubber industry since the industrial use of DCP as vulcanizing agent. Recently, in our lab it has been shown that sulphur cure like scorch control could be achieved with peroxide vulcanization using DCP/stable free radical/co-agent combination.

Free radicals are highly unstable moieties, generally formed in situ during chemical reactions and are highly active species. During peroxide vulcanization, DCP dissociates at high moulding temperatures like 160 -1900C, generating oxygen centered free radicals which immediately abstract hydrogen atoms from the rubber molecules forming carbon centered rubber free radicals. Two such rubber free radicals combine immediately after its generation leading to C-C cross–link formation. Since these reactions are extremely fast, the scorch time in peroxide vulcanization is very low which

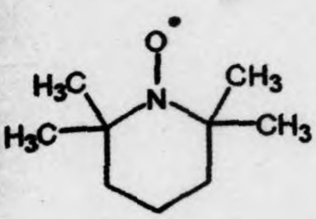

Fig.3. TEMPO (2, 2, 6, 6 - tetramethylpiperidine-1-oxyl) stable free radical

is manifested as the very low breadth of the trough region in Fig.2b.

Stable free radicals are a class of chemical which can remain as free radical at room temperature and also at high temperatures. One of the very important examples is TEMPO (2,2,6,6,- tetramethylpiperidine-1-oxyl) (Fig.3). It is an oxygen centered stable free radical which reacts very quickly with carbon centered free radicals while remaining inert to oxygen free radicals. When TEMPO is added to rubber compound containing DCP, the carbon centered rubber free radicals formed during vulcanization will react with TEMPO thereby eliminating the chance of formation of C-C cross-link until all the added TEMPO is consumed. This can extend the scorch time in peroxide vulcanization as shown in curve2 of Fig.4 (curve 1 for peroxide vulcanization with DCP (2.4 parts per hundred rubber {phr}) alone and curve 2 with DCP and 1.2 phr TEMPO). The scorch time increased from 1.5 minutes in DCP alone system at 1700C to to 3.7 minutes when 1.2 phr TEMPO was added.

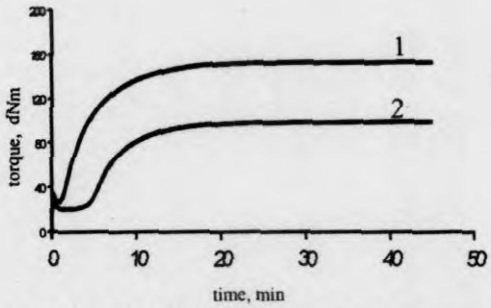

Fig.4. Effect of TEMPO concentration on scorch time (170^{0}C)

(Curve 1 -2.4 phr DCP, Curve 2- 2.4 DCP and 1.2 TEMPO)

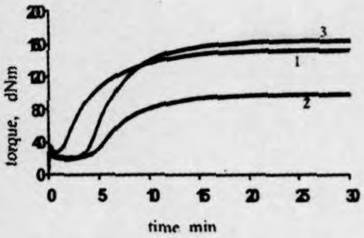

Fig.5. Effect of TEMPO/coagent combination on scorch time

(Curve 1 -2.4 phr DCP, Curve 2- 2.4DCP +1.2 phr TEMPO, Curve 3- 2.4 DCP+ 1.2 TEMPO + 4phr SR25)

However, the height of the plateau regions of the cure curve containing TEMPO (Curve 2 in Fig.4) is reduced (reduction in MH value) indicating loss of cross – link density which can lead to inferior vulcanisate properties. The reduced height of the plateau region in TEMPO containing compounds (curves 2 in Fig 5) compared with that of DCP alone compound (curve 1 in Fig.5) could be regained or even surpassed by adding suitable co-agents. Curve 3 in Fig 5 shows that addition of 4 phr co-agent SR25 (N, N'- m- phenylene dimaleimide) could regain the lost cross-links without affecting the scorch time.

Concluding remarks on industrial potential

It has been shown that the capability of stable free radical (TEMPO) to selectively react with carbon centered rubber free radicals generated during peroxide vulcanization can be utilized to induce scorch control in peroxide vulcanization. The loss of cross –link density due to the reaction of TEMPO and rubber free radical could be compensated using a suitable co-agent. Thus scorch time or process safety in peroxide vulcanization could be controlled in a way similar to the sulphur/accelerator cure.

This breakthrough technology developed at the Advanced Centre for Rubber Technology in RRII of Rubber Board could provide an excellent opportunity for the rubber products manufacturers to utilize the finding to broaden the range of production of rubber articles prepared using peroxide vulcanization which could not have been possible earlier due to low process safety. It may be noted that some of the TEMPO derivatives are available from Chinese suppliers at a price range of Rs.300-500/- per kilogram when purchased in bulk. ■