Role of Phenolic and substituted Phenolic Resins on Vulcanization of Butyl Rubber

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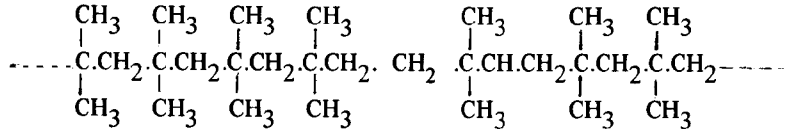
(Received 3rd June, 1981)

In the early 1930s, chemists at I.G. Farben Laboratory, W. Germany stumbled upon a laboratory curiosity. They would amuse the visitors by coverting isobutylene, to a liquid at dry ice temperature, and then add a few drops of boron-trifluoride, a powerful catalyst for polymerization. As soon as the drops hit the surface of the liquid, there would be a noiseless explosion and a white, rubbery snow ball would form and buldge spectacularly over the edge of the glass. However the German scientists could find no way of vulcanizing the substance. Some years later, American chemists learnt that the addition of butadiene, a plentiful and inexpensive gas, would remedy the shortcoming. The resulting butyl-rubber is strong, elastic and so impermeable to air that it serves specially well for inner tubes, tubeless tyres and similar products.

In 1943, German production of this man-made rubber reached well over 100,000 tons annually. When the Japanese cut off the supply of natural rubber in early 1942, Franklin Roosevelt the American president, focussed attention on the rubber problem and siad that if we failed to secure a large new rubber supply our war efforts and our domestic economy will both collapse. The results of all collaborative efforts soon became manifest. In 1942, the first desparate year, production of synthetic rubber was about 20,000 tons but by 1945, it had reached 700,000 tons.

Butyl rubber was made commercially by polymerization of isobutylene with a small amount of isoprene (1.5 to 4.5). A portion of the structure of the polymer may be represented as under.



By introducing the light degree of un-saturation into the chain, an elastomer results which can be vulcanized with sulphur and phenolic resins. The normal range of the molecular weight is 40,000 to 80,000. Butyl rubber is practically colourless tasteless and nontoxic.

Natural rubber was usually vulcanizated by the incorporation of sulphur in the vulcanizate in the early stage of vulcanization techniques, and the disulphide link was considered as the cross-linking bond between the polymer units[1].

Later, with the development of synthetic rubbers, the mode of vulcanization also changed. The action of phenolic resin with rubber was reported in 1935[2]. Most olefinic substances are able, by virtue of their olefinic unsaturation, to combine with phenol and formaldehyde at some stage in the inter-condensation of the latter. The author strongly favoured the view that the dry oil esters are able to combine with simple p-cresol formaldehyde condensation products because of their unsaturation.

The first recorded vulcanization of the phenolic resin as vulcanizing agent was carried out in 1936, by a French chemist Betterich, for the vulcanization of butyl rubber[3]. He produced a better quality vulcanizate by using phenolic resin instead of sulphur. Cunneau *et al* in 1943, noticed that vulcanization with phenolic resins had assumed a considerable importance in curing of butyl rubber[4]. Attempts were also made to combine phenolic resin with rubber and encouraging results were obtained.[5].

In 1948, comparative studies of sulphur vulcanization and phenolic vulcanization were carried out for the first time by Zapp *et al*[6]. It was noticed that when sulphur based vulcanizate softens during exposure to high temperature, the sulphide link between polymer chain breaks down to the thiol group. However, such phenomenon was not observed in case of phenolic resin-based vulcanization of

butyl rubber. So with these observations the superiority of phenolic resin on sulphur was established on scientific grounds. After observing the better performance of phenolic resins (phenol-formaldehyde resins), the research workers tried substituted phenolic resins for the vulcanization of butyl rubber. The comparative study of the substituted groups was carried out to establish the best substituent for vulcanization process[7]. The study of intrinsic viscocity was carried out to evaluate the substituents, and the intrinsic viscosity increased in the order butyl (1.52), chloro (1.40) – bromo (1.46), in a similar fashion as in the vulcanizate.

In 1954[8] Neal reported that butyl rubber can also be vulcanized with phenol formaldehyde resin. Two patents were filed in 1954[8] and 1956[10].

Houwink[11,12] experimented with phenolic resin as a reinforcing agent in rubber and got a better vulcanizate, without knowing the actual function of the resin. The extreme thermal stability imparted to butyl rubber by vulcanizing with phenolic condensation led to the search for catalysts or vulcanization accelerations.

Arnold Giller[13] reported that age resistance of butyl rubber resin vulcanizate is determined by the reaction system depending greatly on the activator. Resin vulcanization is inhibited by basic ingredients, anti-oxidants and accelerators for sulphur vulcanization. Resin vulcanization and sulphur vulcanization are not compatible.

In 1967, Semevova *et al*[14] reported that the inter-action between the resin and rubber occurs either by a methylene mechanism that predominates in the first stages of the treatment or by binding of resin units to the double bond of the rubber.

Halogenated phenolic resins[15] were tried for the vulcanization of butyl rubber and for the comparative study of the effect of different types of halogens on the rate of vulcanization. Bromide substituted resins were found to be better as compared with other halogen derivatives. Due to the better performance of brominated phenolic resins further investigations were concentrated on the different aspects of these resins.

Tawney[16] also used phenolic resin derivatives for the vulcanization of butyl rubber and found that high temperature application, such as tyre curing bags which were formerly corss-linked with sulphur showed no deterioration with phenolic resin as observed in sulphur. He reported the rapid reversion in sulphur vulcanizate with no reversion in phenolic vulcanizate even after 20 days.

Peterson and Batts[17] observed that vulcanization of butyl rubber by phenolic condensation polymers is strongly catalyzed by metallic halides such as iron diydrate. The performance of tin chloride was better as compared with other halides.

Pankratora *et al*[18] investigated the effect of bromine content in the resin on the vulcanizate. The author reported that vulcanization temperatures of butyl rubber also decreased with increasing bromine contents in the resin.

Daroskikh *et al*[19] brominated butyl rubber first and then carried out the vulcanization with phenolic resin. The author culculated that the vulcanization rate of brominated butyl rubber is three times as fast as that of butyl rubber. Later a group of scientists[20], carried out the effect of resin contents in the resin vulcanizate and it was found that vulcanization rate increased with increasing phenolic resin contents.

Joubeet[21] has investigated the effect of substituents on vulcanization. The author has reported that the number of methylol group, and the number and nature of halo groups (Cl, Br) in the resin have little effect on the vulcanization rate and other chemical properties of the vucanizate. A brominated phenolic resin gives the best vulcanizate results with a higher (20%) modulus and shorter (40 vs 80 min.) vulcanization time than the other resins. The brominated phenolic resin and halogen-free phenolic resin proved the best ageing resistance during heat ageing of the rubber compounds.

Zateer *et al*[20] used alkyl phenol formaldehyde resin for the vulcanization of butyl rubber. The vulcanization rate increased and the viscosity of the mixture decreased with the increasing phenolic resin content.

Later on Novikova *et al*[22], investigated the vulcanizing activity of the resins having different Br contents. The activity of the resin increased with the increase of bromine content and vulcanization temperature decreased with increasing bromine content in the resin.

Ali *et al*, used brominated phenol formaldehyde resin to vulcanize butyl rubber, in the presence as

well as in the absence of carbon black. Unfilled vulcanizates were confirmd to Mooney-Rivilin Equation in their stress enlongation behaviour. Cross-linking efficiency of the resin was reduced and gel point was found in the vicinity of concentration 0.5 PHR of resin.

The authors clearly showed that PHR 0.5 of bromine resin is the amount required for vulcanization. On the other hand the amount of vulcanizate has minimum value at 8 parts of resin per PHR. According to the authors net work denisty is due to the higher molecular weight of the resin and lower cross-linking efficiency. Chloroprene rubber was also used as an activator in the resin vulcanization and better results were obtained.

For the investigation of the mechanism of the vulcanization two major factor should be considered.

i. Incorporation of bromine in butyl rubber before or during vulcanization,

ii. The effect of phenolic resin as vulcanizing agent. Experimently it has been investigated that the incorporation of bromine before vulcanization or through the vulcanizing agent gives similar types of products. It clearly indicates that the substitution reaction takes place for the incorporation of bromine in polymer chain. The addition reaction is not probable because it reduces unsaturation in butyl rubber which is very much necessary for the vulcanization. Thus according to the authors the substitution reaction takes place when bromine is reacted with butyl rubber, as a similar behaviour is observed in chlorination of vinyl chloride for the formation of chlorinated poly vinyl chloride.

The second factor which required attention is the comparison between sulphur linkage and phenolic linkage in the butyl vulcanizate. It has already been investigated that phenolic resin vulcanizate is far more superior as compared to sulphur linkage. Because sulphide linkage in sulphur vulcanization can convert itself into thiol-linkage at the high temperature. Due to this disadvantage phenolic resin based vulcanization are getting commercial importance.

An investigation is going on to elaborate the effect of salts ($SnCl_2$, $ZnCl_2$) on the vulcanization of butyl rubber with phenolic resin. Infra red techniques is used for the study absorption effect of salts on the rate of vulcanization.

List of phenolic resins derivative used for butyl rubber vulcanization

1. P-terbutyl penolic resin.[14]
2. P-alkyl phenolic resin.[20]
3. Butyl phenolic resin.[21]
4. Chloro phenolic resin.[21]
5. Halomithyl phenolic resin.[21]
6. Methylol phenolic resin.[21]
7. Brominated phenolic resin[22,23]

References

1. Polymers and Resins, *D. Van Nostrand Company Inc., New Jersey;* 404.
2. T. P. Hilditch and C. J. Smith, *J. Soc., Chem. Ind,* **54**, 111 (1935).
3. *Societe Francaise Beckacite,* French Patent 804552, Oct. 27 (1936)
4. J. I. Cunneen, E. H. Farmer and H. P. Koch, *J. Chem. Soc.,* 472 (1943).
5. J. S. Searer, *Rubberage* (N.Y.), **62**, 191 (1947).
6. R. L. Zapp, *Ind. Eng. Chem.* **40**, 1508 (1948).
7. *Encyclopedia of Polymer Science and Technology,* 2, Interscience 782 (1966).
8. A. M. Neal, *Rubberage* (N'Y), **53**, 31 (1953).
9. *United States Rubber Co.* B.P. 714907 (1954).
10. *United States Rubber Co.* B.P. 753868 (1956).
11. R. Houwin and J. Van Alphen, *J. Polymer Science,* **16**, 121 (1955).
12. J. Van Alphen, *Proc. Third Rubb Technol Conf.* London, 670 (1954).
13. Arnold Giller, *Kautshuk Gummi Kunststoffe,* **19**, (4), 188 (1966).
14. L. P. Semenova, N. A. Kaluzen, M. S. Feldshtein. *Zh. Prikl. Spektrosk.* **6** (6), 759 (1967).
15. M. D. Howered, (National friction products corp.) U.S. 3, 354, 243 (cl 264-25) Nov 21 (1967); *Chemical Abs.,* 68, 13905 c, (1967).
16. P. O. Tawney, J. R. Little and P. Viohl, *Ind. Eng. Chem;* **51**, 937 (1959).
17. L. C. Paterson and H. J. Batts, U.S. Patent 2726334, Dec. 6 (1955).
18. V. A. Pankrative, O. A. Zakharkin, and N. D. Zakharov, *Izgotov Leniya Rezin Semesèi,* 132, 138 (1977).
19. G. T. Darovkish, A. V. Agapova, and L. V. Marmalyukova, *E. N. Gromova Khim Khin Tekhmol,* **21**, (7), 1079 (1978).

20; V. S. Zateer, V. A. Shvetsov, V. G. Aschenko, and E. I. Churkina, *Kauch Rezina*, **10**, 23 (1978).
21. Joubeet J. Francoise (Fac. Sci. Aix Marseille) *Rev. Gen. Coantch*, **599**, 73 (1980).
22. L. A. Novikova, I. F. Luchko, Z. A. Khlyupina and F. S. Tolslukhina *Kauch Rezina*, **9**, 13 (1978).
23. S. Ali, S. T. A. Bokhari, K.M. Janjua and E. Ali, *J. Chem. Soc. Pak*, **3**, 93 (1981).
24. S. Ali, S. T. A. Bokhari, K. M. Janjua and E. Ali; (Unpublished work).