CHEMICALS FOR VULCANIZATION

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The most significant discovery in the development of rubber industry has been that of vulcanization, which has transformed the crude methods of product fabrication into a scientifically based high-tech industry. The process converts a viscous entanglement of long chain molecules into a three-dimensional elastic network by chemically linking these molecules at various points along the chain.

Sulphur is the oldest and the most widely used vulcanizing or crosslinking agent and a majority of the present day systems involve the generation of sulphur crosslinks, usually with elemental sulphur. As the reaction between sulphur and rubber is very slow, even at elevated temperatures, it is customary to speed up the reaction with chemicals which are called accelerators and activators.

Chemicals required for vulcanization, which are otherwise known as curatives, include vulcanizing agents, accelerators, activators and retarders

With the development of very efficient accelerators and activators and their combinations with sulphur, it has been possible to carry out vulcanization at rates which are so fast as to necessitate the use of chemicals called retarders to control the reaction and to avoid premature vulcanization or scorch. Thus the chemicals required for vulcanization, which are otherwise known as curatives, include vulcanizing agents, accelerators, activators and retarders. The following brief review covers their range, functions advantages and limitations.

Vulcanizing agents

Ever since Goodyears' time, sulphur has been the most widely used vulcanizing agent. Even the term 'vulcanization', coined by Brockedon, was derived from the association of heat and sulphur with Vulcan of Greek mythology. Though many alternatives

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have been tried with some degree of success, none have competed successfully with sulphur as a general purpose vulcanizing agent. However, one limitation imposed upon its use is that the rubber must contain at least a low level of unsaturation. In saturated rubbers, other chemicals such as organic peroxides have been found quite useful. Vulcanizing agents can, therefore, be considered in two groups: one comprising elemental sulphur and sulphur donors and the other non-sulphur vulcanizing agents.

1. Sulphur and sulphur donors

(i) Sulphur

Sulphur exists in different allotropic forms. The rhombic form is normally used for vulcanization. It is an yellow powder with a specific gravity of 2.07 and melting point 112.8 -119°C. It has a cyclic (ring) structure composed of eight atoms, S_8. The amorphous form of sulphur also is used as vulcanizing agent. It is also an yellow powder, but with a specific gravity of 1.92 and melting point above 110°C. It is a metastable high polymer with a molecular weight of 100,000 to 300,000 and is insoluble in most solvents and rubber and hence the name 'insoluble sulphur'. Taking advantage of its insolubility , amorphous sulphur is used to minimise blooming on uncured rubber mixes where it is necessary to maintain building tack. Insoluble sulphur shall not be processed above 100 -105°C, as it may revert to the rhombic form.

The usual dosage of sulphur is in the range of 1 - 3 parts per hundred rubber (phr). Commercially both forms of sulphur are available in forms that have been treated with small amounts of materials such as magnesium carbonate which produces free-flowing, noncakng powders. Oil-sulphur mixtures or oil reated sulphur are used occasionally to mprove dispersion.

(ii) Sulphur donors

The main purpose of using sulphur donors is to improve the efficiency of sulphur vulcanization. These are used to replace part or all of the elemental sulphur normally used, in order to produce vulcanized products containing fewer sulphur atoms per crosslink. Thus these materials make more efficient use of the available sulphur. The most common sulphur donors are the disulphides: tetramethylthiuram disulphide (TMTD) and dithiodimorpholin (DTDM). The former acts as an accelerator as well as a sulphur donor. Their use results in improved thermal and oxidative ageing resistance. However, they can also be used to minimise the possibility of sulphur bloom and to modify curing and processing characteristics.

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2.Non-Sulphur vulcanizing agents

Though sulphur vulcanizing systems are more popular, there are special cases and speciality rubbers where non-sulphur systems are necessary or desirable.

(i) Peroxides

Peroxides decompose under vulcanizing conditions forming free radicals which attack the polymer molecules leading to the formation of polymer free radicals. Two polymer free radicals mutually combine to form a direct crosslink. Thus in perxoide vulcanization, direct carbon-carbon crosslinks are formed between rubber molecules as against sulphur crosslinks in sulphur vulcanization. Peroxides can be used to crosslink a wide variety of saturated and unsaturated rubbers, while sulphur vulcanization is possible only in the latter.

In general, the carbon-carbon bonds resulting from peroxide cure are more stable than the carbon-sulphur-carbon bonds from sulphur vulcanization. Thus, peroxide vulcanizates often give superior ageing properties. However, peroxides are more expensive and call for greater care in storage and processing. A wide range of organic peroxides are available including products such as benzoyl peroxide and dicumyl peroxide. Choice of a peroxide is based on its activity, stability, intended cure temperature and effect on processability.

(ii) Resins

Certain defunctional compounds form crosslinks by reacting with rubber molecules. Thus quinone dioximes and phenolic resins are used in butyl rubber, epoxy resins in carboxylated rubbers, and dithiols or diamines with fluorocarbons. The most important of these is the use of phenolic resins to cure butyl rubber for bladders used in the curing of new tyres and curing bags used in the retreading industry, taking advantage of the fact that resin-cured butyl vulcanizates have improved thermal stability. The low level of unsaturation in butyl rubber demands activation of resin cure by halogen containing materials such as stannous chloride.

(iii) Metal oxides

Chlorine containing polymers such as polychloroprene and chlorosulphonated polyethylene can be vulcanized with metal oxides. Usually a combination of zinc oxide and magnesium oxide is used for the purpose of controlling the reaction and for absorbing the hydrogen chloride formed. An accelerator such as ethylene thiourea accelerates the vulcanization process when very fast cures are required. It is believed that the principal curing site is the location of the 1,2 addition con[illegible]uration of the monomer unit in the polymer chain. This crosslinking site occurs relatively infrequently in the linear chain. The chlorine in the 1, 2 addition configuration is allylic and hence, labile. One zinc oxide molecule takes away one chlorine atom each from two molecules of the polymer producing an oxygen bridge between them and gets itself converted into zinc chloride, which catalyses the reaction. Formation of zinc chloride may thus cause scorching problems. However, this is minimised by the addition of magnesium oxide which reacts with zinc chloride to form magnesium chloride.

(iv) Urethane system

The principle behind the urethane vulcanization system is one of a minor chemical modification step first to provide pendent groups which are subsequently used for crosslinking by reactions with a suitable di- or polyfunctional reagent. Use is made of the nitrose addition reaction to give aminophenol groups along the NR chain, which could be utilised for crosslinking by the addition of a diisocyonate. However, the latter reaction is so fast that scorching invariably occurs. Use of a diisocyonate generator could minimise this problem to a large extent. This principle was further developed by the Malaysian Rubber Producers' Research Association and based on their work[1] urethane crosslinking agents have been commercialised under the trade name 'NOVOR' (derived from Nitroso Vulcanization of Rubber). Accelerators as used in sulphur vulcanization are not necessary, but the efficiency of the process is improved by the presence of free diisocyonates and by ZMDC. The latter catalysed the reaction between the nitrosophenol and the polymer chain to form pendent groups.

2-Mercaptobenzothiazole (MBT)	Thiazoles	Primary
Dibenzthiazyl disulphide (MBTS)		
N-Cyclohoxyl-2-benzthiazyl-ulphenamide (CBS)	Sulphenamides	
N-Tert-butyl-2-benzthiazil sulphenamide (TBBS)		
2-(Morpholinothio benzothiazole)(MBS)		
N-Dicyclohexyl benzothiazyl sulphenamide (DCBS)		
Diphenyl guanidine (DPG)	Guanidines	Secondary
Diorthotolyl guanidine (DOTG)		
Tetramethyl thiuram monosulphide (TMTM)	Thiurams	
Tetramethyl thiuram disulphide (TMTD)		
Zinc diethyldithiocarbamate (ZDC)	Dithiocarbamates	
Zinc dimethyldithiocarbamate (ZDMC)		

The main advantage of these systems lies in the high thermal stability of the crosslinks which give minimum reversion even on extreme overcure. Problems can occur with their lower scorch time, rate of cure and modulus. However, modulus and fatigue life retention on ageing is very good.

Accelerators

Although the use of organic accelerators to speed up the vulcanization reaction, started only in the early 1990's, the idea of using accelerators had been there even earlier. Even the first patent on vulcanization by Goodyear [2] involved the use of a combination of sulphur and white lead. However, the real breakthrough has been achieved only with the development of organic accelerators.

Accelerator systems are chosen on the basis of their ability to control the following processing/performance properties of rubber compounds.

1. Time delay (Scorch safety) before vulcanization starts.

2. Speed of the reaction once it is initiated.

3. Extent of the reaction in terms of modulus, tensile strength etc.

4. Type of crosslinks formed.

5. Other factors such as adhesion of the compound to fibre or steel, blooming tendency, cost etc.

The proliferation of accelerator types should be viewed as an opportunity, as it gives the compounder a change to fit curing systems to his processing/performance needs.

Classification of accelerators

Accelerators are classified based on their chemical structure and on their mode of action. The major chemical classes are: aldehyde-amine, guanidines, thiazoles, sulphenamides, dithiophosphates, thiurams and dithiocarbamates. Functionally they are classified as primary and secondary. Primary accelerators usually provide considerable scorch safety, medium-to-fast cure rates and good modulus development. Secondary accelerators, on the other hand, produce scorchy, very fast curing stocks. A generally accepted functional classification of the common types of accelerators is given below:

By proper selection of these accelerators and their combinations, it is possible to vulcanize rubbers at almost any desired time and temperature. But it must be remembered that the rate of vulcanization is not the same in all rubbers. Rubbers containing 100 per cent unsaturation (NR, BR) cure faster with a given vulcanization system than those rubbers containing fewer double bonds such as SBR (85 mol % unsaturation) and NBR (50-75 mole % unsaturation). In these rubbers it is usual to use higher accelerator levels and less sulphur.

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Among the various accelerators, by far the most widely used are the thiozoles and the sulphenamides. Hence these two groups are discussed below in detail.

Thiazoles

The thiazoles give a medium scorch time and a faster onset of cure than sulphenamides, but much slower than thiurams and dithiocarbamates. Used alone, thiazoles are not particularly efficient, giving only a relatively low degree of crosslinking. The situation, however, changes completely when basic substances or secondary accelerators are present in the mix. Even the presence of (basic) furnace blacks, is sufficient to give excellent properties. Mechanical properties of such mixes are also considerably improved by stearic acid.

Sulphenamides

Sulphenamides, in general, gives a substantially delayed onset of cure and this is the main reason for their popularity. The extent of delayed action is related to the bulkiness of the chemical group. Thus CBS gives less scorch safety than MBS which is still less than DCBS. The last of these accelerators has an extremely strong retarding action and is therefore, widely used where high processing temperatures of longer flow distances are encountered.

The total curing times of all mixes containing sulphenamide accelerators are short in relation to their scorch times. Thus accelerators belonging to this class have a favourable flow time/curing time ratio. This makes them particularly suitable for press curing, especially when intricately shaped mouldings are concerned and also for transfer and injection mouldings. All sulphenamide accelerators give a higher degree of crosslinking than straight thiazoles. The vulcanization plateau resulting from sulphenamides are moderately broad. but in this respect they are inferior to thiazoles but superior to the ultra accelerators.

Unlike most other accelerators, sulphenamides are particularly suitable for low sulphur vulcanization. Such systems combine several important advantages including short overall curing times, still better flow time/curing time ratio and broad vulcanization plateaus, along with other favourable vulcanizate properties. As with thiazoles, the rate of cure and degree of crosslinking can be varied substantially by using sulphenamides in conjunction with other substances, though to some extent the latter have different effects. Bases, for example, cause very little secondary acceleration or activation. But strong synergistic effects can be obtained with dithiocarbamates and thiurams. DCBS is highly sensitive to dithiocarbamates, which have a very strong secondary acceleration effect. In mixes containing sulphenamides, if ordinary zinc oxide is replaced with active zinc oxide, scorch safety is significantly reduced while the overall cure time remains unchanged. Other accelerators do not respond in this way to active zinc oxide.

Efficient vulcanizing (EV) systems impart remarkable resistance to reversion and ageing and low set vulcanizates

Efficient vulcanizing systems

In a conventional sulphur vulcanizing system the dosage of sulphur is in the range of 2 to 3 phr and that of accelerator 0.5 to1 phr. Such systems result in vulcanizates with predominantly polysulphidic linkages. Ageing resistance of the vulcanizates is generally inadequate. By reducing the sulphur dosage and proportionately increasing the accelerator level it is possible to ensure a more efficient use of the sulphur resulting in the formation a higher proportion of mono-and disulphidic crosslinks which have greater thermal stability than the polysulphidic crosslinks. In vulcanizates thus prepared the extent of main chain modifications is also less than that in conventional vulcanizates. Such low sulphur high accelerator systems are known as efficient vulcanizing (EV) systems. These systems impart remarkable resistance to reversion and ageing and low set to vulcanizates. However, the strength and fatigue properties of efficient vulcanizates are slightly inferior to those of conventional systems. Semi-EV systems represent a compromise between EV and conventional systems.

EV systems are developed by the total replacement of sulphur by a sulphur donor or by the use of a very high ratio of accelerator to sulphur. Early development of EV systems was based on the use of TMTD. This system is known to give almost exclusively mono-/disulphide crosslinks. However, this approach is undesirable as the levels of TMTD required will almost invariably cause serious blooming and scorch problems. In practice, EV systems are developed by using the less expensive TMTD upto the solubility level and using a non-blooming sulphur donor such as DTDM, to reach the total sulphur donor level required. In semi-EV systems the sulphur level is usually in the range of 1-1.5 phr and proportionately adjusting the accelerator dosage.

Activators

Realization of the full potential of most organic accelerators requires the use of inorganic and organic activators. Zinc oxide is the most widely used inorganic activator, but other metallic oxides such as magnesium oxide and lead oxide are also used. The most important organic activators are the higher fatty acids, although weak amines, polyalcohols and aminoalcohols are also used.

In a majority of rubber compounds, a combination of zinc oxide and stearic acid is used as the activator system. It may be noted that in the absence of an accelerator, zinc oxide and stearic acid are ineffective. The addition of zinc oxide alone to an accelerated stock may give a dramatic effect and produce a well cured stock. However, for zinc oxide to be fully used, it must be present in a form that can react with the accelerator system. This means that a very fine particle zinc oxide must be used and/or the zinc must be in a soluble form. Most natural rubbers and some synthetics contain enough fatty acids to form soluble zinc salts which can react with the accelerators. To ensure that sufficient acid is available, it is common to add 1-2 phr of stearic acid or a similar fatty acid. The fatty acid serves as a plasticiser and/or lubricant to reduce the viscosity of the stock and to solubilise the available zinc. This permits full development of crosslinks by the organic accelerator.

Low volatility organic acids such as benzoic acid, phthalic anhydride and salicylic acid can also be used as retarders

Basic zinc carbonates are more soluble in rubber than fine prticle zinc oxide and can, therefore, be used in higher concentrations. Soluble zinc salts of fatty acids are also used to provide better dispersion and solubility of zinc. Common salts are zinc stearate and zinc 2-ethylhexanoate

Retarders

The problem of prematuration vulcanization (scorch) has been experienced ever since the development of accelerators and activators. many of the accelerated vulcanizing systems are not safe enough to be processed, especially at high temperatures. Under such circumstances it may become necessary to retard the onset of vulcanization. N-nitroso compounds of secondary aromatic amines such as N-nitrosodiphenylamine (NDPA), which can very much retard vulcanization, are no longer in good demand for toxicological reasons. Low volatility organic acids such as benzoic acid, phthalic anhydride and salicylic acid can also be used as retarders. However, most of these chemicals may retard the whole vulcanization process in addition to retarding its onset, and hence cannot be considered ideal. With the introduction[3] of N-cyclohexylthiophthalimide (CTP) in the 1970's, one of the long cherished desires of rubber compounders has been fulfilled. This chemical behaves more or less like an ideal retarder especially in mixes accelerated with sulphenamides. The usual dosage is in the range of 0.1-0.2 phr. CTP does not cause any discolouration or staining. It does not significantly affect the overall vulcanization time also.

References

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2. Charles Goodyear. US Patent 3633 (1844).

3. C. D. Trivetta Jr., E.Morita and O.W. Maender. Rubber Chem. Technol. 50, 570 (1977) ☐