Electrical conductivity, crystallinity and glass transition in vulcanised rubber

N P DAW and R C BHUNIYA*

Department of Chemistry,

*Department of Physics, Indian Institute of Technology, Kharagpur 721 302, India

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Abstract. Temperature variation of electrical conductivity has been measured for rubber vulcanised with different concentrations of sulphur. Change of amorphous character with sulphur concentration has also been measured from the amorphous halo of the Debye-Scherrer x-ray photographs of the samples. The conductivity of vulcanised rubber in glassy state shows a slow and gradual increase; but during glass transition it increases suddenly to a high value which again exhibits gradual increase in high elastic state. X-ray studies show that with increase of sulphur, the amorphous region decreases due to formation of cross-links by the chain units. The decrease of conductivity with increase of sulphur is then due to decrease of amorphous region. The fast decrease of conductivity with sulphur at low concentration in the high elastic state indicates high rate of formation of cross-links at such concentration.

Keywords. Electrical conductivity; glass transition; x-ray powder photograph; vulcanised rubber; crystallinity.

1. Introduction

Electrical and mechanical uses of rubber are numerous. Depending on its use, its properties can be controlled which is usually done by using various types of fillars during vulcanisation (Bras 1957). Thus, the rubber produced by using inorganic fillars are more resistant to deformation and have high dielectric constant while those produced by using organic fillars are somewhat softer compounds with good electrical conductivity. Carbon blacks are in common use for the preparation of conductive rubber upon which a good deal of work has been done (Bras 1957; Mcpherson 1956). For electrical insulation, the dielectric strength and the resistivity of the rubber should be maximum while its dielectric constant and dielectric loss should be minimum. Natural rubber at room temperature is in the high elastic state. When its temperature is decreased to -70°C it passes to glassy state (Tager 1972). Vulcanisation changes the glass transition temperature which has been studied by measuring the physical properties like deformation, elasticity etc. Natural rubber is a polymer of isoprene in which the isoprene units are arranged in a head to tail manner. Cross-links of chain units are formed through fillars in three dimensions during vulcanisation (Bras 1957; Batman 1963) which decreases the amorphous character of the sample and increases its crystallinity. Like other physical properties,

electrical conductivity should also vary with glassy and high-elastic states or with amorphous and crystalline character of the vulcanised rubber. It is with this aim that the present investigation was undertaken to correlate glass-transition and crystallinity of sulphur vulcanised rubber with electrical conductivity.

2. Experimental

The samples were prepared by applying a pressure of 5000 psi ($\sim 340 \text{ kg/cm}^2$) at a curing temperature of 150°C and with a curing time of 50 min. The prepared samples are designated *A*, *B*, *C* and *D* according to the amount of sulphur content. The applied pressure, curing temperature and curing time were the same in all cases. Each type of the samples had 100 parts by weight of natural rubber, 5 parts by weight of zinc oxide, 2 parts by weight of stearic acid with varying amount of sulphur and accelerator. Benzothiazyl disulphide, an organic compound, was used as the accelerator. The amounts of sulphur and accelerator in *A*, *B*, *C* and *D* were as follows: *A* (2.4 parts by wt of sulphur, 0.0 parts by wt of accelerator); *B* (1.5 parts by wt of sulphur; 1.5 parts by wt of accelerator); *C* (0.6 parts by wt of sulphur, 2.4 parts by wt of accelerator); *D* (0.0 part by wt of sulphur, 3 parts by wt of accelerator).

The x-ray photographs of the samples *A*, *D* and natural rubber were taken with a Debye-Scherrer camera. The samples were exposed for 10 hr with x-rays obtained from Phillips micro-apparatus Cu-target x-ray tube operated at 35 kV and 10 mA.

To measure the electrical conductivity, samples of dimensions $1 \times 1 \times 0.25 \text{ cm}$ were coated with silver paint on larger surfaces. Electrical field was applied along the dimension of 0.25 cm. This is the same direction through which pressure was applied during vulcanisation. The electrical conductivity was measured as a function of temperature by placing the samples inside a cylindrical furnace between two silver electrodes provided with guard rings. The steady electric currents at different temperatures were measured with an EKKO electronic vibrating-reed electrometer. The details of the experimental arrangement have been given earlier (Bhuniya 1971).

3. Results

The Debye-Scherrer photographs of the samples *A* and *D* exhibit distinct lines over and above the central amorphous halo. These distinct lines are, however, absent in the photograph of natural rubber which shows only the amorphous halo. The presence of distinct lines in the photographs of the samples *A* and *D* indicates the presence of crystallites in the vulcanised rubber. The lattice parameters calculated from these lines are the same as those of zinc oxide crystal. This shows that a part of zinc oxide powder added for vulcanisation remains unchanged in vulcanised rubber. The central halo of the photograph is a characteristic of the amorphous material (Statton 1967; Agrawal and Tilley 1955). Its intensity is a measure of the amount of amorphous matter present in the sample (Levy *et al* 1959; Mathews *et al* 1949). The intensity of the halo was measured with a photometer and the diffracted ray intensity is plotted as a function of the diffraction angle. These plots shown

Figure 1. Angular variation of the intensity of the central halo of the Debye-Scherrer photograph for different samples *a.* sample *A*, *b.* sample *D*.

in figure 1 for the samples *A* and *D* indicate that the intensity of the halo decreases on increasing the concentration of sulphur during vulcanisation. Since the intensity of the halo is proportional to the amount of amorphous matter present in the sample, the amorphous character of the vulcanised rubber decreases on increasing the sulphur concentration. Most workers (Tager 1972) believe that the chains in amorphous polymers are approximately parallel to one another and therefore the angle corresponding to maximum intensity of the halo is proportional to the mean distance between the adjacent chains. Figure 1 shows this angle as 9.7° in sample *A* and 10° in *D*. The mean distance between the adjacent chains in these samples has been calculated from the formula $1.68 d \sin \theta = \lambda$, where d is the mean distance between adjacent chains, θ is the angle corresponding to the maximum intensity of the halo and λ is the wavelength of x-rays used for diffraction (Tager 1972). The d values found in these samples is about $5 \text{ \AA}$ which agrees well with the values $4\text{--}5 \text{ \AA}$ found by other workers (Tager 1972). Natural rubber is a polymer of isoprene in which the isoprene units are linked together in a head-to-tail arrangement. On vulcanisation the units are cross-linked through sulphur in three dimensions (Batman 1963). The formation of cross-links has decreased the amorphous character of rubber and hence increased its crystallinity.

The steady-state conductivity of vulcanised rubber is found to obey ohm's law for electric field from 200 to 1200 V/cm at different temperatures. The temperature variation of conductivity was measured at an electric field of 250 V/cm. The logarithm of conductivity is plotted against $1/T$ (T temperature in $^\circ\text{K}$) for vulcanised as well as natural rubber and is shown in figure 2. It can be seen that the conductivity plot of natural rubber exhibits a single range throughout the whole temperature range of measurement. But the plots of vulcanised rubber divide themselves into two linear regions separated by a transition region. The lower temperature region is termed as region I while the higher temperature one is termed as region II. The conductivity in region I varies little with sulphur concentration. It increases very slowly with temperature until it exhibits a very fast increase in the transition region.

Figure 2. Temperature variation of electrical conductivity for different samples. **a.** sample A. **b.** sample B. **c.** sample C. **d.** sample D. **e.** natural rubber.

Figure 3. Variation of electrical conductivity with concentration of sulphur in high elastic state.

The conductivity also varies slowly with temperature in region II where it depends strongly on the concentration of sulphur, showing a decrease with the increase of sulphur content.

The conductivity of samples *A*, *B*, *C* and *D* at 400°K in region II has been plotted as a function of sulphur concentration and is shown in figure 3 wherein it can be seen that the rate of decrease of conductivity is very high for low concentration of sulphur and it saturates to a low value for high concentration. The activation energies have been calculated from the slopes of the curves of figure 2 in both regions. In region I the activation energy is the same for all the samples while it is different for different samples in region II *viz.* 0.24 eV for *A*, 0.28 eV for *B*, 0.35 eV for *C* and 0.36 eV for *D* showing a decreasing trend with increase of sulphur concentration. It is to be noted that the activation energy (0.35 eV) of natural rubber is of the same order of magnitude as those for samples *C* and *D* which contain less amount of sulphur.

4. Discussion

When the temperature of a polymer is increased, it passes from glassy state to high elastic state and then to visco fluid state (Tager 1972). When rubber assumes a high elastic state from glassy state, all its properties change, it loses the properties characteristic of the solid state and acquires the properties of a liquid. These changes do not occur jumpwise but gradually over a certain temperature interval. This is the glass transition temperature interval. The mean of this interval is the glass transition temperature. The pronounced difference in the behaviour of electrical conductivity in regions I and II of the conductivity plots and their separation by a transition region indicates that the region I corresponds to the glassy state and region II to the high elastic state, the transition region indicating the glass transition interval. The glass transition temperature intervals found from the conductivity plots are 82–96°C for *A*; 76–96°C for *B*; 66–96°C for *C* and 50–82°C for *D*. This shows that with increase of sulphur content the transformation from glassy state to high elastic state starts at higher temperature but the transformation is complete at nearly the same temperature for all the samples. Glass transition temperature of natural rubber is –70°C (Tager 1972). So the glass transition temperature of sample *D* which does not contain sulphur has also increased from –70°C although the increase is lower than that of samples containing sulphur. It is to be remembered that the samples were prepared by applying a pressure of 340 kg/cm² at a temperature of 150°C in presence of an accelerator and ZnO. It is known (Tager 1972) that pressure as well as temperature alone can produce cross-linking of the chain units in rubber. Cross-linking reactions also occur with metallic oxides like ZnO. Hence, in the absence of sulphur, cross-linking of chain units *i.e.* vulcanisation of rubber does take place. Presence of sulphur only enhances the formation of cross-links. Also the number of rubber molecules forming cross-links together, that is, the size of the cross-linked regions, increases with increase of sulphur concentration. Above the glass transition temperature, rubber assumes the properties characteristic of a liquid. In the liquid state the cross-linked regions of rubber molecules move as a whole and the rubber molecules in the amorphous regions

are also mobile. Since the size of the cross-linked regions is larger and their number is more in samples having high sulphur content, the transition temperature is also higher in such samples. It has been found from x-ray studies that the samples having high sulphur content are more crystalline compared to those having less or no sulphur. This also shows that sulphur enhances the formation of cross-links in rubber.

It has been pointed out by some workers (Tager 1972) that the electrical conductivity of a polymer in glassy state depends on the free ions not connected chemically with the macromolecules and that the low molecular mass impurities present in the polymer serve as the source of these ions. But Lupu (1974) has attributed the steady-state conductivity in polymer to the hopping conduction of electrons. In vulcanised rubber, the electrons need different activation energies for hopping through crystalline and amorphous regions. As the amounts of crystalline and amorphous regions are different in different samples the activation energy should vary with concentration of sulphur in glassy state in case of conduction by hopping electrons. The same activation energy in all the samples in region I shows that the charge carriers move through similar environment in both crystalline and amorphous regions. This is possible only when the charge carriers are ions which can move through the space between rubber molecules. Since the atoms of the rubber molecules are joined by covalent bonds, thermal production of ions from it will destroy the molecule which is not possible at least up to 150°C at which the samples are prepared. Hence the low molecular mass impurity ions present in rubber are most probably the charge carriers as proposed by Tager (1972). The movement of these ions in cross-linked regions will be along a zig-zag path, but in amorphous region it can move straight through the space between the linear chains. Hence the effective mobility of the ions is greater in the amorphous region than in the crystalline region. As the amorphous region decreases with increase of sulphur content the conductivity in glassy state is also lowest in sample A. During the on-set of glass transition, rubber starts acquiring the properties characteristic of liquid when the cross-linked regions move as a whole and also the chain units in amorphous region. The chain proper is not charged and does not participate in the transfer of electric charges, but their movement reduces the hindrance to the migration of impurity ions and hence increases their mobility. The conductivity as a result shows a fast increase during glass transition. The increase of conductivity in both glassy and high elastic state is slow as it is due only to the temperature variation of mobility of the charge carriers. Whereas in the glassy state, the conduction is due to migration of impurity ions, in the high elastic state it involves migration of both impurity ions and chain units. Hence the activation energy of conduction is comparatively higher in this range. In the high elastic state also the movement of impurity ions is along zig-zag paths through cross-linked regions. The cross-linked regions themselves have random motion which is superimposed on the motion of impurity ions. As a result the effective mobility of the impurity ions is reduced compared to its value in amorphous region. Hence the conductivity in the high elastic region is also least in sample A whose crystallinity is more compared to other samples. The variation of electrical conductivity with crystallinity is also more pronounced in high elastic state than in glassy state because of higher mobility of impurity ions in the former state. Figure 3 shows that the conductivity of rubber in the high elastic state decreases very fast

with increase of sulphur for low concentration; the rate of decrease saturates to a low value for high concentration. This then shows that the rate of formation of cross-links by the chain units through sulphur is very high for low concentration of sulphur and saturates to a low value for high concentration. This same conclusion has also been drawn by Batman (1963) from other measurements. So the net effect of vulcanisation of rubber with sulphur is to increase its crystallinity which in turn reduces the electrical conductivity in both glassy and high elastic state.

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