

A Possibility of Nitration of Elastomers in Solid State

Elastomer nitration in the solid state has been carried out by means of solid nitrating agents that decompose at a temperature range where no degradation occurs. The decomposition process is as follows:



where B is NO_2 , HNO_3 , or N_2O_4 .

As nitrating agents, salts of the type $\text{Me}(\text{NO}_3)_{x/y}\text{N}_2\text{O}_4$, $\text{Me}(\text{NO}_3)_{x/y}\text{H}_2\text{O}$, urea nitrate, pyridine nitrate, 1,4-dioxan N_2O_4 , etc., were used,^{1,2} where Me is metal.

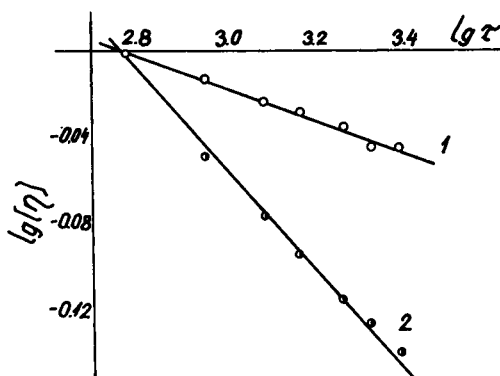


Fig. 1. Change in intrinsic viscosity against rolling time: (1) natural rubber; (2) natural rubber with urea nitrate in molar ratio 1:0.1.

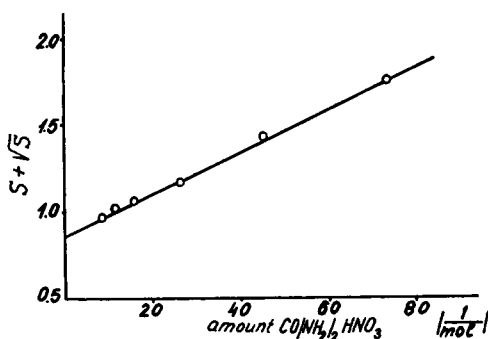


Fig. 2. Relationship between sol fraction and urea nitrate amount at heating of natural rubber-urea nitrate blend at 150°C for 20 min.

Natural rubber was plasticized 10 min followed by adding 0.1 molar units finely ground urea nitrate. A well-shaped constant-thickness sheet (ca. 3–4 mm) was obtained and heated at 110 – 150°C for 5 to 60 min in inert medium.

The interaction between natural rubber and the nitrating component (HNO_3) of the involved urea nitrate displaces the equilibrium of eq. (1) to the right, and salt decomposition occurs at a lower temperature.²

When urea nitrate is added in 20 min and mechanically involved salt is thoroughly eliminated, nitrogen bond content varies within the range of 0.9–1.1%. The intrinsic vis-

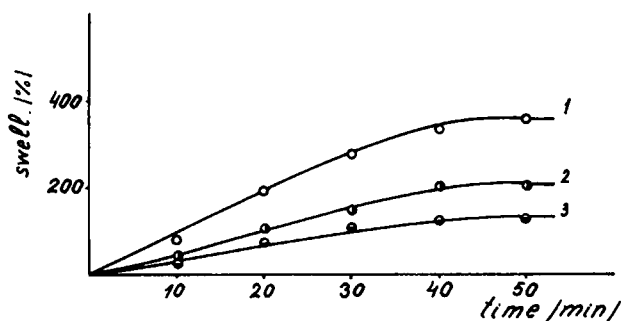


Fig. 3. Change of swelling degree in (1) water (2) acetone and (3) ethyl alcohol against heating time of natural rubber-urea nitrate blend in molar ratio 1:0.1 at 150°C.

cosity varies parabolically according to the rolling time (Fig. 1). Degradation of the natural rubber-urea nitrate blend is more intensive in composition when the pure elastomer is plasticized for the same time period (20 min instead of 10 min).

An active interaction takes part between natural rubber and the urea nitrate decomposition products after heating of the blend at 150°C for a period of 20 min. This leads to new degradation and formation of a crosslinked structure.

The graphical relationship between the sol fraction ($S + S^{1/2}$) and the reciprocal value from the amount of involved urea nitrate at a texture has a straight-line character,³ and there is good indication that the degradation slightly predominates at the chosen conditions (Fig. 2).

As a result of the chemical modification, the rubber decreases in strength and loses its elastic properties very considerably. The rubber becomes darker and its structure becomes more porous. The maximum values of the degree of swelling in polar solvents increase (Fig. 3).

The underlying water solubility is explained by the appearance of polar groups that contain oxygen, and their presence is proved spectrometrically.⁴

The quantity of nitrogen fixation depends very much on the conditions of the modification. Sometimes the nitrogen fixation exceeded the constant which is obtained at full nitration of the rubber from the nitrogen acid during the decomposition of the complex salt.

It is thus useful to assume an interrelation between the modified molecule of the natural rubber and the urea.⁴

References

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