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Abstract

Full Text

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PROPERTIES OF GUTTA-PERCHA IN THE AMORPHOUS STATE

If a crystalline polymer is melted and then cooled, it crystallizes, and in the process an ordering arises in the mutual arrangement of the chain molecules. It is difficult to imagine that rapid cooling of a polymer in which the chain molecules are arranged completely chaotically and are strongly entangled could lead to very rapid, complete, and deep crystallization.

It is obvious that the molecular ordering readily detected in a crystalline polymer must already be prepared in the amorphous state. We assumed that, if the mutual arrangements of chain molecules were fixed by some method, it would be possible to detect differences in the properties of such amorphous polymers, since the ordering of amorphous polymers can vary within very wide limits and, under certain conditions, can reach high values (¹⁻⁴). Undoubtedly, molecular ordering in polymers in the amorphous state must be a prerequisite for the process of rapid crystallization.

Fixing the mutual arrangement of chain molecules should also affect the rate and depth of crystallization (⁵⁻⁸), and consequently also the physical and mechanical properties of crystalline polymers.

The purpose of the present investigation was to detect the influence of the degree of ordering of chain molecules on the properties of a polymer. Gutta-percha was chosen as the object: a natural crystalline polymer that readily passes from the crystalline into the amorphous state at 55° and rapidly crystallizes upon cooling of the melt. Since the ordering of molecules depends to a considerable extent on temperature, the fixation of different states of molecular ordering could be accomplished by vulcanization at different temperatures.

Vulcanization was carried out at 143° with finely dispersed sulfur, at 70° and 20° in vapors of S_2Cl_2 , and at 20° by mixing a solution of gutta-percha in CCl_4 with a solution of S_2Cl_2 in ether. In the latter case, during the process of film formation from the mixture of solutions, vulcanization of the gutta-percha occurred. The amount of bound sulfur was determined by a chemical method.

Table 1 and Fig. 1 present data obtained in the investigation of the initial gutta-percha and of gutta-percha vulcanized under different conditions, containing approximately the same amount of bound sulfur. It was found that, at a content of about 4% bound sulfur, complete amorphization of gutta-percha occurred

only when vulcanization was carried out at temperatures above the melting temperature of the crystals, i.e., at 143 and 70°.

In those cases in which the process of film formation and vulcanization were combined, the structural and mechanical properties of gutta-percha testified to its considerable amorphization while the crystalline state was retained. Apparently, the decrease in the intensity of thermal motion and the slow evaporation of the solvent during film formation create favorable conditions for the ordering of chain molecules, and therefore, despite

Table 1

Dependence of the mechanical and physical properties of gutta-percha on vulcanization conditions

Vulcanization conditions	Content of bound sulfur, %	Phase state at 20°	Strength at 20°, kg/cm ² *	Elastic modulus at 20°, kg/cm ²	Relative elongation at rupture (20°), %	Glass-transition temperature, °C
At 143°	4.2	Amorphous; does not crystallize even after 10 months of storage at 20°	25	20	500	-40
At 70°, in S ₂ Cl ₂ vapors	4.0	Amorphous, but crystallizes after 6 months of storage at 20°	20	65	60	0

Vulcanization conditions	Content of bound sulfur, %	Phase state at 20°	Strength at 20°, kg/cm ² *	Elastic modulus at 20°, kg/cm ²	Relative elongation at rupture (20°), %	Glass-transition temperature, °C
At 20°, solution of gutta-percha in CCl ₄ with S ₂ Cl ₂ solution	4.0	Retains a weak crystalline structure	100	120	80	—
At 20°, in S ₂ Cl ₂ vapors	5.6	Retains crystalline structure	180	2000	40	—
Initial gutta-percha	—	Crystalline	200	2000	350	—

* Calculated for the initial cross-section.

the crystalline structure is retained to a considerable degree during vulcanization.

An even greater difference in the properties of gutta-percha was found when the vulcanization of finished films was carried out in S₂Cl₂ vapors at 70 and 20°. In the first case, at 4% bound sulfur, the gutta-percha became amorphous and did not crystallize even on cooling to 20°; in the second case, at a content of 4% and even 5.6% bound sulfur, the gutta-percha retained a crystalline structure (Table 1).

Thus, by fixing different states of gutta-percha at different temperatures, we obtained the possibility of determining what mechanical properties gutta-percha will possess in passing from the maximally disordered state to a highly ordered state.

Fig. 1. Effect of vulcanization temperature on the mechanical properties of gutta-percha at 20°. 1—vulcanized at 143° with finely dispersed sulfur, containing 4.2% bound sulfur; 2—vulcanized at 70° in S₂Cl₂ vapors, containing 4.0% bound sulfur; 3—vulcanized at 20° in a mixture of solutions, containing 4.0%

bound sulfur; 4—vulcanized at 20° in S₂Cl₂ vapors, containing 5.6% bound sulfur; 5—initial gutta-percha.

From the data presented it follows that the degree of amorphousness of structured crystalline polymers depends not only on the number of cross-links formed, but also to a considerable extent on the state of the polymer in which it was during the structuring process. The less ordered the polymer was during structuring, the smaller was the extent of subsequent crystallization.

Attention should be drawn to the interesting experimental fact that, at one and the same content of bound sulfur, it is possible to obtain two types of amorphous gutta-percha possessing completely different physical and mechanical properties (Table 1, Fig. 1).

The difference in the properties of the two types of amorphous gutta-percha is apparently connected with the fact that, as the temperature is raised, owing to the increase in thermal motion, the orderliness of the arrangement of chain molecules decreases, and at higher vulcanization temperatures a more disordered arrangement of the chain molecules is fixed.

From consideration of the experimental data obtained by us, it is evident that increased deformability and lower values of the elastic modulus and glass-transition temperature correspond to amorphous gutta-percha vulcanized at the higher temperature (143°). Comparatively small deformations and higher values of the elastic moduli and glass-transition temperature correspond to gutta-percha vulcanized at 70°, i.e., at a lower temperature, close to the melting temperature of the crystals.

It might have been supposed that the difference in the properties of the two types of amorphous gutta-percha is due to the fact that, during vulcanization with sulfur chloride, bonds of a monosulfide character are formed^(9, 10), whereas during vulcanization with finely dispersed sulfur, bonds of a polysulfide character are formed⁽¹¹⁾. However, the new experimental facts obtained indicate that the difference in the properties of amorphous gutta-percha is determined not only by the presence of mono- and polysulfide bonds. Amorphous gutta-percha vulcanized at 143° did not crystallize after ten months of storage at 20°, whereas amorphous gutta-percha vulcanized at 70° became crystalline already after six months of storage.

Such a phenomenon could have occurred only owing to a more ordered arrangement of the chain molecules in the gutta-percha samples vulcanized at 70°, as compared with the samples vulcanized at 143°.

Thus, from the foregoing it follows that the fixation of different degrees of orderliness of the polymer chain molecules within the limits of their amorphous state leads to the formation of polymers possessing different mechanical and physical properties.

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