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Dynamic Mechanical Behavior of Chitin and Chitosan

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Introduction

Recently, much attention in the many fields has been paid to chitin(Poly-N-acetyl-D-glucosamine), which is formally considered an aminocellulose derivative that occurs widely in nature, for example, in the hard shell of insect and crustaceans, cuttlefish bone, and the cell walls of fungi, and its derivative, chitosan (Poly-D-glucosamine), which is readily obtained from chitin by N-deacetylation with alkali. However, there has been few papers concerning the physical properties of these polysaccharides. FUKADA et al.(1975) examined the piezoelectricity of highly crystalline α-chitin, and found that a temperature dispersion appears only around -95°C, which has been assigned to the water strongly bound to α-chitin. More recently, BRADLEY et al.(1976) studied dynamic mechanical properties of some polysaccharides such as cellulose, amylose, and dextran containing various amount of water, and have characterized four mechanical transitions.

In this paper, we report the effect of water on the dynamic mechanical properties of chitin and chitosan as a function of temperature.

Experimental

Chitin was isolated from shrimps according to Hackman's method(HACKMAN, 1954). Chitosan was prepared by N-deacetylation of chitin with 40% aqueous sodium hydroxide solution. N-Deacetylation was confirmed from the negligible intensity of absorption of $\nu_{C=O}$ in N-acetyl group at about 1650 cm^{-1}(Amide I band) in the ir spectrum of chitin. The films of both samples were cast from a hexafluoroacetone sesquihydrate(HFAS)/water (1:9, by volume) solution.* The films obtained were dried at 120°C in vacuum(Dry film) and were highly

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** CAPOZZA(1976) reported that HFAS is good solvent for chitin. We found that chitin and chitosan used in this work are soluble in the mixed solvent.*

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moisturized in a desiccator at high relative humidities. The crystallinity of each sample was checked by x-ray method. The dynamic mechanical measurements were made by a RD-10(Rhesca Co., Ltd.)free-oscillation torsion pendulum at a norminal frequency of 1 Hz over temperature range -160° to 200°C. The samples were 5 cm long between clips, 1 cm wide, and 0.05 cm thick. The real (G') and imaginary(G")parts of the complex shear modulus were calculated by the usual equation(SINNOT, 1966).

Results and Discussion

The temperature dependence of the real(G') and imaginary(G") parts of the complex shear modulus for dry and highly moisturized(wet) chitin films are shown in Figure 1. In the dry sample, a clear loss peak at about -120°C(γ-relaxation) and the gradual increase in G" above 0°C are found. On moisturing the sample, the peak intensity increases and a new loss peak appears at around 50°C(β_1-relaxation). Corresponding data for chitosan to those given for chitin are shown in Figure 2. In the dry chitosan, two loss maxima at about -75° and 140°C are clearly seen. The low temperature loss peak may correspond to the γ-peak of chitin. The high temperature relaxation, designated here as an α-relaxation can be attributed to the glass transition of the dry chitosan as indicated by the corresponding steep decrease in G'. The dynamic mechanical properties of chitosan are greatly affected by the presence of water as compared with chitin. On moisturing the chito-

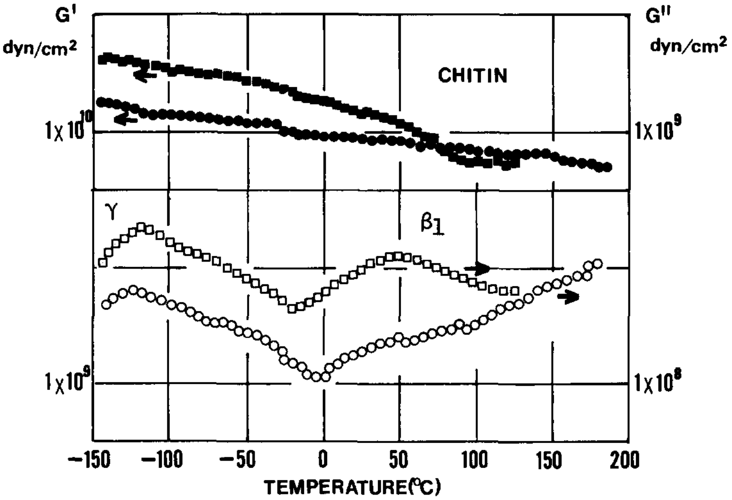

Fig.1 Temperature dependence of the complex shear modulus for chitin. G' (●) and G"(○) for dry sample, and G' (■) and G"(□) for wet sample.

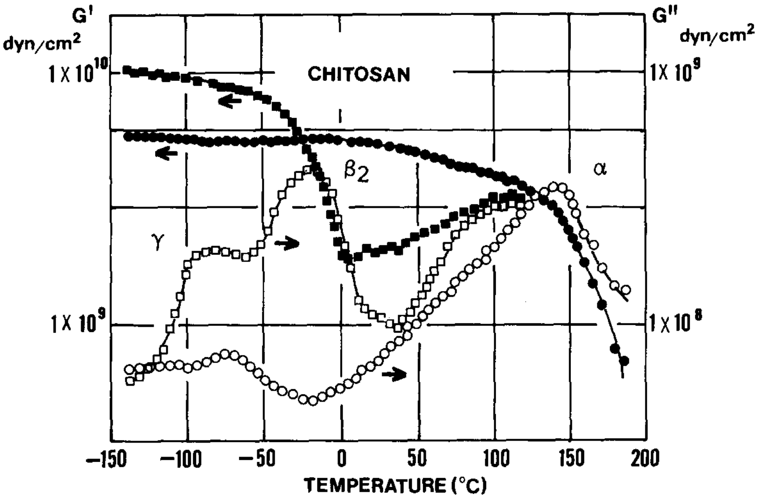

Fig.2 Temperature dependence of the complex shear modulus for chitosan. G'(●) and G"(○) for dry sample, and G'(■) and G"(□) for wet sample.

san, the γ-peak is seen to increase markedly in intensity and shift to the low temperature side. Furthermore, a new loss peak at around -20°C(β_2-relaxation) with a corresponding large decrease in G' is found on the high temperature side of the γ-relaxation. The apparent G" maximum observed for wet chitosan at about 100°C seems to be caused by the loss of water from the sample coupled with the mechanical relaxation due to the micro-Brownian motion which is activated during the loss of water, because in this temperature region, G' increases monotonously with temperature. Above 125° C, the G' is again predicted to increase and G' decrease, and overlap with those of dry chitosan, as predicted in chitin.

At the present time, we cannot characterize the origin of the γ-relaxation for chitin and chitosan; however, it may be related to the rotation of methylol and/or methylol-water complex as suggested for cellulose(BRADLEY et al., 1976) or water bound to the specimen as proposed for α-chitin(FUKADA et al., 1975).

For chitin and chitosan, the real component of shear modulus is found to be different between the dry and wet specimens, especially in chitosan. At temperatures below the β_1 and β_2 transitions, both the wet samples have a higher shear modulus than the dry specimens. The plasticizing effect of water at temperatures above the β_1 and β_2 changes into an antiplasticizing one below the transitions. Similar observations have been reported for cellulose(BRADLEY et al., 1976) and for nylon 6(PREVORSEK et al., 1971). Prevorsek et al. have proposed that the water must reduce the free volume of the system, which in turn leads to the observed increase in the modulus while the system is in the glassy state. Consequently, they have assigned a transition exhibiting a large increase in the real part of tensile modulus with decreasing temperature to the glass transition of the polymer plasticized with water. It seems to be reasonable to assign the the β_1 and β_2 loss peaks corresponding to the large decreases in G'(with increasing temperature) to the glass transition of chitin and chitosan plasticized with water.

The dry chitosan exhibits the α-relaxation(glass transition); however, the dry chitin showed no clear loss peak below the decomposition temperature of the sample. This is consistent with the x-ray diffraction results that the chitin was highly crystalline while the chitosan was poorly crystalline. The steady increase in G" with the corresponding gradual decrease in G' with temperature around 150°C suggests an occurrence of the glass transition of the dry chitin above 175°C.

The effects of adsorbed water on the dynamic mechanical properties(changes in loss peak intensity and temperature, and in real part of the shear modulus) are more prominent in chitosan as compared with chitin. Chitosan has a lower crystallinity as compared with chitin. Therefore, much more water may be able to be adsorbed on chitosan as compared with chitin.

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