

Influence of Water on Thermal Transitions in Natural Polymers and Synthetic Polyamides

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A B S T R A C T

The glass transition temperature T_g and to some extent the melting temperature T_m of collagen, cellulose, polyamide 6 and 66, and of the statistical copolyamide 6/66 were investigated with the differential scanning calorimeter after equilibration of the specimens at various humidities at 295K. The results showed that smaller amounts of absorbed water cause a pronounced shift of T_g to lower temperatures due to the breaking of hydrogen bonds and the reduction of the cohesive energy between the polymer chains. Additional water molecules form clusters with previously absorbed water and T_g decreases are less pronounced. The plasticizing effect of water on natural polymers exceeds by far the effect on synthetic polyamides, as does its influence on T_m in the case of collagen.

I N T R O D U C T I O N

The glass transition temperature T_g of polymers depends on the intermolecular forces between the chains of the macromolecules, i.e. the cohesive energy (HAYES 1961, KREIBICH and BATZER 1979, 1981 in press). In structural proteins such as collagen, elastin and keratins, in cellulose (MACGREGOR and GREENWOOD 1980, WARD and COURTS 1977) and in the synthetic polyamides (CHAMPETIER and PIED 1971), T_g is markedly higher due to additional hydrogen bonding between the molecular chains. The results of previous investigations on the influence of tanning agents on collagen, elastin, and polyamide 6 suggested that the tanning process can be explained as dehydrating plastification (BATZER et al. 1952, 1953). Lower amounts of water are present in macromolecular systems in a molecular dispersed form that has physical and physiological influences differing from those of water clusters. The breaking of hydrogen bonds by water molecules leads to a reduction in T_g , an effect which has been investigated for polyamides (PAPIR et al. 1972, GOLDBACH 1973, REIMSCHUESSEL 1978, STARKWEATHER 1980), elastin (KAKIVAYA and HOEVE 1975), gelatin (MARSHALL and PETRIE 1980), and cellulose (OGIWARA et al. 1970).

The following paper shows the influence of water on thermal transitions in collagen, cellulose, polyamide 6 and 66, and in copolyamide 6/66. A comparison of the effects in different polymers with strong hydrogen bonding leads to interesting conclusions about their dependence on chemical structure.

EXPERIMENTS

The polyamides were investigated using polyamide 6 (Grilon nature A28, Emser Werke AG) and polyamide 66 (Ultramid A3K, BASF). The statistical copolyamide 6/66 was prepared by a melt condensation process from caprolactam and AH-salt (synthesized from equivalent amounts of adipic acid and 1,6-diaminohexane) in the ratio 50:50 (weight %). After the polymers had been dried under vacuum at 353K, sheets of PA 6, PA 66, and PA 6/66 about 0.2 mm thick were pressed at about 510 K, 550 K, and 460 K using an electrically heated hydraulic press.

The coreum of calf skin was used to investigate collagen. Cellulose was investigated using cotton fabric which had not been given any pretreatment.

The polymers were dried under high vacuum at elevated temperatures (polyamides at 358 K, collagen and cellulose at 328 K) for several days until weight constance. The water content of the materials was varied by equilibration of the sheets at various relative humidities at 295 K, either by using saturated solutions of salts in deionized water or by immersing the polymers in deionized water.

The equilibrium absorption of water was controlled with a Mettler microbalance. The glass transition temperature T_g and the melting temperature T_m were measured at a heating rate of 10K/min using a DuPont 1090 thermal analysis system equipped with a high-pressure DSC cell. The specimens were encapsulated in commercially available, hermetically sealed aluminium DSC pans. Below room temperature the experiments were performed without pressure and with liquid nitrogen as cooling agent. At elevated temperatures a pressure of 20 bar was applied to prevent the evaporation of water.

RESULTS AND DISCUSSION

The diffusion of water molecules into a polymer leads to a pronounced shift of T_g to lower temperatures due to the reduction of the cohesive energy between the macromolecular chains and the breaking of hydrogen bonds (Figure 1). The higher the T_g of the polymer, i.e. the greater the difference between the T_g of the components of the binary system, the more pronounced is the reduction in T_g , providing that strong interaction forces between polymer and solvent induce high solvent-uptake by the polymer. Hence determination of the reduction in T_g can be used as an analytical tool to measure the water content of natural polymers (further details will be given in a succeeding paper).

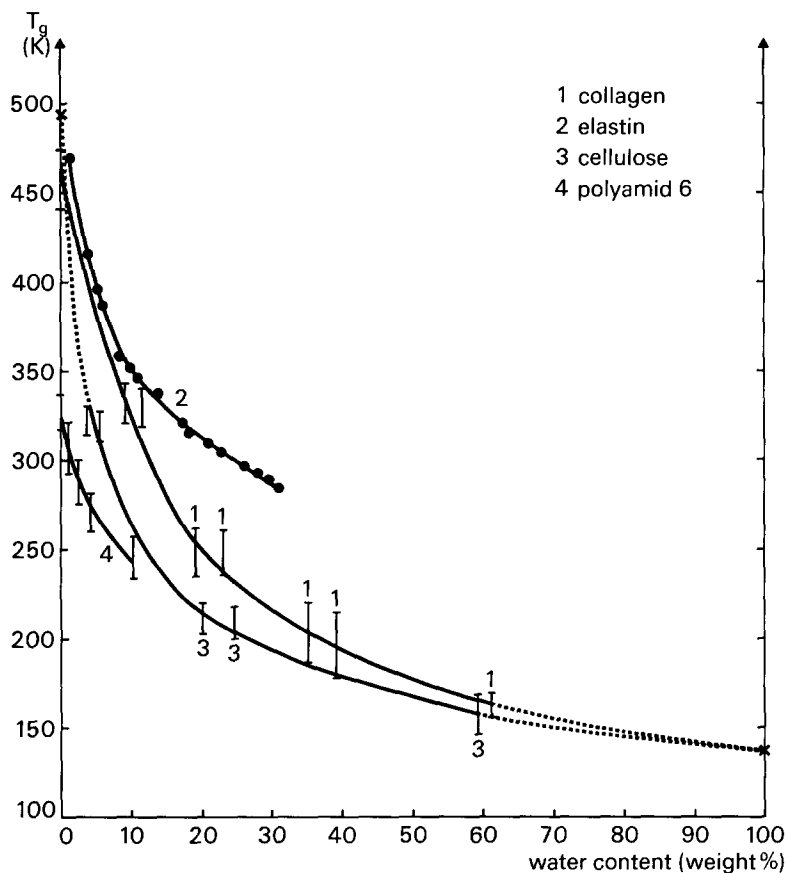


Figure 1: Influence of the water content on the glass transition T_g of some natural polymers and PA 6 (T_g of dry cellulose from KARGIN et al. 1960, T_g of water from RASMUSSEN and MACKENZIE 1971)

Cellulose and collagen show a rather similar significant decrease in T_g under the influence of water, whereas the effect on elastin is not so marked. This could be due either to a higher cross-linking density or to a reduced polarity of elastin.

The T_g of the polyamides is affected less by water absorption than that of the natural polymers (Figure 2). Its decrease as a function of water content is rather similar in PA 6 and 66. The statistical copolyamide 6/66 with its lower melting temperature and crystallinity due to a lower degree of order of the molecular chains (BATZER and MOESCHLE 1957), shows a lower T_g in the dry state and increased absorption of water. However, once the water content exceeds 5 %, the chemical structure between the amide groups makes no further contribution to added reduction in T_g .

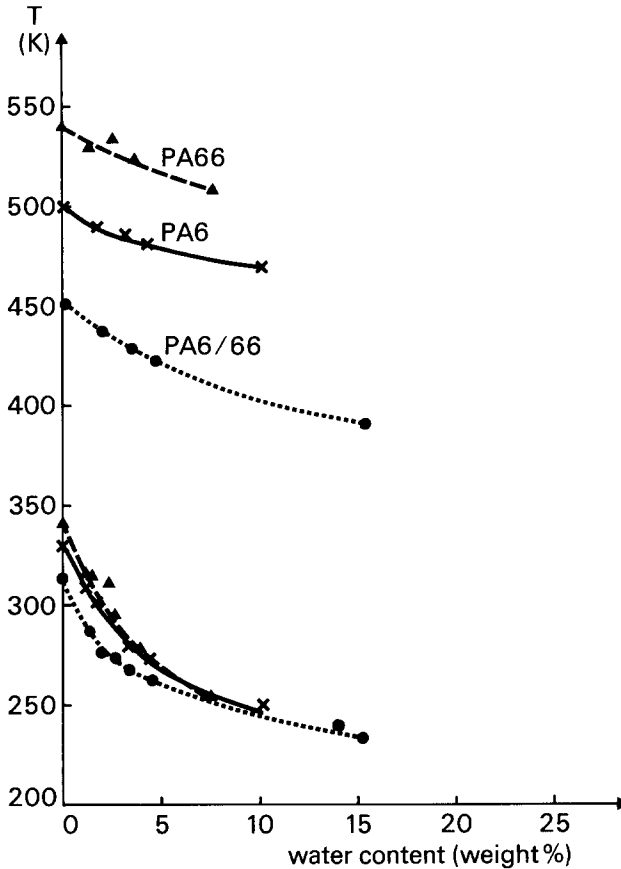


Figure 2: Glass transition temperature T_g and melting temperature T_m of PA 6, PA 66, and PA 6/66 in function of the water content

Additional water is known to form clusters with the previously absorbed water molecules following complete hydrogen bonding of the available groups in the polymer to the penetrating water molecules (STARKWEATHER 1975, KALUTSKAYA and GUSEV 1980). In cellulose the melting of absorbed frozen water was observed when the water content of the system was about 20%, and in collagen at about 35%. No melting of the ice was observed in the polyamides. At higher water contents the formation of hydrate structures has only limited influence on T_g since the hydrogen bonds between the macromolecular chains are already broken.

Figure 3 shows that water has a pronounced effect on melting temperature or helix-coil transition in collagen. Its effect on the crystalline melting temperature of the polyamides is less marked. The comparison of the ratio $T_g/T_m \sim 0.67$ for PA 6 and ~ 0.93 for

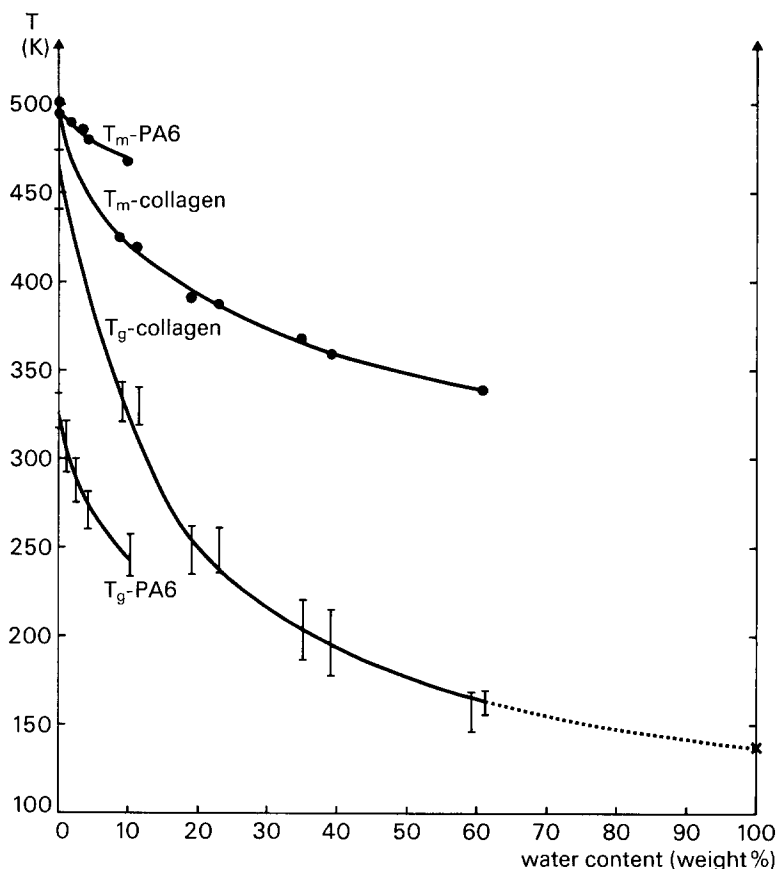


Figure 3: Comparison of the influence of water on the glass transition T_g and on the melting temperature T_m of a natural and a synthetic polyamide

collagen reflects the high asymmetry of the protein due to substituents, side groups, and the influence of supermolecular structures.

In summary, the properties of the synthetic polyamides with a rather simple structure differ quite distinctly from those of the natural polymers with sophisticated chemical and supermolecular structures. The results of the investigations carried out do, however, give some insight into means used by nature to flexibilize proteins and polysaccharides and to enable life processes.

A C K N O W L E D G E M E N T S

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