ABSTRACT

Tanning is the process of conversion of raw hides and skins into imputrescible leather; thereby the later acquires resistance to chemical, thermal and microbial forces. Tanning, specifically stabilization of collagen could be accomplished by many substances. It is of profound interest to understand the forces involved not only in stabilization of collagen, but also in biodegradability of finished products on disposal. Conversely, biodegradable tanning systems proposed in the present work refers to processing of leathers using suitable tanning system, which is easy for biodegradation under defined environmental conditions. Three representative carbohydrate biopolymers such as starch, cellulose and alginate were modified as dialdehydes and used for the stabilization of collagen. The ability of the three modified biopolymers i.e. dialdehyde starch (DAS), dialdehyde cellulose (DAC) and dialdehyde sodium alginate (DSA) as polyaldehydes in rendering leathers with matching physical properties to that of the chrome tanned or vegetable tanned leathers were assessed. The amenability of these leathers for biodegradation was also verified. An attempt to understand the molecular level mechanism of these polyaldehydes with stabilization of collagen is presented.

Hydrothermal stability of collagen cross linked using dialdehyde starch (DAS), dialdehyde cellulose (DAC) and dialdehyde sodium alginate
(DSA) was found to be more than 80° C; and in the ascending order of DAC, DSA and DAS. Thermodynamics with respect to denaturation temperature, rate of shrinkage, activation energy and enthalpy change were also found to be in the same order. A similar trend was observed for enzymatic stability of collagen against degradation of collagenase. The increase in thermal and enzymatic stability was found to be dependent on the degree of oxidation. Autoclaving of DAS resulted in hydrolysis and lower molecular weight (MW) oligomeric species. The presence of lower molecular species (DAS-Dimer) was found to be the cause for better shrinkage temperature, enzymatic stability and tanning effect using DAS. Hydrolysis of DAS was also achieved by acid, alkali and enzyme. Cross linking ability was found to be better for DAS-Dimer and in the decreasing order of DAS-Dimer, DAS-Trimer, DAS-Tetramer, DAS, DSA and DAC. The cross linking density of DAS-Dimer was found to be 12 cross links per collagen molecule. The value for DAS-Trimer, DAS-Tetramer, DAS, DSA and DAC are 9, 8, 11, 8 and 6 number of crosslinks formed per collagen molecule respectively.

There is no significant secondary structural alteration in collagen on treatment with DAS, DAC, DSA and oligomeric species of DAS. However, marginal changes in Rpn ratio in the case of DAS and DSA was observed. DAC does not elicit any change in the CD spectra of collagen. No concrete evidence for loss of triple helicity or conformational changes on reaction of collagen with all the developed polyaldehydes was observed. However, the secondary structure of collagenase was altered considerably by DAS, DAC and DSA and induced changes in conformation of collagenase. DAS
promoted helix to random coil conformation, whereas DSA and DAC resulted in \(\beta\)-sheet transitions. Non competitive inhibition was exhibited by all the three polyaldehydes. Quaternary structural alterations resulted in qualitative changes in banding density for DAS-Dimer and DAS-Trimer. Changes in D-Periodicity were observed for DAS-Dimer and DAS-Trimer treated collagen. However, no change in D-periods of collagen treated with tetramer, DAS, DAC and DSA was seen. Polyaldehyde induced aggregation of collagen from aqueous solution resulted in similar D-period pattern for native and DAS-Dimer. A fibrous network was observed for trimer. Polyaldehydes stabilized collagen substratum is biocompatible and enhances cell proliferation. Tanned leathers from DAS, DAC and DSA resulted in leather properties that are suitable for upper and garment leathers. The biodegradability of polyaldehyde tanned leathers was within international standards as compared to conventional chrome and vegetable tanned leathers. The biodegradability of polyaldehyde tanned leathers was found to be better than chrome tanned and vegetable tanned leathers. The present work investigates the molecular insights into the mechanism of polyaldehyde tanning as an integrated biodegradable tanning system.