

INVESTIGATIONS OF CROSSLINKING SYSTEMS IN THE GRAFT POLYMERIZATION OF CHROMIUM-TANNED COLLAGEN

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These investigations are being conducted to combine the desirable properties of leather with those of synthetic polymers and thus produce a new leather product with easy-care properties. Graft copolymers of collagen in the form of chromium-tanned sheepskins have been made by a redox-initiated emulsion polymerization using butyl acrylate or methyl methacrylate for the purpose of imparting some of their beneficial properties to leather. Previous investigations had demonstrated that vinyl-type monomers could be grafted onto tanned or untanned collagen and would lend their properties to those of collagen without altering the natural appearance of the resulting leather.

Animal skins are composed of collagen fibers arranged in a three-dimensional woven fabric. Collagen itself is made up of three approximately equal-molecular-weight polypeptides arranged in the form of a triple helix and has a combined molecular weight of 300 000. It is about 14 Å in diameter and 2 900 Å long. These molecules form into protofibrils, which further aggregate to form eventually the fiber bundles that make up the three-dimensional woven fabric. Tanning makes the collagen nonputrescible, and we obtain leather, the oldest known crosslinked polymer to be made and used by man.

Impregnation of leather gives a transient combination of leather and polymer properties and also interferes with the desirable aesthetic values of leather. Our approach was to use graft polymerization to combine the desirable properties of both natural and synthetic polymers.

Because of the special nature of this system, not all the polymer was grafted. The redox system supplied the primary,

ionic free radical, which then generated a secondary free radical on the insoluble collagen matrix. The monomer reacted with both types of free radicals to produce a true graft copolymer as well as homopolymer. The properties of the collagen-g-polymer did not follow exactly predictions based on that particular polymer's bulk properties. In one of the early studies, two conventional crosslinking monomers were used and favorably increased the amount of bound polymer and also the break load during tensile strength testing. In addition, acrylic acid or methacrylic acid was found to have a similar effect, presumably through ionic bonding with the collagen, and probably also involved the chromium-collagen complex which was formed during tanning.

In this study we expanded the types and number of polyfunctional comonomers studied and determined the resulting improved chemical and physical properties when compared to the untreated substrate. Five comonomers had di- or tri-vinyl functionality. Five more had one or two ionic groups in addition to a vinyl group. Two levels of monomer (s) were chosen to yield leather products containing a theoretical maximum of 29% or 50% synthetic polymer on the product basis. The polyfunctional comonomer comprised 8% of the total monomer offered.

By means of chemical and physical tests, the properties of the resulting collagen-g-polymer were compared to those of chromium-tanned skins. These studies were used to evaluate the utility of the graft polymerization process for making leathers with new and improved properties by imposing the beneficial properties of synthetics on the leather but without visibly affecting the leather's appearance.

Within the limits imposed by the non-uniform water content of the leather being grafted and those of the analytical

methods used on the grafted leathers, essentially theoretical yields of polymer were observed when using either butyl acrylate or methyl methacrylate. Thus the two levels of monomer that were used would be expected to yield products containing 29% or 50% of their total weight as polymer. In practice not all of this polymer was actually grafted. Regardless of the level of monomer used, only 13 to 16% of the product weight was grafted polymer; the difference between this value and the expected value was extractable with appropriate solvents. By replacing 8% of the monomer offered with one of the polyfunctional comonomers, the extractable portion of the total polymer could be reduced or even eliminated. Some of the polyfunctionality of the comonomer could be ionic; however, the effectiveness in reducing polymer extractability was greater for the comonomers that contained only vinyl functionality.

All graft-polymerized leathers showed increases in thickness compared to the controls. The increases in thickness ranged from 9% to as much as 159%. This increase was statistically best related to the amount of total polymer with $R = 0.774$ and .95 confidence limits of 0.59 to 0.88.

The percent tensile elongation values were increased in all but 5 cases for the treated leathers, and all but one of the load values were increased. The reasons for these increases were not fully explainable. In general, the tensile elongations were greater when butyl acrylate was used instead of methyl methacrylate, whether or not any of the comonomers were included. This trend may be related to the different Tg values

for poly *n* butyl acrylate and poly methyl methacrylate: -40°C and 106°C , respectively. Within the butyl acrylate series or the methyl methacrylate series, the inclusion of comonomers did show some aberrations regarding the percent changes in elongation.

A hypothesis is proposed to explain the increase in thickness observed in the course of graft polymerization as carried out in our system. This hypothesis suggests that the lack of ability to carry completely the properties of a bulk polymer to the collagen-g-polymer hybrid situation is due to the relative isolation and fixed site of each growing chain.

The irregular changes in tensile elongation and the increases in tensile breaking loads may well be due to interfibrillar displacements caused by the growing polymers, resulting in a pseudo-lubrication effect that permits the fibers varying amounts of movement before rupture during the tensile test. The amount of branching in the various polymer chains and the possible presence of interpenetrating polymer networks can also be contributing factors.

These results suggest that it is practical to make leather that can withstand increased stress, is more uniform in thickness, and has a range of stretchabilities to meet a particular need. In addition, preliminary studies suggest that the grafted leather may have improved adhesion for specialty films (laminated foils, etc.) or finishes, improved gluing characteristics, and improved performance as a leather upper for use in shoes with injection-molded soles.