IR SPECTROSCOPIC ANALYSIS OF GRAFT CO-POLYMERS OF CELLULOSE AND ITS DERIVATIVES WITH VINYL FLUORIDE

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Graft co-polymers of cellulose with certain vinyl monomers have been analyzed by spectroscopy methods by other workers /1-5/ but, with certain exceptions, they failed to provide spectroscopic evidence of the formation of a chemical bond between the cellulose and the grafted polymer. Such evidence is very important for demonstrating the formation of graft co-polymers and for an analysis of the mechanism of the grafting reaction. In this communication the results are reported of an analysis of the IR spectra of the graft co-polymers of cotton cellulose, regenerated cellulose and cellulose acetate with vinyl fluoride the polyvinyl fluoride side chains of which sharply increase the resistance to rotting, chemical agents and light of the fibres and reduce their flammability.

A comparison of the IR spectra of the original cellulosic materials and their mechanical mixtures with polyvinyl fluoride (PVF) and of those of the graft co-polymers containing various proportions of PVF yielded information about the changes in these spectra which enabled conclusions to be drawn about the formation of a chemical bond between the original and grafted polymers and thus to demonstrate the formation of the graft co-polymer, to determine the changes taking place in the original polymer as a result of the grafting of the vinyl fluoride, and to ascertain the most likely sites for the formation of the active centres which initiate the reaction of graft co-polymerization.

The graft co-polymers were produced by exposing the polymer and vinyl fluoride containing impurities 10^-5 wt.% together to Co60 radiation. The IR spectra were obtained on a UR-10 spectrophotometer. The specimens were prepared by compressing 5 mg of the polymer thoroughly mixed with 500 mg potassium bromide at a residual pressure of 10^-3 mm Hg. The spectra obtained were those of the graft co-polymers, of the original polymers irradiated under the same conditions, and of the mechanical mixtures of the original polymers with PVF.

The IR spectra of the graft co-polymers (Figs. 1-3) contain new absorption bands in non-overlapping regions which are absent in the IR spectra of the original polymers and are connected with the presence of PVF chains, viz. valence groups of C - F in the frequency regions 1040 and 1060 cm^-1, CH2 deformation groups of PVF chains (pendulum type at 835 cm^-1, scissor type at 1415 cm^-1, fan type at 1455 cm^-1), valence groups of the same type (CH at 2860 cm^-1, symmetric CH2 groups at 2960 cm^-1, and asymmetric CH2 groups at 2980 cm^-1). However, the development of these absorption bands cannot serve as evidence of the formation of a chemical bond between the original polymer and the grafted monomer since they appear also in the IR spectra of their mechanical mixtures. In this context maximum interest attaches to changes in those absorption bands in the IR spectra of the graft co-polymers which are characteristic of the original polymers.

These changes can be divided into several kinds, viz. a decrease in the intensity of the absorption bands for specific functional groups in the original polymers; a change in the intensity of the absorption bands sensitive to a disturbance of the structure of the original polymer; the development of new absorption bands in connection with the conversion of certain functional groups in the original polymer as a result of the grafting of vinyl fluoride; and a shift of the oscillation frequency of certain groups.
in the original polymer along which or on which the monomer is grafted. The latter is
difficult to discern since as a rule this frequency shift results merely in a broadening
of the absorption band concerned. The first three kinds of changes in the absorption
bands, on the other hand, are easily identifiable in the IR spectra of all graft co-
polymers.

The IR spectra of the graft co-polymers of cotton cellulose (Fig. 1) show that an
increase in the proportion of the grafted vinyl fluoride results in a decrease in the
intensity of absorption bands 1645 cm\(^{-1}\) (symmetric deformaional oscillation of water
molecules adsorbed on the cellulose), 1170 cm\(^{-1}\) (valence fluctuation of the C-O bond
in the hydroxyl group of the sixth carbon atom of the cellulose unit), 1320 and 1345 cm\(^{-1}\)
(defomational fluctuation of the primary hydroxyl group), 3400 - 3500 cm\(^{-1}\) (valence
fluctuation of the hydroxyl groups combined with hydrogen bonds), and 900 cm\(^{-1}\) (pendulum
oscillation of the CH\(_2\) group characteristic for the rotational isomers in the structurally
unordered regions of the cellulose) /7/.

The decrease in the intensity of absorption
band 1645 cm\(^{-1}\) remained even when the cellulose
specimens were subjected to high-vacuum treatment
and a radiation dose of 10 mR and in the spec-
tra of the mechanical mixtures with PVF. This is
evidently connected with the elimination of the
adsorbed water as a result of the formation of the active grafting centres on the released
hydroxyl groups. The decrease in the intensity of bands 1170, 1320 and 1345 cm\(^{-1}\) is explained by
the fact that the grafting proceeds on the primary
hydroxyl groups at the sixth carbon atom of the
-glucoside unit. A similar phenomenon was noted
in the oxidation of cellulose under mild condi-
tions which affected only the primary hydroxyl
groups /7/.

It is well known /7/ that a disturbance of
the structural order of cellulose always results
in a decreased intensity of absorption bands
1320, 1340 and 1430 cm\(^{-1}\) (scissor oscillation of
CH\(_2\) groups characteristic for rotational isomers
in the tightly packed regions of the cellulose)
with a simultaneous increase in the intensity of
absorption band 900 cm\(^{-1}\). In the graft co-polymer-
ization the intensity of absorption band 900 cm\(^{-1}\)
increased without a noticeable change in the in-
tensity of band 1430 cm\(^{-1}\). This indicates the
probability of preferred grafting in the loosely
packed regions of the cellulose. The decrease in
the intensity of band 1320 - 1340 cm\(^{-1}\) can be
attributed equally to grafting and to a distur-
bance of the structure of the original cellulose
which results in a decrease in the intensity of
absorption bands 3400 - 3500 cm\(^{-1}\).

An increase in the proportion of grafted
PVF in the graft co-polymer results in the de-
velopment of an absorption band at 1725 cm\(^{-1}\) which
can be attributed to valence oscillation of the
carbonyl groups coming into being evidently from
those hydroxyl groups on which the radicals ini-
tiating the reaction of the graft co-polymeriza-
tion are formed.

The change in the intensity of the absorp-
tion bands of the CH\(_2\)OH groups in the cotton
cellulose thus shows that the graft co-polymeriza-
tion reaction proceeds on the primary hydroxyl
groups in the loosely packed regions.

Fig. 1. The IR spectra of the graft
copolymer of cotton cellulose
with PVF: 1) pure cotton cellulose,
2, 3) and 4) graft co-polymers
with weight increments of 3, 13
and 30% PVF resp., 5) mechanical
70/30 mixture of cotton cellulose
and PVF.