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Radiation Grafting of Vinyl Monomers Onto Wood Pulp Cellulose. Part I

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Synopsis

The effect of dose, dose rate, monomer type, and monomer concentration on the water transport behavior in grafted cellulose pulp and hand sheets was studied. At low dose rates, grafting rates of styrene onto wood pulp were less with hand sheets than with the pulp itself. Grafting was also found to be decreased by increasing the dose rate. Grafting mixtures of styrene and acrylonitrile gave better yields than styrene alone. Excellent grafting yields were obtained by treating the pulp or hand sheets with water before adding vinyl monomers. In this way, solvents such as dioxane could be eliminated from the grafting mixture. The hand sheets, grafted with mixtures of acrylonitrile and styrene, had good mechanical properties although less than the corresponding ungrafted sheets. Grafting decreased the moisture regain in pulp and hand sheets. Gamma irradiation of wood pulp under ambient conditions without additives reduced the water sorption considerably.

INTRODUCTION

Grafting vinyl monomers to cellulose is an effective method for modifying cellulose and imparting a desired property (e.g., water sorption) without affecting greatly other properties of interest (e.g., mechanical behavior). A considerable amount of literature has been published on this subject and adequate recent review articles are available.[1-4]

Extensive studies of high-energy-radiation-induced grafting onto cellulose have been reported by many investigators: for example, acrylonitrile was used[5,6] for radiation-induced modification of cotton, while styrene was used for radiation-induced modification of cellulose in the form of cellophane and cotton[7]; of cotton linters, cotton cloth, and rayon[8]; and of wood.[9] Grafting studies of wood pulp and paper have been considerably less numerous although some have been reported.[10-12] A number of others are reviewed by Arthur.[4] Some investigators have studied the high-energy-radiation-induced grafting of a mixture of acrylonitrile and styrene onto cellulose and observed a high increase in grafting rates compared with either monomer alone.[13,14,16]

It has been shown by extensive grafting work onto cellulose that swelling of the cellulose substrate is necessary to render the active growth sites accessible to monomers thus allowing propagation of the grafted chain.

Water was found to be one of the more obvious swelling agents and has been used alone[6] or mixed with a third component, normally a solvent which enables the hydrophobic monomer to tolerate the addition of water in a single phase. Dioxane has been found to be an excellent cosolvent with water for styrene grafting to cellulose.[7] Huang et al.[8] reported that swelling in water alone and subsequent immersion in styrene or other vinyl monomers were sufficient to bring about substantial grafting of vinyl polymer onto cellulose on exposure to gamma radiation.

Some properties of cellulosic materials can be changed dramatically as the result of graft copolymerization. Sanders and Sovish[6] reported that grafting acrylonitrile to cotton improved its rot and mildew resistance while the mechanical properties were not affected significantly, provided the radiation dose was less than 5 Mrads. Wellons et al.[15] and Kesting and Stannett[16] have demonstrated that water vapor regain in cellulose and cellulose acetate can be reduced by controlled radiation-induced grafting of styrene.

Recent work in this laboratory[10,11] on grafting styrene onto wood pulp has shown that by the use of gamma ray initiation with a dioxane–water swelling system, 70% by weight styrene was grafted onto unbleached kraft softwood pulp containing 84% α-cellulose at a dose of 5 Mrad. Measurements of the amount of water sorbed in the modified wood pulp revealed that the equilibrium regain of water decreased with respect to that of the unmodified pulp, while the diffusion coefficient of water increased with grafting. Grafting of more polar monomers such as ethyl acrylate and acrylonitrile cause a comparable decrease in water sorption at low relative humidity, but the reduction in water sorption tended to disappear at high humidities; the water diffusion coefficient decreased with increasing polarity of the grafted polymer.

The work reported here is an extension of the above styrene studies to the case of the graft copolymerization of acrylonitrile–styrene onto wood pulp and the corresponding hand sheets. It was hoped that this combination would reduce the radiation dose levels needed to bring about adequate grafting without great sacrifice of the water regain improvements. An extensive study of the grafting in binary mixtures of acrylonitrile and styrene to cellulose has recently been published.[17] In addition, it was hoped that adding the more polar acrylonitrile to styrene would lead to somewhat greater strength properties compared with styrene alone. The results obtained revealed that all of these expectations were indeed realized.

EXPERIMENTAL

Materials

Two different forms of cellulose were used in this work: (a) unbleached kraft soft wood pulp containing 84% α-cellulose and 4% lignin; (b) hand sheets made from the pulp described in (a).

Styrene monomer was treated with a 1% sodium hydroxide solution to eliminate the inhibitor, washed several times with water, dried, and then distilled under vacuum. Acrylonitrile was distilled under atmospheric pressure, while the other reagents were used as received.

As radiation sources, three cobalt 60 gamma ray sources of intensities 1.05 Mrad/hr, 0.135 Mrad/hr, and 0.073 Mrad/hr were used.

Procedure

Two methods were used for the preparation of graft copolymer. In one, dioxane containing a small amount of water was used as the swelling agent and irradiation was carried out in vacuo. In this method, the sample was placed in an ampoule and covered with the monomer or with the mixture of monomers and swelling agents. Degassing was carried out by repeated freeze–thaw cycles of the tube contents under 10^{-5} mm Hg pressure. The tube was then sealed and the contents were equilibrated for 24 hr and then irradiated to the desired dose.

In the other procedure, water alone was used as a swelling agent and irradiation was carried out without degassing. This was achieved by adding the desired amount of water directly to the hand sheets placed in test tube, the tube was tightly covered, and the hand sheets were preconditioned for 24 hr. The mixture of acrylonitrile–styrene was added until it just covered the sample. The tube was again tightly covered and then directly irradiated to the desired dose.

In case of small strips of wood pulp, the homopolymer was removed by Soxhlet extraction with a suitable solvent (benzene was used for styrene grafts while dioxane was used for acrylonitrile–styrene grafts) and the samples were oven dried at 60°C under vacuum.

In the case of grafted hand sheets, the homopolymer was removed by soaking the samples in the proper solvent which was changed several times and the sheets were then air dried at room temperature.

The percentage graft was calculated as

$$\frac{W - W_0}{W_0} \times 100$$

where W = final weight of the sample after grafting, W_0 = initial weight (oven dried).

Physical Properties

The bursting strength, breaking length, and folding endurance of the modified hand sheets were determined according to Tappi standard methods T-403M, T-404M, and T-423M, respectively.

RESULTS AND DISCUSSION

Effect of Dose and Dose Rate on Grafting Yield

The effect of dose and dose rate on the grafting of styrene onto unbleached kraft wood pulp containing 84% α-cellulose (and 4% lignin) was determined using cobalt 60 gamma ray sources of intensities 1.05, 0.135, and 0.073 Mrad/hr. The same method and the optimum concentration of monomer and swelling agent as described elsewhere[7] were used, i.e., 33 ml styrene and 67 ml dioxane containing 2.3% water. The irradiation was carried out in vacuo.

The results, which are presented in Figure 1, show that the per cent graft increased monotonically with dose although the grafting rate decreased progressively with time. Increasing the dose rate resulted in a decrease in grafting yield at the same total dose although the actual initial rate of grafting increased with roughly the one half power of dose rate. This is in good agreement with the results previously obtained by grafting vinyl monomers to wood[9] and many other materials.

The results of grafting styrene on wood pulp and its corresponding hand sheet using the low cobalt 60 dose rate of intensity 0.135 Mrad/hr and the same method are shown in Figure 2. It can be seen that the hand sheets gave considerably less grafting yield than the pulp itself; probably the reaction is more controlled by the slow diffusion of the monomers to the active sites in the hand sheets which have reduced swelling after drying.

Gamma-Ray-Induced Graft Copolymerization of Mixtures of Acrylonitrile and Styrene

Grafting styrene onto pulp was found to decrease the water regain of the pulp, yet increase the rate of diffusion of water.[10] It would be desirable to find some other monomers that do not give rise to the increased rate of diffusion. Acrylonitrile tended to meet this requirement[11]; moreover, it has been found to improve the sheet properties.[16] Therefore, grafting a mixture of acrylonitrile and styrene was studied.

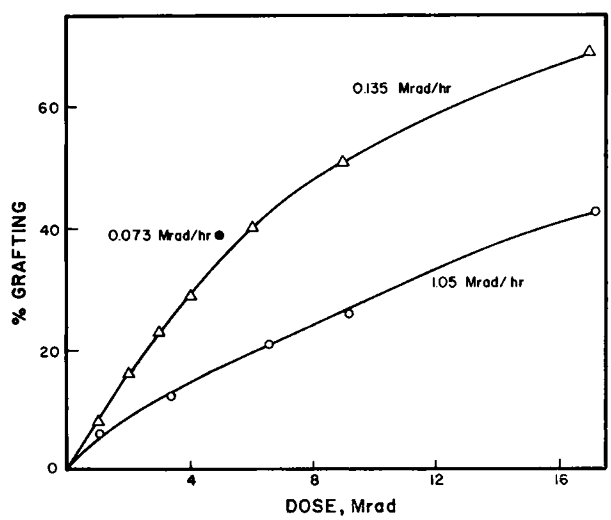

Fig. 1. Effect of dose rate on grafting styrene onto pulp (33 ml styrene plus 67 ml dioxane containing 2.3% water, irradiation in vacuo).

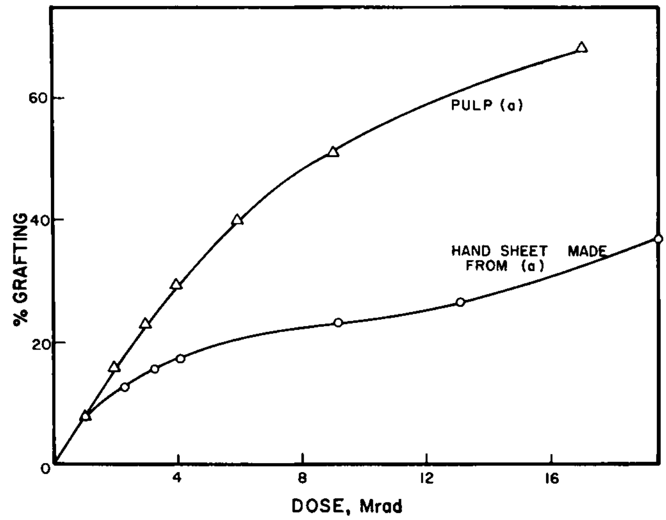

Fig. 2. Effect of grafting styrene onto pulp and its corresponding handsheet (33 ml styrene plus 67 ml dioxane containing 2.3% water, irradiation in vacuo with ^{60}Co, 0.135 Mrad/hr).

Preliminary tests were carried out on the grafting yield with different ratios of acrylonitrile and styrene. The results showed that the grafting rate was greatly increased by the use of these two monomers, and the best yield was obtained with one part acrylonitrile to three parts styrene, which is close to the concentration of the two monomers at the eutectic copolymerization point.

The increase in grafting by the use of a mixture of acrylonitrile and styrene over that of styrene alone, with photoinitiated systems, was observed by Geacintov et al.[19] and Rapson and Kvasnicka[14] with gamma radiation.

A number of reasons can be postulated to explain the increased rate. The copolymerization rate is much faster than that of styrene alone; furthermore, the acrylonitrile increases the sorption and diffusion of the monomers into cellulose. Another possible reason could be the enhanced gel effects often found with acrylonitrile systems due to the poor swelling of the polymer in the monomer mixture (see also Harris and Arthur[17]).

The ratio of the two monomers was calculated according to their concentration at the eutectic point; the swelling agent was dioxane containing 2% water, and hence the standard mixture was 12.6 ml acrylonitrile, 33.4 ml styrene, and 54 ml dioxane containing 2% water. Irradiation was carried out after degassing and preconditioning for 24 hr; the homopolymer was removed by extraction with dioxane.

The results of grafting acrylonitrile–styrene mixtures on pulp and hand sheets are presented in Figure 3. It was found that grafting on either pulp or hand sheets gave similar grafting yields when using the relatively high

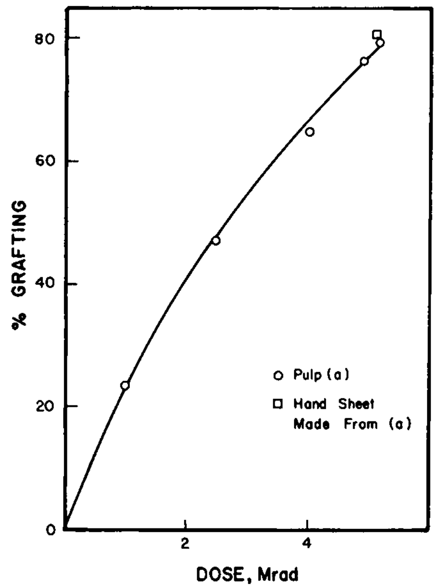

Fig. 3. Effect of grafting acrylonitrile–styrene on pulp and its corresponding hand sheet using dioxane recipe (12.6 ml acrylonitrile, 33.4 ml styrene puls 54 ml dioxane containing 2% water, irradiation in vacuo with ^{60}Co, 1.05 Mrad/hr.

cobalt 60 dose rate (1.05 Mrad/hr), presumably because of the gel effect and reaction rate being more significant than site accessibility. However, the efficiency of grafting was considerably enhanced over that achieved with styrene alone. Thus, at 2.5 Mrads, the grafting yield was 47.5% compared to 10.6% with styrene only.

Elimination of Dioxane from the Grafting Solution

The use of the dioxane system as a swelling agent for grafting styrene to cellulose was first developed by Chapiro and Stannett,[7] and it was preferred over other swelling systems because it gave considerably less homopolymerization and led to grafting under conditions in which, although water was present to swell the cellulose, the polymerization itself took place in homogeneous solution. It was later shown[11] that the dioxane system led to lower moisture regains in styrene-grafted pulps. Although this swelling system has been used successfully here for grafting styrene and acrylonitrile–styrene onto cellulose, attempts were made to eliminate the toxic solvent dioxane from the grafting mixture and replace it by water alone. However, the addition of water to the mixture of monomers was found to be ineffective because of the immiscibility of water in the used concentration of the monomers. To overcome this difficulty, water was added directly to the cellulose substrate.

The appropriate amount of water was added directly to the strips of hand sheet placed in test tube, then the mixture of monomers [12.6 ml

TABLE I
Effect of Water Content on the Grafting Onto Cellulose

Water in pulp sample, %	Grafting, %
7	4.6
45	53.2
60	55.9
72	79.0

TABLE II
Effect of Preparation Technique on the Grafting of Styrene and Acrylonitrile Onto Cellulose

Method used	Grafting, %
40% Cellulose—60% water + mixture of monomers; preconditioned for 24 hr, irradiated in vacuo	55.9
40% Cellulose—60% water + mixture of monomers; preconditioned for 24 hr, irradiated in air	54.4
40% Cellulose + 60% water; preconditioned for 24 hr, *then* mixture of monomers added and irradiated in air	66.5

acrylonitrile, 33.4 ml styrene] was added until the strips were just covered. Degassing, preconditioning, and removal of homopolymer were carried out in the usual manner; irradiation was achieved by cobalt 60 of intensity 1.0 Mrad/hr for a total dose of 1.2 Mrad.

The effect of using different concentrations of water on the grafting yield are shown in Table I. The results show that grafting was greatly enhanced by increasing the water concentration up to 60%; above this concentration the grafted pulp was contaminated with some gel-like structure which was not removed by exhaustive extraction with dioxane. This is attributed to the fact that addition of more than 60% water to cellulose causes some of it to remain in suspension as immiscible droplets, and these water-rich regions nucleate the formation of the gel-like structure. Accordingly, 60% was considered to be the optimum water concentration.

The effect of air and the effect of preconditioning the cellulose in water alone were studied using the same optimum concentration as in the above experiments. Irradiation was carried out by cobalt 60 of intensity 1.0 Mrad/hr for a total dose of 1.2 Mrad. The results are summarized in Table II. The results indicate that the presence of air had no significant effect on the grafting yield when the cellulose was preconditioned in the presence of the monomer mixture. Conversely, soaking the cellulose in water alone for 24 hr increased the grafting yield and reduced the time of contact of cellulose with the mixture of monomers to a minimum. Hence,

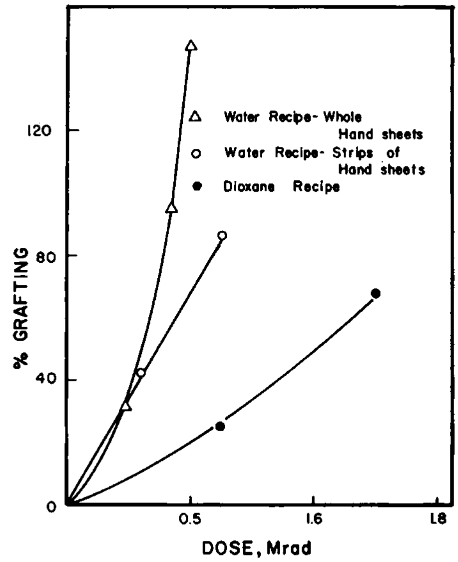

Fig. 4. Effect of using dioxane recipe and water recipe on grafting yield (^{60}Co, 0.130 Mrad/hr).

the following recipe was used: Water was added directly to the hand sheet in the ratio of 40:60 cellulose:water and the mixture was preconditioned for 24 hr; the mixture of monomers was then added (12.6 ml acrylonitrile and 33.4 ml styrene) before subjecting the system to irradiation.

The effect of total dose on grafting the mixture of monomers onto strips of hand sheet (~0.3 g) was studied using the above recipe and cobalt 60 of intensity 0.13 Mrad/hr. Comparing the results, which are shown in Figure 4, with those previously obtained using dioxane and the same radiation dose rate, it was found that the grafting yield is greatly increased. This may be attributed to the increase in the concentration of the monomers and to the increased efficiency of the swelling agent plus the large gel effect associated with the styrene–water system. Moreover, it was found that applying the same method on a large scale, i.e., on large hand sheets (~6 g) gave similar grafting yields, as shown in Figure 4.

Physical Properties of Hand Sheets Modified with a Mixture of Acrylonitrile–Styrene or with Styrene Alone

In order to determine the effect of grafting level and the method of grafting on the physical properties of the hand sheets, a mixture of acrylonitrile and styrene was grafted on total hand sheets using the dioxane-free recipe and cobalt 60 at an intensity of 0.13 Mrad/hr. For the sake of comparison, grafting was carried out under different conditions: (a) grafting on hand sheets using the dioxane-free recipe but without removing the homopolymer, i.e., the sheet air dried after irradiation; (b) grafting

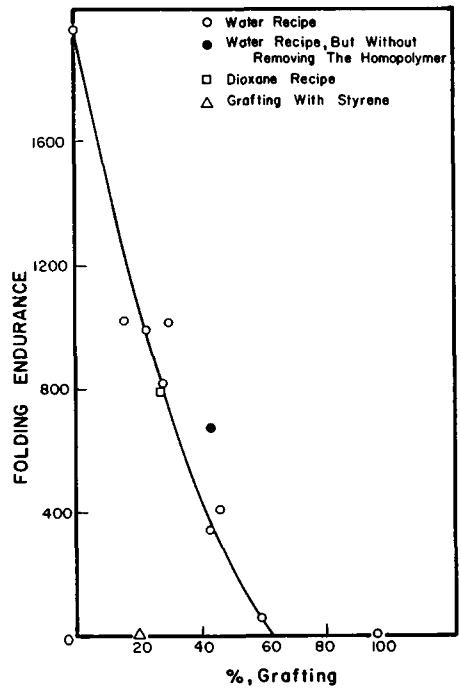

Fig. 5. Effect of grafting on folding endurance (tension 1 kg).

on hand sheets using dioxane; and (c) grafting styrene on hand sheets using the standard mixture of 33 ml styrene and 67 ml dioxane containing 2.3% water.

The results presented in Figures 5 and 6 show that the folding endurance of the treated sheets decreased almost linearly with increasing the grafting level, while their breaking length and their specific bursting strength were found to decrease considerably only after 30% graft.

The strength of the unextracted sheets containing grafted polymers as well as homopolymer was found to be higher than the strength of those which had been extracted to constant weight. This may be attributed to the fact that the homopolymer in the grafted sheet perhaps formed a coating layer which reinforced the sheet to some extent. In any case, it is gratifying that no expensive solvent extraction procedure seems necessary for the development of optimum properties.

Grafting on hand sheets using the dioxane and dioxane-free recipes produced no significant difference in physical properties between the two methods. This was a gratifying result, inasmuch as the dioxane would be an expensive, toxic, and highly complicating factor in the grafting process itself.

Grafting styrene alone to hand sheets tended to make them very brittle and friable, with low folding endurance and poor bursting and tensile strengths. The advantages gained in these properties by copolymerization

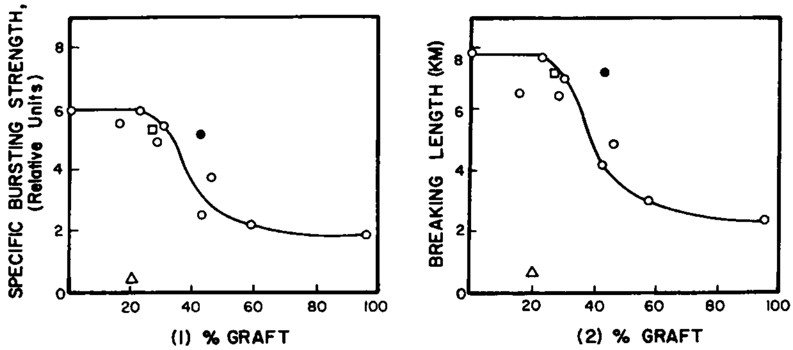

Fig. 6. Effect of grafting level on (1) specific bursting strength, (2) breaking length: (O) water recipe; (●) water recipe without removing the homopolymer; (□) dioxane recipe; (△) grafting with styrene.

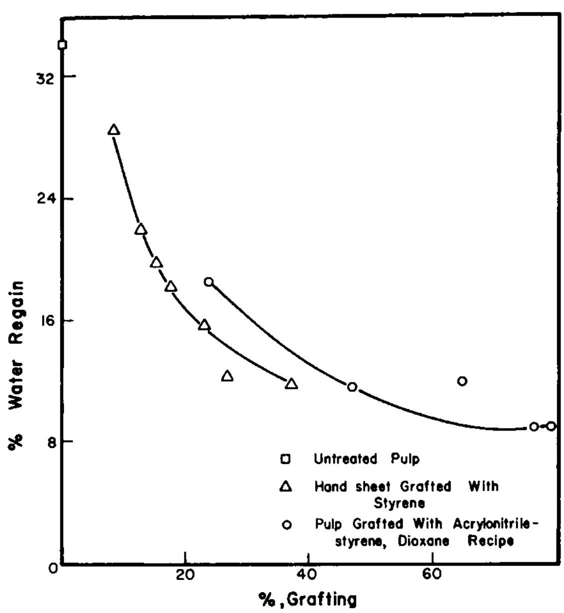

Fig. 7. Effect of grafting level on water regain of modified cellulose (^{60}Co, 1.05 Mrad/hr).

with acrylonitrile are clearly shown by the results presented in Figures 5 and 6.

Moisture Regain of Modified Cellulose

The estimation of the moisture regain at 100% relative humidity by the hand sheets modified with styrene and pulp modified by grafting the mixture of acrylonitrile–styrene was made at several different levels of grafting.

The results presented in Figure 7 show that there is a decrease in moisture regain with increase in grafting level. As expected, the acrylonitrile–

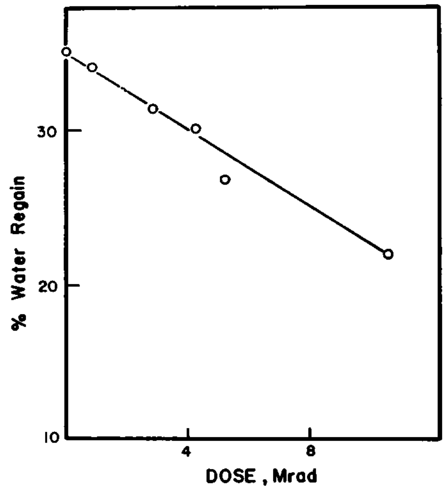

Fig. 8. Effect of dose on water regain of pulp (^{60}Co, 1.05 Mrad/hr).

styrene grafts sorbed more water than the corresponding pure styrene grafts. For example, the acrylonitrile substitution for a portion of the styrene resulted in 23% more sorption at 30% graft.

Effect of Gamma Ray Irradiation on Water Regain of Pulp

It has been reported recently by Mares and Arthur[20] that a reduction of both water retention and vapor sorption was achieved by irradiation of cotton and wood pulp under ambient conditions of air. This effect was studied here by the exposure of pulp in air under ambient conditions of temperature and relative humidity to gamma rays from a cobalt 60 cell of intensity 1.05 Mrad/hr. The results are shown in Figure 8 and are in good agreement with those reported by Mares and Arthur[20]; for example, a 37% reduction in moisture regain was obtained after irradiation to a total dose 10.4 Mrads.

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