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Radiation-Induced Copolymerization of Vinyl Monomers onto Husk and Stem of Rice Cellulose

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ABSTRACT

The husks and stems of grain comprise major products of agriculture processes and not very widely used in industry. The present study deals with refining such materials to suitable products. A detailed study on the graft copolymerization of styrene and acrylonitrile onto husks and stems of rice cellulose was carried out, a Co-60 source being used as a means of producing ionizing radiation. The effect of different factors, e.g., dose, water content, temperature, and monomer concentration, in the graft copolymerization was studied and optimum conditions are proposed for the reactions.

INTRODUCTION

The husk and stem of grain is one of the by-products of cereal agriculture which has been neglected for its possible use in industry as well as in domestic use. A method was initiated to refine such cellulose to a suitable product having widespread applications.

A series of vinyl monomers were grafted onto the husks and stems by using radiation from a Co-60 source. Such grafting gives rise to a material with high strength and flexibility which can be easily modified to any size and dimension [1, 2].

The interaction of ionizing radiation with cellulose leads to the formation of free radicals which are trapped in the polymer matrix and are stable at ambient temperatures [3, 4]. These radicals are polymeric species, due to the fact that they are formed on the cellulose molecule and can therefore be used to initiate a graft copolymerization reaction with vinyl monomers under conditions where monomer can diffuse into the polymer matrix and reach trapped radical sites [5].

This work presents a detailed study on the graft copolymerization of styrene and acrylonitrile on the husks and stems of rice by irradiation from a Co-60 source. To ascertain ideal conditions for the reactions and for the comparison of the results, both simultaneous and pre-irradiation methods were studied [6-8].

EXPERIMENTAL

Sample Preparation

The husks and stems of rice contain 10% (by weight) of cellulose as well as lignins (esters, alcohols and some other complex compounds). Before the start of any graft reaction, they were washed with methanol for about 4 hr and then dried under vacuum. A series of vinylic monomers as styrene and acrylonitrile were grafted onto the husks by using the techniques already mentioned.

For the simultaneous technique the grafting process was carried out in excess of styrene in different proportions of CH_3OH/H_2O as solvents and evacuated up to 10^{-4} Torr. The styrene was chosen because of its low $G_{R\cdot}$ (radical) value relative to that of cellulose and the ease of separation of its homopolymer from both the grafting matrix and the bulk solution [9]. After irradiation at different doses, the reactive mixture was kept at 40-70°C for about 14-24 hr, then, after the samples were exposed to air, the homopolymers were extracted in benzene and toluene.

In the pre-irradiation technique, after irradiation of husks at atmospheric pressure, they were mixed (at room temperature) with different proportions of styrene/dioxane/water or styrene/acrylonitrile/water as the solvent, respectively. The samples were evacuated up to 10^{-4} Torr and this was repeated for many times as mentioned at following section. Then, they were kept at constant

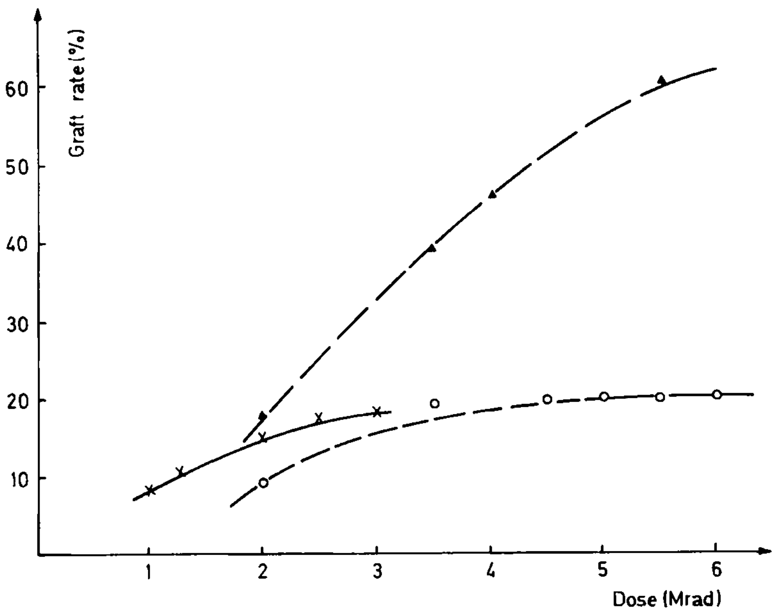

FIG. 1. Influence of dose on grafting rate under various conditions of polymerization: (×) simultaneous grafting, styrene/methanol/H_2O = 72/20/8; (○) pre-irradiation grafting, swelling with vapor; (▲) pre-irradiation grafting, without swelling, styrene/dioxane/H_2O = 76/22/2.

temperatures of 45-90°C for times varying from 14 to 24 hr. After the reaction was completed, the products were washed with toluene/DMF to eliminate the homopolymers.

For both the above mentioned methods, the grafting rate was determined by measuring the increase in the weight after the homopolymer extraction process was complete. The rate of grafting was calculated by use of the simple equation:

$$\text{Grafting rate} = \frac{\text{Weight after irradiation} - \text{Weight before irradiation}}{\text{Weight before irradiation}} \times 100$$

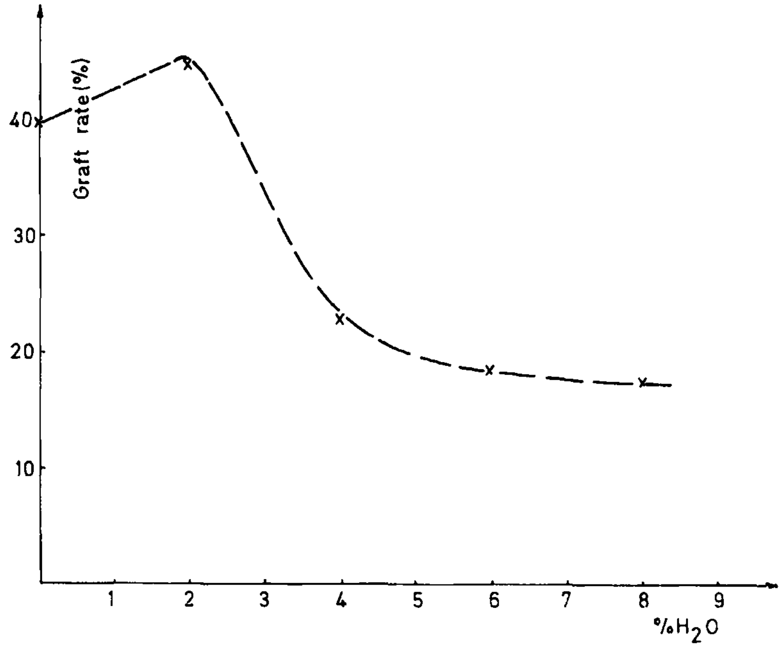

FIG. 2. Influence of water on grafting rate. Radiation dose, 2.5 Mrad; dose rate, 310 rad/min; radiation temperature, 25°C; polymerization time, 24 hr; polymerization temperature, 50°C.

Irradiation Facilities

The irradiation was carried out by using a 3400 Ci Co-60 source (AECL Gamma Beam 150/B) at the Nuclear Research Center, of AEOI, for radiation studies. The sample mixtures were prepared as freeze-and-thaw systems in Pyrex ampoules or in the presence of air. They were irradiated at different distances from the source. Dose rates were varied within the range 55-1300 rad/min, as measured by the ferrous sulfate dosimeter assuming $G_{Fe^{3+}} = 15.5$.

Materials

The vinylic monomers used were provided by Merck with a high degree of purity. To get rid of small traces of hydroquinone (0.02%) as a strong stabilizer of the styrene and acrylonitrile, they were

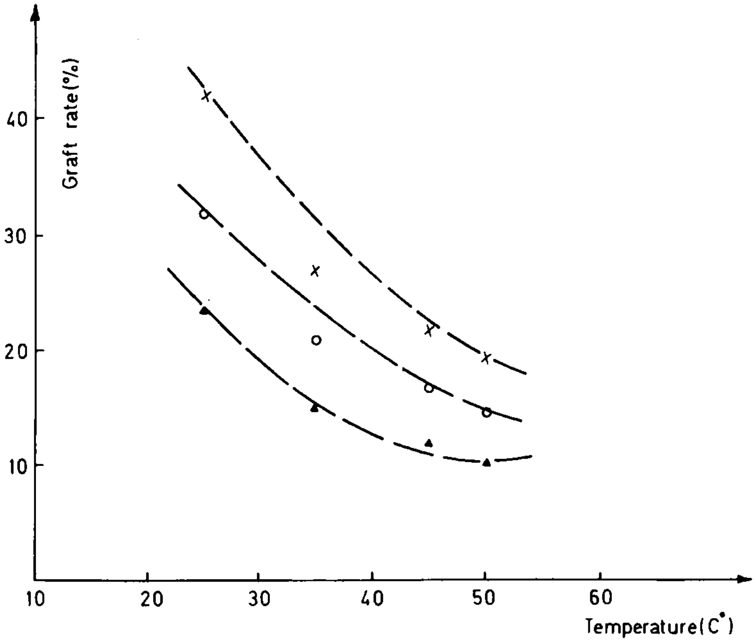

FIG. 3. Influence of temperature during irradiation on grafting rate: (x) styrene/methanol/H_2O = 76/22/2; (○) styrene/methanol = 80/20, no water; (▲) styrene/methanol/H_2O = 72/20/8. Irradiation dose, 1.28 Mrad; dose rate, 1300 rad/min; polymerization temperature, 50°C.

redistilled under high vacuum with nitrogen pressure of about 10 Torr at 33.6°C and at atmospheric pressure at 72°C, respectively.

RESULTS AND DISCUSSION

Influence of Dose

As mentioned previously, different methods were tried for the study of reaction, and the results are compared. The relationship between the radiation dose and graft polymerization of styrene with methanol or dioxane as a solvent was studied. In simultaneous and pre-irradiation techniques, dose rates of 1300 and 570 rad/min with polymerization

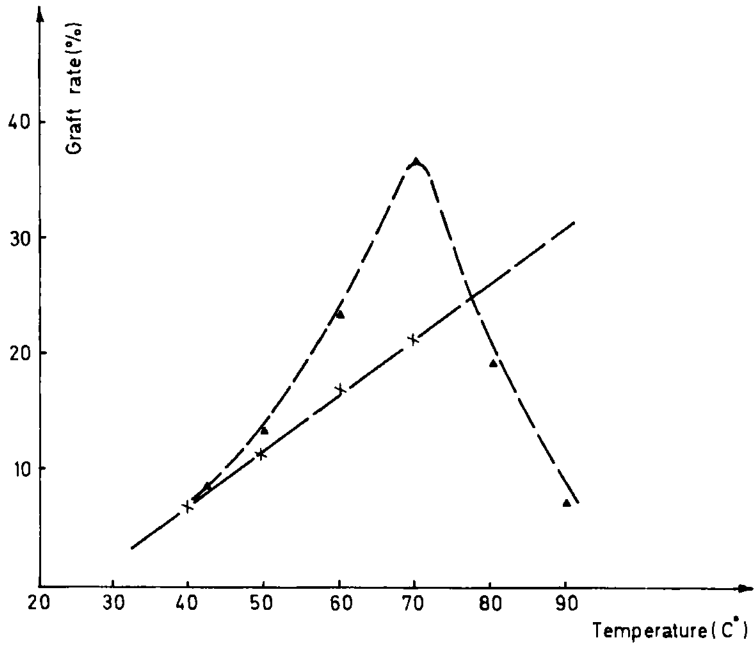

FIG. 4. Influence of graft polymerization temperature on grafting rate: (x) simultaneous grafting, styrene/methanol/H_2O = 72/20/8; (▲) pre-irradiation grafting, styrene/dioxane/H_2O = 76/22/2. Radiation dose, 2 Mrad; dose rate, 1300 rad/min.

temperature of 50 and 70°C were chosen, respectively. As it is seen in Fig. 1, the grafting yield and the rate of homopolymerization, respectively, increase up to 3 Mrad, and then reach a state at which they deviate from linearity. Thus, the number of trapped radicals produced during the reaction is proportional to the dose in the range studied. Consequently it appears that the degree of grafting is proportional to the concentration of the trapped radicals. Swelling of the cellulose in water vapor before irradiation leads to higher percentage of grafting and saturation dose.

Influence of Water

The influence of water on graft polymerization of styrene was tested with methanol as a solvent. Addition of water to the styrene system enhances grafting considerably, since the radiolysis products of water contribute to the overall reaction.

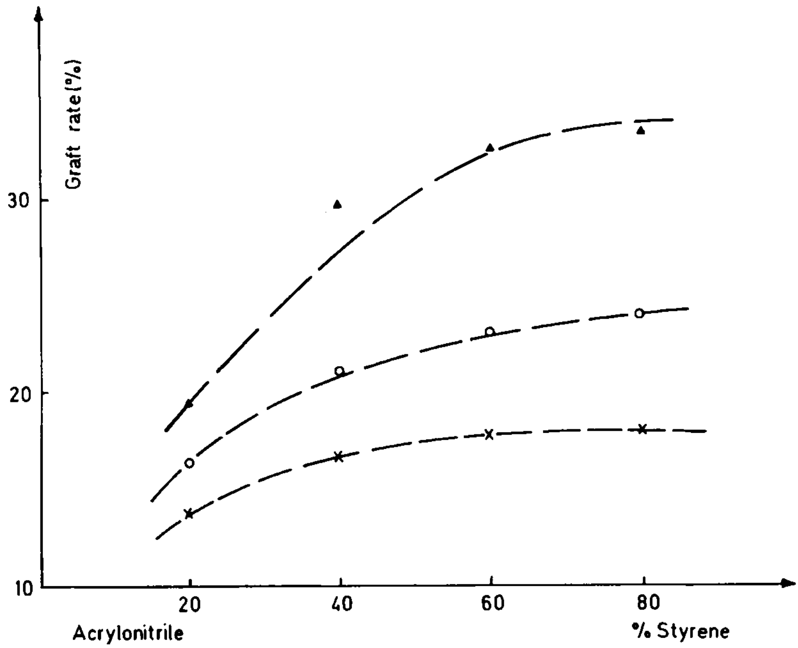

FIG. 5. Influence of styrene content on grafting rate: (x) dose 4 Mrad; (○) dose 6 Mrad; (▲) dose 8 Mrad.

Radicals such as $H_3O^\cdot$ and $OH^\cdot$ serve to abstract hydrogen from molecules, thus creating activated sites which serve as centers of grafting.

The results in Fig. 2 show a maximum at 2% of water mixture at 25° C. The grafting rate is reduced if the samples are saturated with water.

Influence of Temperature during Irradiation

Figure 3 represents a correlation between temperature during irradiation (25-50° C) and graft rate in the simultaneous system.

It was observed that in different compositions of styrene, methanol and H_2O, the rate of graft reaction is lowered to approximately 45% with increasing temperature and saturation in water.

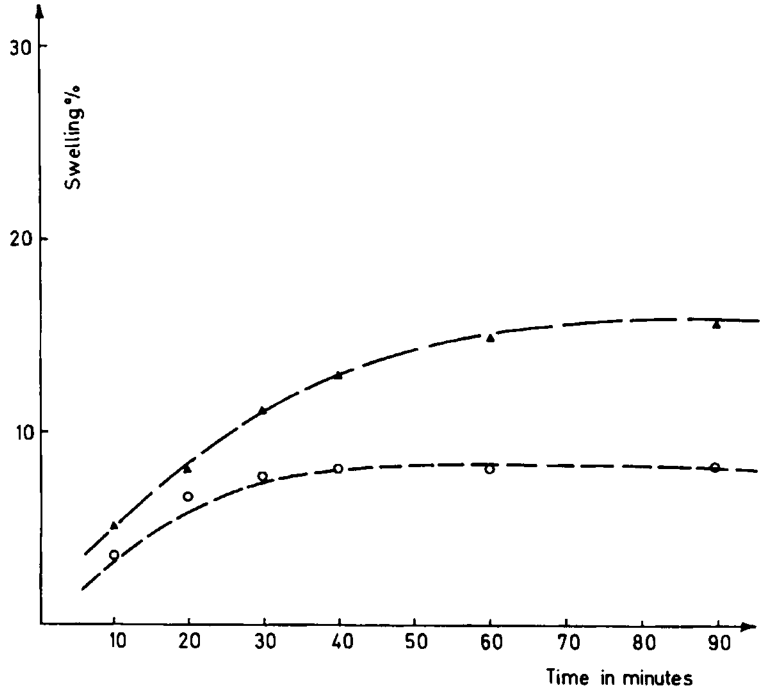

FIG. 6. Effect of water on the swelling of rice husks: (▲) 2% water; (○) no water.

Influence of Graft Polymerization Temperature

The effect of temperature studied in the range of 40-90°C. A maximum is observed after 24 hr of reaction at 70°C (an optimum condition), as shown from the diagram of variation of percentage grafting versus temperature (Fig. 4). This maximum can be interpreted as due to the balance between penetration of the reacting solution and thermal termination which is achieved by the particular temperature.

Influence of Monomers Concentration

The variation of percentage grafting with the contents of grafting monomers (styrene/acrylonitrile) is shown in Fig. 5. As is observed from this figure, there is a maximum in the percentage of grafting at

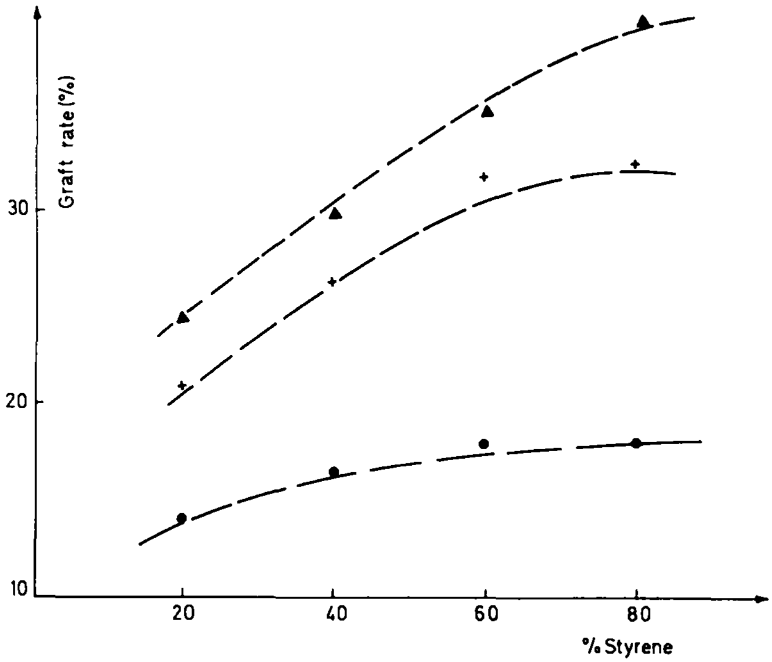

FIG. 7. Influence of water and water vapor on grafting rate: (▲) dose 4 Mrad, 2% water; (+) dose 4 Mrad, water vapor present; (●) dose 4 Mrad, no water present.

about 80% styrene in acrylonitrile. Obviously, the grafting rate is increased with the dose.

Effect of Water as a Swelling Agent on the Graft Copolymerization

In order to minimize the main-chain degradation of cellulose in high dose and dose rates, the effect of water and water vapor on the reaction was studied. The results shown in Fig. 6 demonstrate the importance of 2% H_2O as a swelling agent for cellulose. As it is shown in Fig. 6, in the absence of water, the degree of swelling reaches an equilibrium more rapidly than observed with when it is absent. This is attributed to the adsorption of the monomer solution onto the husk rice surface but not its penetration into the substrate.

The water and water vapor present in the system favor the reaction of grafting on cellulose (Fig. 7). For example, the weight gain observed with the dose of 1 Mrad is 18%, whereas when the reaction mixture is completely saturated with water vapor the weight gain is 32.5% and in a system with 2% water, 40.1%. Thus under optimum conditions (80: 18:2 styrene; acrylonitrile; water), when the dose is lowered from 8 to 4 Mrad, the grafting percentage is increased considerably.

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