

# Radiation-Induced Wood Plastic Composites Under Combinations of Monomers

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## SYNOPSIS

Radiation-induced wood plastic composites (WPC) were prepared from five varieties of Bangladeshi timbers, using seven different types of monomers. The mixtures of double and triple monomers were investigated along with the single-monomer system for the preparation of composites. Among the three systems, single-monomer process showed the highest polymer loading with butylmethacrylate (BMA). Tensile strength (TS) property, represented as  $T_f = TS_{\text{WPC}}/TS_{\text{wood}}$  was determined. Highest  $T_f$  values were achieved with the soft wood. The effects of dose and dose rate, monomer concentration, and swelling agent were also studied. Suitable total dose was found to be 3 Mrad at 0.8 Mrad/h, and methanol exhibited the best swelling ability for the woods at a ratio of 1 : 9 v/v in all the monomer investigated.

## INTRODUCTION

Composites are prepared with wood when suitable monomer is impregnated into the wood, normally under pressure, and then the monomer undergoes polymerization either by heat or by radiation to form a plasticlike material that is very similar to cellulose constituent of wood. Polymerization may form homopolymer and copolymer, and their ratio depends on the nature of monomer and the binding capacity of the substrate with monomer units. The binding capacity is, in turn, dependent on the structure of wood and the nature of the monomer used. Thus, a single monomer or a combination of monomers may influence the composite formation with a particular substrate system. It has been reported earlier<sup>1</sup> that wood plastic composite (WPC) formation was studied with ten different types of monomers using six kinds of soft and hard timbers. In each case a single monomer was used. Under the present investigation, cross combination of several different types of monomers was used with five varieties of timbers from Bangladesh.

## EXPERIMENTAL

Wood samples were prepared from long grained plank of kadom (*Anthocephalus cadamba*), simul (*Salmalia malabarica*), koroi (*Samanea samane*), mango (*Mangifera indica*), and debdaro (*Polyalthia longifolia*). Their respective densities were 0.36, 0.40, 0.44, 0.51, and 0.71 g/cm<sup>3</sup> under oven-dry condition. They were uniformly polished with sandpaper. Beakers containing wood samples were placed in a desiccator that was then evacuated for one hour at 50 mmHg. Without interrupting the vacuum, a solution of monomer or mixture of monomers in methanol with a ratio of 9 : 1 v/v was introduced. All the samples were kept completely immersed in the solution for 15 h. The samples were then taken out of the solution, wiped out, encapsulated with polyethylene bags, and then placed for irradiation. Styrene (ST), methylmethacrylate (MMA) butylmethacrylate (BMA), methylacrylate (MA), vinyl acetate (VA), acrylonitrile (AN), and methacrylonitrile (MAN) were used as monomers while methanol was used as the swelling agent, which was found to be the best among all other alcohols used as the swelling agents. Samples were irradiated at room temperature by gamma rays from <sup>60</sup>Co source (50 KCi) of Bangladesh Atomic Energy Commis-

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sion, at a dose rate 0.2–1.4 Mrad/h and the total dose was 1–4 Mrad. Untreated monomer was completely removed from the irradiated samples by heating them at 60°C under vacuum (50 mmHg). Polymer loading (PL) was calculated by using the following equation:

$$PL = \frac{W_2 - W_1}{W_1} \times 100$$

where  $W_1$  = weight of untreated sample and  $W_2$  = weight of treated sample. Tensile strength (TS) of treated and untreated woods was directly measured by the tensile strength machine of INSTRON, (Model 1011, U.K.) integrated with a personal computer (Amastrad PC 1640 HD20, U.K.).  $T_f$  is a tensile strength factor that can be determined from the TS values of WPC divided by the TS values of the untreated wood samples, i.e.,  $T_f = TS_{wpc}/TS_{wood}$ .

## RESULT AND DISCUSSION

Wood plastic composite formation was studied with five wood species and seven types of monomers. In this particular investigation, polymer loading was determined to monitor the change of tensile strength of the composites formed in the presence of a single monomer, double monomers, or triple monomers. However, it was necessary to find out the optimum dose needed for the maximum polymer loading. It is also known that the swelling property of the wood fiber enhances the copolymerization process. Thus, it was needed to investigate the swelling affinity of the wood for a number of swelling agents.

### Dose and Dose Rate

Percentage of polymer loading of MMA into simul and mango was determined at different dose rates (e.g., 0.20, 0.25, 0.80, and 1.40 Mrad/h) as well as at different total doses from 0.5 to 4 Mrad. The results are shown in Figure 1, and these indicate that PL increases with total dose up to 3 Mrad for simul and mango, and the increase is also observed as the dose rate is enhanced. The PL is found to increase with the enhanced dose rate, but this is true only up to 0.8 Mrad/h. When the higher dose rate of 1.40 Mrad/h was used, PL was minimum. Many primary radicals are produced at such high dose rates, most of which combine with each other and do not initiate polymerization.<sup>2</sup>

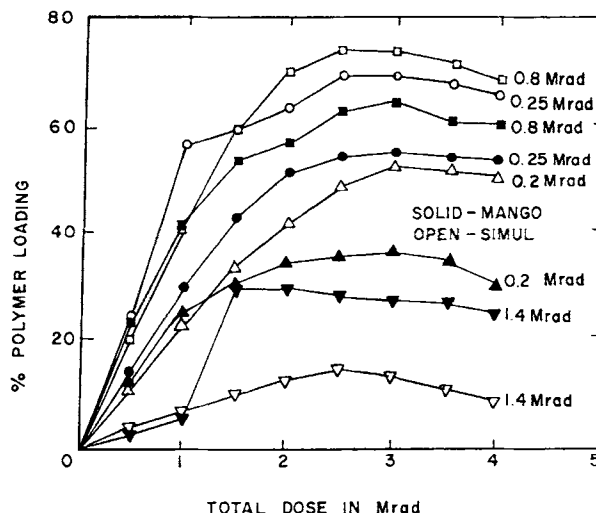
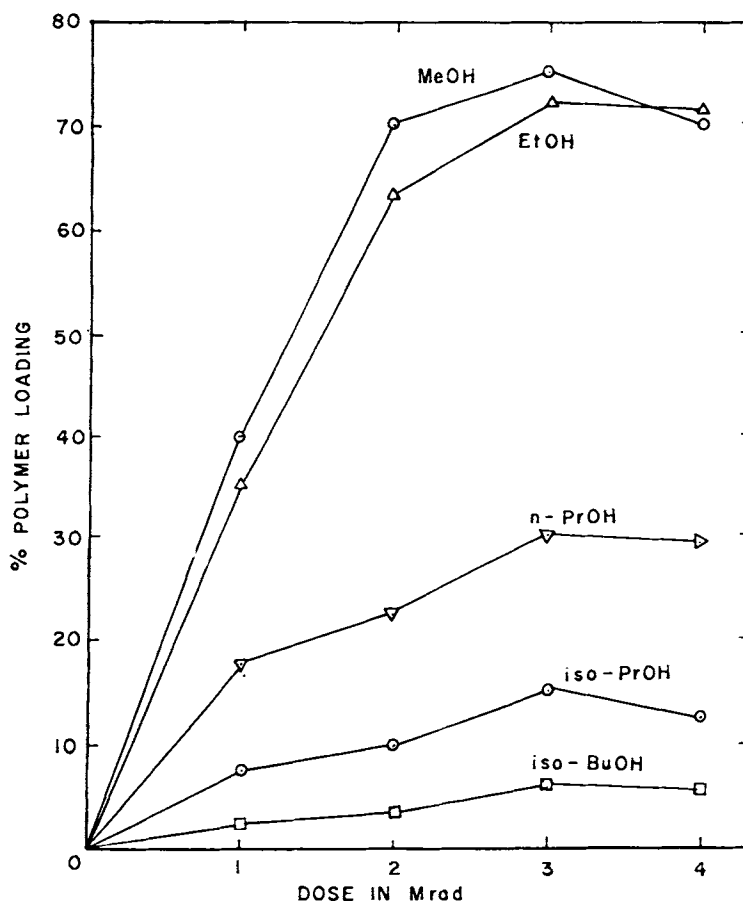


Figure 1 Polymer loading is plotted against irradiation dose as a function of dose rate.

### Swelling Agents

Polymer loading of MMA into simul was studied using different types of alcohol, such as methanol, ethanol, *n*-propanol, iso-propanol, and iso-butanol as swelling agents at a fixed dose rate of 0.8 Mrad/h but using different total doses from 1 to 4 Mrad. In each case the ratio of monomer–alcohol was 9 : 1 v/v. From these data of Figure 2, it is obvious that as the chain length of the solvent alcohol is increased from the methanol to butanol there is a significant and rapid decrease in the PL of MMA in simul. Thus methanol is the best of the alcohols for radiation grafting of monomer to cellulose. The methanol effect was attributed predominantly to swelling of the trunk polymer (cellulose), although radiolytic effects were also important. The observation of extensive grafting in methanol may be related to several phenomena. First, methanol not only possesses a swelling power approaching that of water, but also has the added advantage of being miscible with monomers in all proportions, thus simplifying its access and diffusion. The situation changes during the course of the irradiation. The increasing volume of the grafted polymer assists the swelling and breaking up of the cellulose structure. A second important advantage of methanol is that solvent radicals as the primary radiation species may activate the trunk polymer. This result is consistent with the swelling property of the cellulose where the relative sorptive and swelling properties fall significantly on proceeding through the alcohol series.<sup>3</sup>



**Figure 2** Effect of various swelling agents on polymer loading of MMA in simul at different doses.

### Monomer Concentration

Polymer loading of MMA into simul was investigated by varying the MMA concentrations from 10 to 100% v/v in methanol at a fixed dose rate 0.8 Mrad/h and total doses from 1 to 4 Mrad. The results are shown in Figure 3. These indicate that percent PL increases initially with increase of monomer concentration up to 90% and decreases beyond this concentration. Reactivity of monomer with cellulose molecules is expected to be enhanced as the concentration of monomers increases; but when the monomer concentration increases beyond 90%, monomer-monomer radical reactions dominate the polymerization process more than the monomer-cellulose reactions. Rate of monomer radical diffusion is affected at higher monomer concentration due to polymer deposit, which causes "gel effect" by increasing viscosity of the monomer medium. Similar observations were also noted by other workers<sup>4</sup> with different types of cellulose.

### Single Monomer

Polymer loading of each of the seven monomers into different wood species was determined and is given in Table I. Total dose used for WPC was up to 4 Mrad. Most of the wood species showed the maximum PL at about 3 Mrad. From Table I it is observed that soft wood (kadom simul, koro, mango) has exhibited more PL than the hard wood (debdaro) in the corresponding monomer system.

### Double and Triple Monomers

Selection of combinations of monomers was made by simple permutation with seven monomers. Thus, 21 sets of solutions with double-monomer systems were studied; however, in the case of triple-monomer systems, only 25 sets of solutions were investigated. Results of the three systems are given in Table II. The results of Tables I and II show that better PL

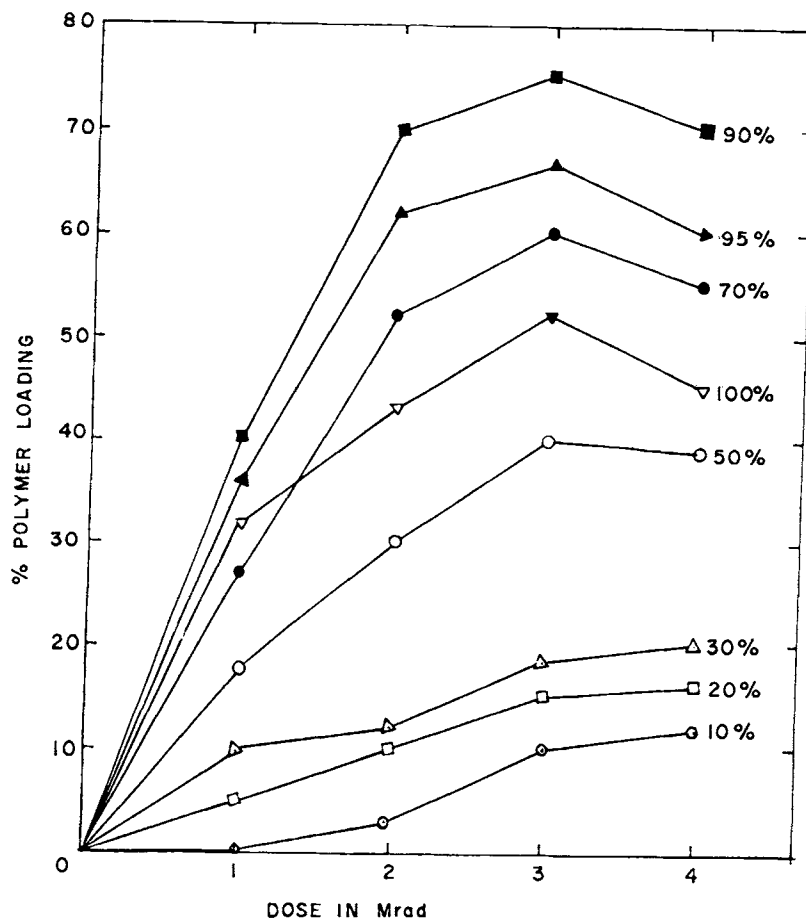


Figure 3 Polymer loading in simul at different MMA concentrations under different doses.

was obtained with the single-monomer system, followed by double- and triple-monomer processes, except for some double-monomer systems. Better PL was also achieved with soft wood than with hard wood in all three cases. These may indicate that during the WPC process, monomer radicals are first formed by radiation; these radicals then undergo

homopolymerization (same monomer units interaction), copolymerization (different monomer units interaction), or grafting (monomer units interaction with wood fiber). In the case of triple and double monomers, copolymerization seems to be dominant whereas grafting (polymer loading) is more plausible in the single-monomer system.

Table I Percentage of the Highest Polymer Loading of Wood Shown against the Total Dose Used for Achieving Highest PL (Single Monomer)

Monomer	Kadom	Simul	Koroi	Mango	Debdaro
ST	56 (3)	41 (3)	35 (4)	30 (3)	16 (4)
BMA	95 (4)	75 (3)	56 (2)	53 (2)	45 (3)
MA	87 (3)	85 (3)	55 (3)	51 (3)	45 (4)
VA	76 (3)	65 (4)	39 (3)	58 (4)	38 (3)
MMA	69 (2)	53 (3)	48 (3)	49 (3)	26 (2)
AN	53 (3)	26 (3)	18 (2)	32 (2)	12 (3)
MAN	24 (3)	18 (3)	15 (3)	18 (4)	17 (3)

**Table II Percentage of Highest Polymer Loading of Wood Shown against the Total Dose Used for Achieving the Highest PL**

Monomers	Kadom	Simul	Koroi	Mango	Debdaro
<i>Double Monomers</i>					
MMA + ST	124 (2)	81 (3)	53 (3)	67 (3)	47 (3)
MMA + BMA	69 (3)	47 (3)	79 (3)	49 (2)	29 (3)
MMA + MA	27 (4)	27 (4)	19 (3)	16 (4)	14 (4)
MMA + MAN	46 (4)	26 (4)	14 (4)	24 (4)	19 (4)
MMA + AN	64 (4)	25 (4)	17 (3)	31 (4)	20 (4)
MMA + VA	30 (3)	22 (4)	14 (4)	19 (4)	11 (4)
BMA + ST	57 (3)	51 (4)	11 (3)	32 (3)	29 (4)
BMA + MA	91 (3)	90 (4)	43 (3)	58 (4)	43 (4)
BMA + MAN	26 (3)	20 (4)	06 (3)	19 (1)	11 (4)
BMA + AN	90 (3)	83 (4)	30 (3)	35 (1)	19 (4)
BMA + VA	51 (4)	47 (4)	25 (4)	31 (4)	48 (1)
MA + ST	90 (4)	26 (2)	22 (4)	42 (4)	37 (4)
MA + MAN	19 (4)	13 (4)	44 (2)	14 (4)	16 (4)
MA + AN	41 (4)	56 (4)	17 (4)	35 (4)	30 (4)
MA + VA	18 (3)	29 (3)	16 (4)	07 (3)	08 (2)
ST + MAN	39 (3)	14 (2)	09 (4)	20 (3)	16 (4)
ST + AN	94 (4)	63 (1)	17 (4)	42 (4)	22 (4)
ST + VA	31 (4)	09 (4)	06 (4)	20 (4)	05 (4)
VA + AN	40 (4)	21 (3)	17 (4)	28 (4)	14 (4)
VA + MAN	10 (4)	11 (4)	08 (4)	07 (4)	09 (4)
AN + MAN	17 (4)	15 (4)	05 (3)	10 (3)	13 (4)
<i>Triple Monomers</i>					
ST + MMA + BMA	76 (4)	44 (4)	20 (4)	41 (4)	15 (2)
ST + MMA + MA	65 (4)	42 (4)	17 (4)	35 (4)	14 (3)
ST + MMA + VA	46 (4)	40 (4)	10 (4)	22 (4)	10 (4)
ST + MMA + AN	53 (4)	51 (4)	19 (4)	42 (4)	11 (4)
ST + MMA + MAN	47 (4)	30 (4)	26 (3)	27 (4)	23 (4)
ST + VA + MAN	53 (4)	24 (4)	15 (4)	18 (3)	10 (4)
ST + VA + AN	48 (4)	42 (3)	16 (4)	34 (4)	13 (3)
ST + BMA + MA	68 (3)	61 (4)	38 (4)	58 (4)	21 (3)
ST + BMA + AN	55 (3)	84 (3)	18 (4)	52 (3)	8 (4)
ST + MAN + MA	28 (4)	15 (4)	12 (4)	16 (3)	11 (4)
MMA + BMA + MA	71 (2)	41 (2)	32 (2)	38 (4)	30 (4)
MMA + BMA + AN	15 (4)	12 (4)	13 (4)	15 (4)	7 (4)
MMA + BMA + MAN	26 (4)	17 (4)	9 (4)	15 (3)	24 (4)
MMA + BMA + VA	25 (3)	22 (2)	22 (4)	21 (4)	16 (4)
MMA + MAN + MA	29 (4)	16 (4)	20 (4)	22 (4)	14 (4)
MMA + MAN + AN	33 (4)	26 (4)	16 (4)	19 (4)	30 (4)
MMA + MAN + VA	18 (4)	18 (4)	13 (4)	10 (4)	7 (3)
MMA + AN + VA	11 (4)	10 (4)	8 (4)	7 (4)	5 (4)
MMA + MA + VA	34 (4)	23 (4)	18 (3)	19 (4)	16 (4)
BMA + MA + AN	20 (4)	20 (3)	22 (4)	24 (4)	26 (4)
BMA + AN + MAN	16 (4)	32 (4)	19 (4)	16 (4)	18 (4)
BMA + VA + MAN	52 (4)	55 (4)	23 (4)	30 (4)	26 (4)
BMA + VA + AN	25 (4)	22 (4)	22 (4)	21 (4)	16 (4)
VA + MAN + AN	22 (4)	16 (4)	19 (4)	15 (4)	13 (4)
VA + AN + MA	29 (4)	25 (4)	22 (3)	19 (4)	16 (3)

Table III Tensile Strength Factor  $T_f$  against the Corresponding PL<sup>a</sup>

Monomer	Wood									
	Kadom		Simul		Koroi		Mango		Debdaro	
	PL	$T_f$	PL	$T_f$	PL	$T_f$	PL	$T_f$	PL	$T_f$
<i>Single Monomer</i>										
ST	56	2.21	17	1.93	15	2.55	31	2.20	16	1.40
BMA	95	1.24	70	1.16	53	3.01	53	2.19	45	2.32
MA	87	2.04	14	1.10	45	1.33	42	2.19	45	1.64
VA	76	1.55	5	1.01	34	2.15	46	1.95	38	1.46
MMA	69	1.53	49	2.73	43	1.77	43	1.03	26	1.39
AN	53	2.15	25	1.63	28	2.04	32	1.93	12	1.05
MAN	24	1.76	18	1.21	15	1.26	69	2.08	17	1.23
<i>Double Monomers</i>										
MMA + ST	50	1.95	70	1.11	43	1.88	59	1.09	12	1.19
MMA + BMA	50	2.25	44	0.99	24	1.99	26	1.11	24	0.81
MMA + MA	23	1.22	18	1.28	18	1.12	12	1.14	08	1.31
MMA + MAN	46	1.26	13	1.31	10	1.51	22	1.27	14	1.09
MMA + AN	51	2.16	20	1.19	17	1.47	—	—	13	1.08
MMA + VA	17	0.76	19	0.70	07	1.34	12	0.68	06	1.58
BMA + ST	57	1.16	38	1.24	10	1.43	23	0.87	21	0.90
BMA + MA	19	0.99	60	0.86	36	1.39	43	1.85	27	0.96
BMA + MAN	22	1.40	13	0.67	05	1.20	10	1.07	08	1.5
BMA + AN	43	0.85	51	1.12	22	1.34	30	1.00	10	1.03
BMA + VA	45	1.34	43	1.29	19	1.61	27	1.02	42	1.35
MA + ST	63	1.21	23	1.43	16	1.63	26	1.16	18	0.95
MA + MAN	06	1.07	06	0.84	04	1.06	06	0.49	06	1.09
MA + AN	126	1.48	44	1.23	06	1.19	24	1.49	09	1.59
MA + VA	08	1.25	29	1.95	16	1.48	05	0.78	08	0.59
ST + MAN	39	0.71	13	1.34	07	1.27	17	1.11	14	1.02
ST + AN	56	1.17	63	1.29	17	1.58	42	1.12	16	1.13
ST + VA	11	1.05	05	0.97	04	1.03	15	0.93	04	1.07
VA + AN	34	1.50	16	1.22	09	1.38	16	0.76	10	1.51
VA + MAN	05	0.88	08	1.09	05	1.48	05	0.69	07	1.24
AN + MAN	13	0.73	07	0.70	04	1.27	07	1.01	07	1.00
<i>Triple Monomers</i>										
ST + MMA + BMA	76	0.74	43	0.94	42	1.57	41	0.84	19	0.96
ST + MMA + MA	64	1.21	35	0.94	14	0.61	42	1.35	17	0.59
ST + MMA + VA	46	0.90	22	1.02	10	1.18	38	1.36	10	0.76
ST + MMA + AN	53	—	42	1.09	10	0.89	51	1.35	18	1.49
ST + MMA + MAN	47	—	27	0.87	27	1.18	30	1.13	23	—
ST + VA + MAN	53	1.84	17	1.05	10	1.41	24	—	15	0.97
ST + VA + AN	48	—	24	1.31	12	1.19	42	0.92	34	1.09
ST + BMA + MA	68	1.99	51	0.93	21	1.81	60	1.06	07	—
ST + BMA + AN	24	1.16	84	1.82	08	1.53	21	0.57	23	1.36
ST + MAN + MA	28	1.15	15	0.84	11	1.42	20	0.90	11	1.81
MMA + BMA + MA	41	0.61	42	0.79	43	1.79	71	0.73	11	—
MMA + BMA + AN	22	0.83	12	1.52	08	0.87	15	1.18	07	0.78
MMA + BMA + MAN	15	1.74	25	0.73	09	1.09	54	1.04	33	1.54
MMA + BMA + VA	06	0.57	42	0.48	05	0.97	05	1.43	07	1.28
MMA + MAN + MA	29	0.56	16	1.05	13	1.26	16	1.16	20	0.47

Table III (Continued)

Monomer	Wood									
	Kadom		Simul		Koroi		Mango		Debdaro	
	PL	$T_f$	PL	$T_f$	PL	$T_f$	PL	$T_f$	PL	$T_f$
MMA + MAN + AN	33	1.06	18	1.34	16	1.77	19	1.12	30	1.12
MMA + MA + VA	34	0.93	18	1.46	18	0.89	23	1.81	19	1.78
MMA + MAN + VA	11	1.64	12	1.24	08	0.77	10	1.07	18	1.82
MMA + AN + VA	22	1.60	11	1.13	—	—	08	0.99	10	1.71
BMA + MA + AN	20	1.17	20	1.35	14	1.15	24	1.19	26	—
BMA + AN + MAN	16	—	32	1.41	19	1.42	16	1.39	18	0.62
BMA + VA + AN	25	—	22	0.78	22	—	21	1.17	16	—
VA + MAN + AN	31	1.13	16	1.18	16	1.29	16	1.22	19	1.12
AN + MA + VA	22	0.81	19	0.67	29	1.36	24	1.01	17	1.95

$$^* T_f = TS_{wpc}/TS_{wood}$$

### Tensile Property

Tensile strength measurement is one of the better ways of determining the extent of improvement of wood property on WPC formation using single, double or triple monomers. Here WPC sample of any PL value was arbitrarily taken, and its TS value was then determined to evaluate the corresponding  $T_f$  values. Results are mentioned in Table III for single-, double-, and triple-monomer systems. The  $T_f$  values of any particular wood system are observed to be higher in the single-monomer profile than the corresponding double- and triple-monomer processes. This would signify that wood species attains better mechanical property (TS) on WPC using single monomer than double or triple monomers. However, there have been some cases with double and triple monomers also where mechanical property has decreased on WPC. Thus, it may be suggested that it is obvious to use single-monomer system for any WPC formation than the double- or triple-monomer systems. In fact, the latter processes are more costly and cumbersome.

The authors acknowledge the cooperation of the members of the radiation chemistry laboratory of the Institute of Nuclear Science and Technology (INST.) and those of the  $^{60}\text{Co}$  source facility of the Institute of Food and Radiation Biology (IFRB). They are grateful to the International Atomic Energy Agency (IAEA) for granting them the financial support under the Technical Assistance Program BGD/8/008.

### REFERENCES

1. M. A. Khan and K. M. I. Ali, *J. Appl. Polym. Chem.*, to appear.
2. A. Chapiro and J. Dannon-Seban, *J. Chem. Phys.*, **54**, 776 (1957).
3. S. Dilli, J. L. Garnett, E. C. Martin, and D. H. Phuoc, *Proceedings of the Symp. on Graft Polymerization onto Cellulose*, Jett. C. Arthur, Jr. Ed., Interscience, New York, 1972, p. 57.
4. H. Haworth and J. R. Holker, *J. Soc. Dyers Colour*, **82**, 257, (1966).

Received August 19, 1991

Accepted October 30, 1991