

Wood Plastic Composite Using Different Monomers in Presence of Additives

MUBARAK A. KHAN* and K. M. IDRIS ALI

Radiation Chemistry Laboratory, Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission, P.O. Box 3787, Dhaka, Bangladesh

SYNOPSIS

Wood plastic composites (WPC) are prepared with low density wood simul under Co-60 gamma radiation using acrylamide (AM), butyl methacrylate (BMA), and styrene (ST) as the bulk monomers at different compositions with methanol used as swelling agent. The effect of additives, e.g., polyfunctional monomers and oligomers, used by 1% v/v or w/v, on the polymer loading and tensile strength of the composites is investigated. Polyfunctional monomers are *N*-vinyl pyrrolidone (NVP), tripropylene glycol diacrylate (TPGDA), and trimethylol propane triacrylate (TMPTA). Oligomer additives are urethane acrylate (UA), epoxy acrylate (EA), and polyester acrylate (PEA). Increased polymer loading (PL) with enhanced tensile strength (TS) are obtained with the composite. Incorporation of a small amount (1% v/v or w/v) of coadditives like sulfuric acid (H^+), lithium nitrate (Li^+), copper sulfate (Cu^{2+}), and urea (U) into the impregnating solutions containing the additives has significantly influenced the PL and TS values of the WPC. Though the H^+ ion has synergistically enhanced the PL, but it has drastically reduced the TS values. Li^+ ion has played a good role for the replacement of H^+ ion. Urea has substantially increased the PL values with relatively small enhancement of TS. Cu^{2+} ions have retained both PL and TS values of the WPC, which could be used as protective and preservative purposes of the composites. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In the wood plastic composite (WPC) preparation, the role of impregnating monomers is very important. Some of the monomers are easily augmentable with the substrate during the composite formation under the impact of heat or irradiation. This depends on the structures and functional groups of the monomers. However, the cellular arrangement of the wood substrates shares similar importance for the composite preparation. Recently, some works were done to prepare the wood plastic composites using simul, a Bangladeshi soft wood in combination with different monomers.¹ The impact of organic and inorganic additives present with the bulk monomers is also studied on the tensile properties of the composites.^{2,3} In the present investigation, a set of three

bulk monomers such as styrene (ST), acrylamide (AM), and butyl methacrylate (BMA) was used to study their roles in the preparation of the composites in the presence of a number of additives from polyfunctional monomers and oligomers, and organic and inorganic coadditives, both used by 1% v/v or w/v.

EXPERIMENTAL

Substrate

Simul (*Salmalia malabarica*) wood samples (6.2 × 0.8 × 0.4 cm) were uniformly polished before removing free water from within the substrate by baking them at 70°C under 50 mm Hg pressure.

Monomer

Styrene (ST), acrylamide (AM), and butyl methacrylate (BMA) were procured from E. Merck and used as received.

* To whom correspondence should be addressed.

Additives

N-vinyl pyrrolidone (NVP), tripropylene glycol diacrylate (TPGDA), trimethylol propane triacrylate (TMPTA), urethane acrylate (UA), epoxy acrylate (EA), and polyester acrylate (PEA) were obtained from Ajax, Australia.

Coadditives

Sulfuric acid (H₂SO₄), copper sulfate (CuSO₄), lithium nitrate (LiNO₃), and urea (U) were procured from BDH, U.K.

Swelling Agent

Methanol (BDH) was used as the swelling solvent.

Method

Impregnating solutions were prepared with a monomer/methanol mixture which was combined with an additive and or coadditive. Wood samples soaked for 15 h in the above solution under vacuum (50 mm Hg) were packed in polyethene bags and were irradiated for 3 Mrad at 8 krad/h. These were then heated at 60°C under 50 mm Hg for removing the monomers, ascertained by the constant weight gain. Polymer loading (PL) was determined by the extent of weight gain by the samples. Tensile strength (TS) was measured with an Instron Model 1011 (U.K.). Change of tensile strength T_f was obtained from the relation $T_f = TS_{wpc}/TS_{wood}$, where TS_{wpc} is for the composite and TS_{wood} is for the wood.

RESULTS AND DISCUSSION

Vinyl monomers are normally used for preparing wood plastic composites by radiation technique, because these monomers can easily generate free radicals required for crosslinking purposes during the polymerization process. Three distinct vinyl monomers are used as the bulk monomers in this investigation. One of them is styrene (ST), containing an aromatic ring attached to the vinyl moiety, and is the cheapest among them, while others are acrylamide (AM) having carboamide group to the vinyl chain and the third monomer is the butyl methacrylate (BMA), which has a relatively long chain aliphatic acid group beside the vinyl backbone. All these monomers are soluble in conventional organic solvents, but only acrylamide is soluble in water at all proportions. When the composites are prepared

with simul wood using these monomers (AM, BMA, and ST) as the bulk monomer at different compositions (10–100%) with methanol as swelling agent, it is observed (Table I) that AM produces the highest polymer loading (PL) among these monomers followed by BMA and ST. In addition, this highest PL is obtained at 70% monomer (AM) concentration compared to 90% with BMA and ST and is more than twofold higher than that obtained with ST. It is believed that an equilibrium concentration of the impregnating solution is attained in the copolymerizing region of the backbone polymer (cellulose) of the substrate. The condition of the region may continually change depending on various factors prevailing during the time of the copolymerization. The partitioning/diffusion⁴ of the monomer and/or components of the impregnating solution is one of the factors in such a copolymerization process. Thus, the structural shape, ionic mobility, and possible affinity for interactions among the components of the impregnating solution are some of the factors to be considered. AM has possibly the most favorable partitioning/diffusion ability among the three monomers due to its structural advantages over BMA and ST; thus, AM may yield the highest PL with the highest tensile strength (TS), about 1.5 times higher than the TS values of the composites obtained with BMA or ST.

Effect of Additives

Two series of organic additives are used in order to study their impact on the copolymerization process between the wood substrate and the monomers as well as on the mechanical strength of the composites prepared in the presence of these additives. One set is chosen from a monomer like NVP, a monofunctional monomer (MFA), TPGDA, a difunctional monomer (DFM), and TMPTA, a trifunctional monomer (TFM). The second set is selected from oligomer, e.g., UA, containing urethane functional group, EA, having epoxy functional group, and PEA, which has a long chain backbone. These additives are used in a minute quantity 1% (v/v or w/v) with bulk monomer. It is observed (Table I) that TMPTA has produced the highest PL in all the three systems (AM, BMA, and ST) at 50% monomer composition. It is also noticed that the BMA + TMPTA system is more favorable to yield the highest PL compared to ST + TMPTA and AM + TMPTA systems. Additive NVP has the lowest influence for the copolymerization⁵ process between the substrate (simul) and the bulk monomer. However, NVP has

Table I Polymer Loadings (PL) in Presence of Additives at Different Monomer/Methanol Compositions

| Monomer | | | | | | | | | | | | |
|---------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|----|----|----|-----|
| Polymer Loading (%) | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | |
| | B | NV | TP | TM | B | NV | TP | TM | B | NV | TP | TM |
| 10 | 10 | 15 | 22 | 20 | 7 | 11 | 26 | 39 | 5 | 8 | 12 | 15 |
| 20 | 12 | 20 | 28 | 47 | 12 | 26 | 32 | 189 | 11 | 21 | 26 | 56 |
| 30 | 51 | 80 | 93 | 183 | 34 | 41 | 78 | 196 | 20 | 32 | 39 | 80 |
| 50 | 68 | 89 | 128 | 202 | 50 | 52 | 83 | 228 | 27 | 35 | 43 | 130 |
| 60 | 86 | 115 | 159 | 192 | 55 | 62 | 108 | 223 | 30 | 39 | 51 | 128 |
| 70 | 102 | 133 | 163 | 187 | 63 | 71 | 145 | 222 | 35 | 48 | 62 | 125 |
| 80 | 82 | 90 | 105 | 145 | 90 | 92 | 160 | 172 | 38 | 46 | 67 | 123 |
| 90 | 74 | 79 | 91 | 123 | 96 | 108 | 164 | 160 | 41 | 43 | 70 | 123 |

| Oligomer | | | | | | | | | | | | |
|---------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|----|----|----|-----|
| Polymer Loading (%) | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | |
| | B | UA | EA | PEA | B | UA | EA | PEA | B | UA | EA | PEA |
| 10 | 10 | 14 | 35 | 40 | 7 | 24 | 43 | 53 | 5 | 6 | 11 | 13 |
| 20 | 12 | 19 | 48 | 68 | 12 | 28 | 52 | 103 | 11 | 18 | 27 | 28 |
| 30 | 51 | 66 | 102 | 152 | 34 | 32 | 89 | 143 | 20 | 23 | 36 | 41 |
| 50 | 68 | 83 | 142 | 184 | 50 | 73 | 83 | 276 | 27 | 31 | 45 | 55 |
| 60 | 86 | 104 | 166 | 248 | 55 | 86 | 103 | 281 | 30 | 36 | 52 | 63 |
| 70 | 102 | 143 | 196 | 279 | 63 | 92 | 156 | 284 | 35 | 42 | 59 | 73 |
| 80 | 82 | 101 | 160 | 101 | 90 | 106 | 204 | 192 | 38 | 48 | 72 | 96 |
| 90 | 74 | 96 | 132 | 123 | 96 | 112 | 201 | 196 | 41 | 51 | 88 | 103 |

B, Blank (monomer + MeOH); NV, = *N*-vinyl pyrrolidone (NVP), 1% v/v; TP, tripropylene glycol diacrylate (TPGDA), 1% v/v; TM, trimethylol propane triacrylate (TMPTA); 1% v/v.

All used by 1% w/v: UA, urethane acrylate; EA, epoxy acrylate; PEA, polyester acrylate.

exhibited the maximum PL values in the presence of AM, the minimum being with ST. The enhanced PL imparted by TMPTA is due to the branching effect of the TMPTA molecule. The trifunctional moiety is more prone to augmentation between substrate backbone polymer (cellulose) and the bulk monomer through its ability for favorable crosslinking process. Thus, the difunctional monomer (TPGDA) has the less potentiality than TMPTA for the crosslinking process between the substrate and the bulk monomer. This may explain the fact that the additive initially combines with the bulk monomer through the free radical mechanism, creating a secondary free radical to the bulk monomer, which, in turn, reacts with the substrate.⁵ Thus, the polymer loading, which is a measure of the extent

of copolymerization, becomes higher as the functionality of the additives (and/or the bulk monomers) increases. However, when the mechanical strengths of the composites are considered, it is observed (Table II) that the composites formed in the presence of NVP are more mechanically strong than those formed with TPGDA and TMPTA. It was explained earlier³ that *N*-containing compound has the ability for better augmentation of the impregnating solution with the substrate backbone polymer (cellulose), though the polymer loading is found relatively low. The lone pair of electrons of the nitrogen may play some role for such behavior. Though TMPTA produces the highest PL values, it has yielded the composites with the second highest TS values in the series.

Table II Effect of Additives on TS of WPC of the Highest PL

| Additives | AM | | BMA | | ST | |
|-----------|-----|-------|-----|-------|-----|-------|
| | PL | T_f | PL | T_f | PL | T_f |
| Blank | 102 | 1.51 | 96 | 1.10 | 41 | 1.07 |
| NVP | 133 | 1.75 | 108 | 1.83 | 48 | 1.31 |
| TPGDA | 163 | 1.36 | 164 | 1.21 | 70 | 1.15 |
| TMPTA | 202 | 1.52 | 228 | 1.56 | 131 | 1.26 |
| UA | 143 | 1.65 | 112 | 1.60 | 51 | 1.31 |
| EA | 196 | 1.18 | 204 | 1.21 | 88 | 1.12 |
| PEA | 279 | 1.26 | 292 | 1.42 | 103 | 1.15 |

TS, tensile strength; $T_f = TS_{wpc}/TS_{wood}$.

It is quite interesting that the additive PEA has produced the highest polymer loading in the series of oligomers (UA, EA, and PEA) used as additives. BMA + PEA system yields the maximum PL while ST + PEA system gives the minimum PL values. The AM + PEA system enhances PL values very close to that of the BMA system. AM + oligomers produces the highest PL at 70% AM composition whereas the highest PL values obtained in ST + oligomers are at 90% ST concentration; but in the case of BMA + oligomers, these values are obtained at 80% BMA with the exception of UA + BMA, which yielded the highest PL at 90%. Among the series, UA yields the minimum PL values with the three bulk monomers. The maximum PL values rendered by PEA may be explained by the fact that polyester acrylate has a long chain backbone which can easily crosslink to form polymer. But epoxy acrylate (EA) has the epoxy groups along the oligomer backbone, which may delay the crosslinking process due to its structural or geometrical shape compared to that of the polyester. Urethane acrylate oligomer produces the minimum polymerization among the series, but the tensile strengths of the WPC formed in presence of UA as the additives are the highest. UA is an N-containing material like NVP. The presence of both these additives (UA and NVP) has been conducive to prepare WPC with enhanced TS. Apart from UA, PEA is more capable of producing WPC with stronger tensile property than EA. This is probably due to the better crosslinking ability of the PEA molecule with the bulk monomer and the substrate polymer backbones. Considering all the factors of PL and TS values, the BMA + simul system seems to be the best.

Effect of Coadditives

Sulfuric acid (H^+), lithium nitrate (Li^+), urea (U), and copper sulfate (Cu^{2+}) were used as coadditives

with the additives of multifunctional monomers (NVP, TPGDA, and TMPTA) and oligomers (UA, EA, and PEA) in order to study their effects on the polymer loading and tensile property of the WPC.

Acid (H^+)

When sulfuric acid is used as the additive, polymer loading values enhance quite substantially; the order of the increment with the bulk monomers is AM > BMA > ST (Table III). Though the PL increases in the presence of H^+ ions, the tensile strengths (TS) decrease (Table IV) below the values of the tensile strength of the untreated wood. H^+ ions break the long chain of the backbone polymer² (cellulose) of the substrate; thus, it renders reduced strength to the composites, even though it helps speed up the copolymerization process through the crosslinking of the individually segmented units of the polymer. When acid is used in combination with any additive selected from the monomer or oligomer series, it is observed that the PL values increase almost synergistically with all the additives except PEA, where PL values are suppressed in presence of H^+ ions. The overall highest PL values are obtained with the BMA (bulk monomer) and TMPTA (additive) systems. Acidification of the impregnating solutions change the mobility of the solution at the equilibrium condition of the components during the copolymerization process at the zone of the reactivity associated with the partitioning of the various components present in the solutions. The rate of reactivity coupled with the partitioning is, thus, enhanced for the overall copolymerization process in the presence of the acid. However, PEA which has a long chain has the delaying effect during the partitioning compared to other molecules of the additives. Thus, the PL values with PEA are reduced in the presence of the acid.

Lithium Nitrate (Li^+)

Incorporation of the lithium nitrate salt (1% w/v) into the formulations causes enhancement of the polymer loading with increased TS values for BMA and ST systems (Tables V, VI). There is, however, a slight reduction of TS values for the AM system when Li^+ ions is added to AM + simul. The Li^+ ion has favored the polymerization process, but this is not to the same extent as that due to H^+ ion addition. The beauty of Li^+ ion is that it does not break, like H^+ ions, the long chain of the backbone polymer (cellulose) during the reactivity. It, rather, retains the tensile property of WPC. Li^+ ion, thus, plays some significant part during the partitioning process in the overall WPC formation. Addition of Li^+ ion

Table III Effect of Coadditive Acid (H⁺) on PL in Presence of Additives at Different Monomer/Methanol Compositions

| Monomer | | | | | | | | | | | | |
|---------------------------------|---------------------|-----|-----|-----|----------------|-----|-----|-----|----------------|-----|-----|-----|
| Monomer (%) in MeOH (v/v) | Polymer Loading (%) | | | | | | | | | | | |
| | AM | | | | BMA | | | | ST | | | |
| | H ⁺ | a | b | c | H ⁺ | a | b | c | H ⁺ | a | b | c |
| 10 | 13 | 60 | 63 | 86 | 33 | 52 | 59 | 192 | 6 | 13 | 16 | 53 |
| 20 | 20 | 81 | 70 | 98 | 43 | 80 | 70 | 240 | 18 | 30 | 25 | 96 |
| 30 | 70 | 145 | 113 | 187 | 56 | 123 | 83 | 269 | 26 | 45 | 46 | 116 |
| 50 | 91 | 129 | 188 | 238 | 89 | 203 | 163 | 269 | 42 | 63 | 68 | 163 |
| 60 | 116 | 218 | 196 | 234 | 92 | 210 | 169 | 270 | 52 | 80 | 82 | 155 |
| 70 | 151 | 230 | 216 | 225 | 94 | 216 | 173 | 278 | 65 | 115 | 99 | 145 |
| 80 | 105 | 180 | 171 | 196 | 106 | 220 | 179 | 290 | 72 | 110 | 100 | 143 |
| 90 | 93 | 152 | 123 | 152 | 118 | 225 | 181 | 282 | 74 | 114 | 109 | 140 |

| Oligomer | | | | | | | | | | | | |
|---------------------------------|---------------------|-----|-----|-----|----------------|-----|-----|-----|----------------|----|----|----|
| Monomer (%) in MeOH (v/v) | Polymer Loading (%) | | | | | | | | | | | |
| | AM | | | | BMA | | | | ST | | | |
| | H ⁺ | d | e | f | H ⁺ | d | e | f | H ⁺ | d | e | f |
| 10 | 13 | 19 | 42 | 40 | 33 | 39 | 41 | 48 | 6 | 10 | 12 | 10 |
| 20 | 20 | 76 | 68 | 61 | 43 | 43 | 62 | 89 | 18 | 28 | 33 | 23 |
| 30 | 70 | 101 | 122 | 138 | 65 | 53 | 78 | 137 | 26 | 42 | 46 | 40 |
| 50 | 91 | 140 | 167 | 153 | 89 | 86 | 103 | 210 | 42 | 62 | 59 | 51 |
| 60 | 116 | 175 | 192 | 214 | 92 | 92 | 105 | 222 | 52 | 65 | 69 | 60 |
| 70 | 151 | 189 | 204 | 252 | 94 | 111 | 108 | 202 | 65 | 73 | 73 | 68 |
| 80 | 105 | 145 | 183 | 151 | 106 | 108 | 121 | 142 | 72 | 82 | 88 | 79 |
| 90 | 93 | 143 | 153 | 112 | 118 | 102 | 131 | 116 | 74 | 84 | 90 | 89 |

a, NVP + H⁺; b, TPGDA + H⁺; c, TMPTA + H⁺; d, UA + H⁺; e, EA + H⁺; f, PEA + H⁺; H⁺, H₂SO₄; 1% v/v.

as coadditive to the formulations containing bulk monomer and an additive (the latter being taken from monomer or oligomer series) causes substantial

Table IV Effect of Acid (H⁺) on TS of WPC with the Highest PL

| Additives and H ⁺ | AM | | BMA | | ST | |
|---------------------------------|-----|----------------|-----|----------------|-----|----------------|
| | PL | T _f | PL | T _f | PL | T _f |
| H ⁺ | 151 | 0.80 | 118 | 0.70 | 74 | 0.72 |
| NVP + H ⁺ | 230 | 1.22 | 225 | 1.09 | 114 | 1.12 |
| TPGDA + H ⁺ | 216 | 0.68 | 181 | 0.65 | 109 | 0.75 |
| TMPTA + H ⁺ | 238 | 0.82 | 290 | 0.88 | 163 | 0.92 |
| UA + H ⁺ | 189 | 0.87 | 111 | 0.68 | 84 | 0.72 |
| EA + H ⁺ | 204 | 1.11 | 131 | 1.01 | 90 | 1.01 |
| PEA + H ⁺ | 252 | 1.03 | 222 | 1.02 | 89 | 0.98 |

enhancement of PL values with almost all the series of AM, BMA, and ST except for the oligomer additives with AM and BMA where there has been some depletion of the PL values when Li⁺ ion is added to AM + oligomers and BMA + oligomers. With some exceptions, in most of the cases, TS values have increased with the enhanced PL. This is an added merit of Li⁺ ions being used as coadditives in place of H⁺ ions.

Urea (U)

When urea is added to the bulk monomer, the PL increases with enhanced TS values with all three systems of AM, BMA, and ST (Tables VII, VIII). This increment in PL values is higher than Li⁺ ion systems but lower than H⁺ ion systems. The enhanced TS values in the presence of urea is very

Table V Effect of Coadditive Lithium (Li⁺) on PL in Presence of Additives at Different Monomer/Methanol Compositions

| Monomer | | | | | | | | | | | | | |
|---------------------------------|-----------------|-----|-----|-----|-----------------|-----|-----|-----|-----------------|----|----|-----|--|
| Polymer Loading (%) | | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | | |
| | Li ⁺ | a | b | c | Li ⁺ | a | b | c | Li ⁺ | a | b | c | |
| 10 | 10 | 16 | 19 | 25 | 14 | 10 | 27 | 42 | 4 | 8 | 11 | 17 | |
| 20 | 18 | 19 | 33 | 53 | 30 | 28 | 33 | 202 | 12 | 23 | 28 | 62 | |
| 30 | 62 | 83 | 107 | 195 | 47 | 45 | 76 | 220 | 23 | 38 | 35 | 92 | |
| 50 | 86 | 96 | 142 | 231 | 82 | 58 | 90 | 240 | 35 | 45 | 52 | 152 | |
| 60 | 101 | 126 | 176 | 208 | 86 | 71 | 118 | 235 | 43 | 53 | 63 | 148 | |
| 70 | 136 | 153 | 183 | 198 | 88 | 89 | 163 | 231 | 52 | 58 | 78 | 142 | |
| 80 | 98 | 97 | 126 | 156 | 97 | 109 | 165 | 183 | 57 | 93 | 83 | 140 | |
| 90 | 83 | 83 | 102 | 133 | 103 | 121 | 169 | 163 | 59 | 88 | 97 | 131 | |

| Oligomer | | | | | | | | | | | | | |
|---------------------------------|-----------------|-----|-----|-----|-----------------|-----|-----|-----|-----------------|----|----|-----|--|
| Polymer Loading (%) | | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | | |
| | Li ⁺ | d | e | f | Li ⁺ | d | e | f | Li ⁺ | d | e | f | |
| 10 | 10 | 13 | 18 | 28 | 14 | 10 | 16 | 26 | 4 | 7 | 13 | 12 | |
| 20 | 18 | 35 | 40 | 51 | 30 | 28 | 32 | 35 | 12 | 24 | 28 | 31 | |
| 30 | 62 | 70 | 90 | 109 | 47 | 71 | 61 | 66 | 23 | 28 | 42 | 42 | |
| 50 | 86 | 98 | 118 | 126 | 82 | 82 | 83 | 93 | 35 | 39 | 51 | 65 | |
| 60 | 101 | 114 | 129 | 143 | 86 | 93 | 96 | 115 | 43 | 40 | 63 | 86 | |
| 70 | 136 | 128 | 142 | 162 | 88 | 109 | 103 | 129 | 52 | 42 | 79 | 98 | |
| 80 | 98 | 121 | 136 | 143 | 97 | 120 | 121 | 138 | 57 | 68 | 87 | 106 | |
| 90 | 83 | 102 | 116 | 120 | 103 | 118 | 131 | 146 | 59 | 78 | 99 | 123 | |

a, NVP + Li⁺; b, TPGDA + Li⁺; c, TMPTA + Li⁺; d, UA + Li⁺; e, EA + Li⁺; f, PEA + Li⁺; Li⁺, LiNO₃; 1% w/v.

significant. Thus, when H⁺ ions, Li⁺, and urea are considered as the additives incorporated to any of the three bulk monomers, it is observed (Tables II,

Table VI Effect of Lithium (Li⁺) on TS of WPC with the Highest PL

| Additives and Li ⁺ | AM | | BMA | | ST | |
|----------------------------------|-----|----------------|-----|----------------|-----|----------------|
| | PL | T _f | PL | T _f | PL | T _f |
| Li ⁺ | 136 | 1.32 | 103 | 1.26 | 59 | 1.16 |
| NVP + Li ⁺ | 153 | 1.59 | 121 | 1.46 | 93 | 1.58 |
| TPGDA + Li ⁺ | 183 | 1.41 | 169 | 1.36 | 97 | 1.32 |
| TMPTA + Li ⁺ | 231 | 1.63 | 240 | 1.66 | 152 | 1.62 |
| UA + Li ⁺ | 128 | 1.26 | 120 | 1.21 | 78 | 1.19 |
| EA + Li ⁺ | 142 | 1.28 | 131 | 1.19 | 89 | 1.21 |
| PEA + Li ⁺ | 162 | 1.23 | 146 | 1.18 | 123 | 1.29 |

V, and VII) that urea is the best additive to be chosen for such purposes, because WPC formed in the presence of urea (1% w/v) yields high PL along with enhanced TS values. Urea is also cheap compared to Li-salt and acid. Electron density around the two carbonyl groups (=C=O) as well as beside the N-atom of the urea molecule may play some important role for diffusion/partitioning of the required component during the copolymerization process at the equilibrium condition phenomena of the system. Use of urea in combination with monomers (NVP, TPGDA, and TMPTA) and oligomers (UA, EA, and PEA) yields WPC, which exhibits sufficiently enhanced PL values with significant increment of TS. The highest TS values attained in the presence of NVP is of much interest. The effect of bulk monomers (AM, BMA, and ST) on PL and TS values in the presence of urea combined with an additive

Table VII Effect of Coadditive U on PL in Presence of Additives at Different Monomer/Methanol Compositions

| Monomer | | | | | | | | | | | | |
|---------------------------------|---------------------|-----|-----|-----|-----|-----|-----|-----|----|----|-----|-----|
| Monomer (%) in MeOH (v/v) | Polymer Loading (%) | | | | | | | | | | | |
| | AM | | | | BMA | | | | ST | | | |
| | U | a | b | c | U | a | b | c | U | a | b | c |
| 10 | 12 | 27 | 24 | 22 | 11 | 23 | 29 | 53 | 6 | 11 | 18 | 22 |
| 20 | 16 | 96 | 43 | 66 | 33 | 68 | 43 | 209 | 18 | 30 | 35 | 83 |
| 30 | 67 | 183 | 153 | 167 | 48 | 82 | 99 | 246 | 25 | 55 | 53 | 113 |
| 50 | 82 | 242 | 202 | 192 | 73 | 101 | 172 | 230 | 35 | 68 | 62 | 156 |
| 60 | 109 | 212 | 268 | 143 | 81 | 123 | 199 | 222 | 42 | 81 | 82 | 152 |
| 70 | 143 | 156 | 216 | 96 | 92 | 143 | 204 | 220 | 49 | 92 | 96 | 143 |
| 80 | 99 | 121 | 148 | 82 | 109 | 176 | 236 | 221 | 56 | 90 | 00 | 140 |
| 90 | 81 | 87 | 119 | 43 | 138 | 222 | 241 | 216 | 62 | 86 | 103 | 141 |

| Oligomer | | | | | | | | | | | | |
|---------------------------------|---------------------|-----|-----|-----|-----|-----|-----|-----|----|----|----|----|
| Monomer (%) in MeOH (v/v) | Polymer Loading (%) | | | | | | | | | | | |
| | AM | | | | BMA | | | | ST | | | |
| | U | d | e | f | U | d | e | f | U | d | e | f |
| 10 | 12 | 16 | 24 | 22 | 11 | 42 | 46 | 51 | 6 | 8 | 12 | 12 |
| 20 | 16 | 38 | 58 | 52 | 33 | 51 | 76 | 102 | 18 | 16 | 28 | 26 |
| 30 | 67 | 75 | 99 | 96 | 48 | 64 | 93 | 153 | 25 | 29 | 41 | 39 |
| 50 | 82 | 102 | 133 | 137 | 73 | 95 | 119 | 296 | 35 | 40 | 53 | 56 |
| 60 | 109 | 135 | 142 | 148 | 81 | 97 | 178 | 298 | 42 | 46 | 58 | 66 |
| 70 | 143 | 151 | 163 | 160 | 92 | 103 | 229 | 303 | 49 | 53 | 66 | 78 |
| 80 | 99 | 120 | 156 | 152 | 109 | 116 | 221 | 210 | 56 | 62 | 91 | 81 |
| 90 | 81 | 105 | 149 | 135 | 138 | 122 | 205 | 213 | 62 | 67 | 97 | 82 |

a, NVP + U; b, TPGDA + U; c, TMPTA + U; d, UA + U; e, EA + U; f, PEA + U; U, Urea, 1% w/v.

(monomer or oligomer) is reflected in these results in the sense that the highest PL and TS values are obtained with AM + NVP + U in the series of AM

+ monomer additives, whereas TMPTA + U shows the maximum PL values in BMA and ST systems in the presence of urea.

Table VIII Effect of Urea (U) on TS of WPC with the Highest PL

| Additives and U | AM | | BMA | | ST | |
|--------------------|-----|-------|-----|-------|-----|-------|
| | PL | T_f | PL | T_f | PL | T_f |
| U | 143 | 1.43 | 138 | 1.36 | 62 | 1.12 |
| NVP + U | 243 | 1.90 | 222 | 1.85 | 92 | 1.78 |
| TPGDA + U | 268 | 1.55 | 241 | 1.45 | 103 | 1.47 |
| TMPTA + U | 192 | 1.63 | 246 | 1.71 | 156 | 1.76 |
| UA + U | 151 | 1.70 | 122 | 1.69 | 67 | 1.25 |
| EA + U | 163 | 1.23 | 229 | 1.24 | 97 | 1.32 |
| PEA + U | 160 | 1.12 | 303 | 1.35 | 82 | 1.48 |

Copper Sulfate (Cu^{2+} Ions)

Cupric ion (Cu^{2+}) is known to play some significant role in the radiation process of the liquid solution, particularly through the electron-transfer mechanism⁶ from the primary free radicals to Cu^{2+} ions. Results in the Table IX show that there has been some depletion of the polymer loading in the presence of Cu^{2+} ions with the bulk monomers. This effect of Cu^{2+} ions is relatively low with ST compared to BMA and AM. It is of interest to note that the composites formed in the presence of Cu^{2+} ions retain their TS values without any reduction, though the PL values have been reduced, to some extent,

Table IX Effect of Coadditive Copper (Cu²⁺) on PL in Presence of Additives at Different Monomer/Methanol Compositions

| Monomer | | | | | | | | | | | | | |
|---------------------------------|------------------|-----|-----|-----|------------------|-----|-----|-----|------------------|----|----|-----|---|
| Polymer Loading (%) | | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | | |
| | Cu ²⁺ | a | b | c | Cu ²⁺ | a | b | c | Cu ²⁺ | a | b | c | |
| | 10 | 0 | 0 | 2 | 8 | 0 | 0 | 8 | 20 | 0 | 0 | 0 | 2 |
| 20 | 8 | 9 | 7 | 36 | 9 | 12 | 17 | 162 | 7 | 9 | 12 | 40 | |
| 30 | 48 | 75 | 83 | 178 | 19 | 29 | 60 | 178 | 16 | 21 | 27 | 71 | |
| 50 | 62 | 83 | 111 | 196 | 41 | 37 | 75 | 159 | 19 | 29 | 33 | 119 | |
| 60 | 84 | 105 | 143 | 189 | 48 | 53 | 98 | 157 | 23 | 32 | 43 | 120 | |
| 70 | 98 | 128 | 152 | 182 | 53 | 81 | 103 | 144 | 28 | 37 | 49 | 108 | |
| 80 | 82 | 86 | 97 | 141 | 87 | 87 | 131 | 133 | 32 | 36 | 56 | 103 | |
| 90 | 71 | 79 | 82 | 119 | 90 | 106 | 132 | 129 | 35 | 34 | 62 | 104 | |

| Oligomer | | | | | | | | | | | | | |
|---------------------------------|------------------|-----|-----|-----|------------------|-----|-----|-----|------------------|----|----|----|---|
| Polymer Loading (%) | | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | | |
| | Cu ²⁺ | d | e | f | Cu ²⁺ | d | e | f | Cu ²⁺ | d | e | f | |
| | 10 | 0 | 3 | 12 | 22 | 0 | 12 | 27 | 34 | 0 | 0 | 0 | 1 |
| 20 | 8 | 8 | 29 | 48 | 9 | 28 | 43 | 62 | 7 | 9 | 11 | 42 | |
| 30 | 48 | 51 | 83 | 143 | 19 | 29 | 93 | 123 | 16 | 17 | 38 | 34 | |
| 50 | 62 | 78 | 136 | 168 | 41 | 66 | 97 | 178 | 19 | 26 | 41 | 49 | |
| 60 | 84 | 97 | 152 | 238 | 48 | 78 | 123 | 267 | 23 | 32 | 48 | 55 | |
| 70 | 98 | 136 | 185 | 268 | 53 | 83 | 179 | 283 | 28 | 38 | 52 | 68 | |
| 80 | 82 | 92 | 151 | 147 | 87 | 98 | 181 | 289 | 32 | 41 | 72 | 83 | |
| 90 | 71 | 82 | 122 | 106 | 90 | 101 | 196 | 293 | 35 | 45 | 82 | 97 | |

a, NVP + Cu²⁺; b, TPGDA + Cu²⁺; c, TMPTA + Cu²⁺; d, UA + Cu²⁺; e, EA + Cu²⁺; f, PEA + Cu²⁺; Cu²⁺, CuSO₄, 1% w/v.

from those of simul + bulk monomer systems. Similar behavior of Cu²⁺ was also observed with the ST + simul system in the presence of these additives.⁷ This is possibly due to favorable Cu²⁺ ionic mobility of the organometallic complex formed at the equilibrium condition of the cellulose backbone of the substrate. This helps better augmentation of the organometallic moiety with the substrate (simul) cellulose backbone for preparing WPC. Copper is also known to be used for preservation and protection purposes. Thus, WPC formed with Cu²⁺ ions retains tensile strength with very little reduction of PL and can act for preservative and protective purposes of the composites. Combination of Cu²⁺ ions with polyfunctional monomers (NVP, TPGDA, and TMPTA) or with oligomers (UA, EA, and PEA)

used as additives increases polymer loadings of the bulk monomer in the order AM > BMA > ST in the case of the polyfunctional monomer series. This increment is in favor of the functionality of the additive monomer. This means TMPTA shows the highest PL values among NVP and TPGDA. The above order of bulk monomers changes to BMA > AM > ST when oligomers are used as the additives. PEA systems show the maximum PL values. The impact of oligomer is more dominant in the presence of Cu²⁺ ions than the polyfunctional monomers. This shows that oligomers have a more favorable partitioning/diffusion mechanism in the presence of Cu²⁺ ions than the polyfunctional monomers. It is observed in Table X that the tensile strength of the composites containing Cu²⁺ ions are

Table X Effect of Copper (Cu^{2+}) on TS of WPC with the Highest PL

| Additives and Cu^{2+} | AM | | BMA | | ST | |
|--------------------------------|-----|-------|-----|-------|-----|-------|
| | PL | T_f | PL | T_f | PL | T_f |
| Cu^{2+} | 98 | 1.53 | 90 | 1.11 | 35 | 1.06 |
| NVP + Cu^{2+} | 128 | 1.72 | 106 | 1.80 | 37 | 1.34 |
| TPGDA + Cu^{2+} | 152 | 1.32 | 132 | 1.20 | 62 | 1.12 |
| TMPTA + Cu^{2+} | 196 | 1.53 | 178 | 1.55 | 119 | 1.22 |
| UA + Cu^{2+} | 136 | 1.28 | 101 | 1.63 | 45 | 1.28 |
| EA + Cu^{2+} | 185 | 1.21 | 196 | 1.26 | 82 | 1.12 |
| PEA + Cu^{2+} | 268 | 1.23 | 293 | 1.40 | 97 | 1.14 |

more or less similar to those (Table II) of the composites without Cu^{2+} ions. Thus, when additives (NVP, TPGDA, and TMPTA) are used to the bulk monomer (AM, BMA, and ST) and then Cu^{2+} ions are incorporated into it, the overall PL and TS values are almost the same as those of the composites without the Cu^{2+} ions; but these composites can be used as preservative and protective materials due to the presence of Cu^{2+} ions in it. The composites can be used for the preservation of arts and antiques.

Mixed Coadditives

It is now understood that sulfuric acid (H^+ ions) used as coadditive in the simul + bulk monomers + additives systems increases polymer loading almost synergistically with a drastic reduction of the tensile properties of the composites. On the other hand, both Cu^{2+} and Li^+ ions play moderate roles as the coadditives in place of H^+ ions. Li^+ ions slightly enhance the polymer loadings and tensile strengths, whereas Cu^{2+} ions retain both PL and TS values almost at the same levels as if no Cu^{2+} ion was used. But WPC formed with Cu^{2+} ions can be used for protective and preservative purposes. Urea plays the best role in the WPC formation. It increases both PL and TS quite significantly. It is worth investigating the impact of mixed coadditives on WPC formation. Since Cu^{2+} ions do not alter PL and TS values of the composites very much, it is desirable that Cu^{2+} ion can be mixed with H^+ ions or Li^+ ions or urea in order to study the impact of the mixed coadditives in the WPC formation.

$\text{Cu}^{2+} + \text{H}^+$ Ions

Table XI shows the polymer loading of the composites formed in presence of $\text{Cu}^{2+} + \text{H}^+$ ions, and bulk monomers and/or additives (monomers or

oligomers). When these results are compared with those of Tables I–IX, it is observed that PL values are slightly enhanced in presence of $\text{Cu}^{2+} + \text{H}^+$ ions, particularly with polyfunctional monomers. In fact, these values of PL are reduced when oligomer additives are used (Table XI). The enhancement due to $\text{Cu}^{2+} + \text{H}^+$ ions is not to the same extent as that due to H^+ ions alone (Table III). Thus, it shows that Cu^{2+} ions have suppressed the copolymerization process which could have occurred in the presence of H^+ ions. One possibility is that some H^+ ions reacted with Cu^{2+} ions in the related organometallic compound and/or some other entities. It is known that involvement of Cu^{2+} ions alone in the WPC formation does not reduce PL and TS values whereas incorporation of H^+ ions into any system reduces the TS values with enhanced PL values. But the TS results given in Table XII show that the composites formed with AM monomer in the presence of $\text{Cu}^{2+} + \text{H}^+$ ions and polyfunctional monomers (additives) have less tensile strength, indicating involvement of H^+ ions as more dominating than Cu^{2+} ions in the WPC formation. This behavior changes as the bulk monomer is replaced by another bulk monomer. For example, WPC with ST yields TS values which are greater than those of the system containing H^+ ions (Table IV) but are very slightly smaller than those with Cu^{2+} ions. This shows that molecular structure of the bulk monomer plays a significant role during the partitioning/diffusion of the molecules at its equilibrium condition.⁴ This is further complicated by the process of ionic involvements. Thus, Cu^{2+} and H^+ ions play their respective roles during the equilibrium condition of the bulk monomer and other related components.

$\text{Cu}^{2+} + \text{Li}^+$ Ions

The behavior of $\text{Cu}^{2+} + \text{Li}^+$ ions is different from other systems. It is already observed in Table V that Li^+ ions have enhanced the PL values, particularly in the presence of the polyfunctional monomers (additives) and slightly reduced PL values when oligomers are used as additives. But this enhancement of PL is slightly suppressed when Cu^{2+} ions are incorporated with Li^+ ions (Table XIII). This is true in both the systems of the additives (monomers and oligomers). Cu^{2+} ions have the tendency to suppress PL values when used alone with retention of the TS property. The overall enhancement of the tensile strengths of the composites in the presence of $\text{Cu}^{2+} + \text{Li}^+$ ions (Table XIV) indicate that both Cu^{2+} and Li^+ ions have played some important roles in the composite formation. It seems

Table XI Effect of Coadditives Copper (Cu²⁺) and Acid (H⁺) on PL in Presence of Additives at Different Monomer/Methanol Compositions

| Monomer | | | | | | | | | | | | |
|---------------------------------|-----------------------------------|-----|-----|-----|-----------------------------------|-----|-----|-----|-----------------------------------|-----|----|-----|
| Polymer Loading (%) | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | |
| | Cu ²⁺ + H ⁺ | A | B | C | Cu ²⁺ + H ⁺ | A | B | C | Cu ²⁺ + H ⁺ | A | B | C |
| 10 | 6 | 52 | 51 | 65 | 18 | 41 | 34 | 267 | 2 | 8 | 7 | 18 |
| 20 | 11 | 72 | 60 | 77 | 29 | 82 | 54 | 267 | 11 | 25 | 34 | 78 |
| 30 | 58 | 123 | 97 | 156 | 51 | 111 | 75 | 268 | 21 | 37 | 46 | 98 |
| 50 | 83 | 105 | 158 | 211 | 83 | 183 | 159 | 275 | 35 | 55 | 59 | 143 |
| 60 | 95 | 186 | 172 | 202 | 82 | 185 | 163 | 255 | 46 | 84 | 63 | 136 |
| 70 | 113 | 201 | 195 | 200 | 89 | 196 | 163 | 261 | 61 | 105 | 88 | 133 |
| 80 | 92 | 161 | 148 | 187 | 95 | 203 | 168 | 269 | 63 | 105 | 90 | 134 |
| 90 | 81 | 129 | 103 | 133 | 112 | 207 | 169 | 268 | 70 | 108 | 92 | 121 |

| Oligomer | | | | | | | | | | | | |
|---------------------------------|-----------------------------------|-----|-----|-----|-----------------------------------|----|-----|-----|-----------------------------------|----|----|----|
| Polymer Loading (%) | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | |
| | Cu ²⁺ + H ⁺ | D | E | F | Cu ²⁺ + H ⁺ | D | E | F | Cu ²⁺ + H ⁺ | D | E | F |
| 10 | 6 | 8 | 28 | 24 | 18 | 33 | 35 | 42 | 2 | 3 | 5 | 6 |
| 20 | 11 | 63 | 52 | 46 | 29 | 38 | 54 | 87 | 11 | 15 | 17 | 18 |
| 30 | 58 | 89 | 96 | 112 | 51 | 47 | 72 | 125 | 21 | 35 | 36 | 33 |
| 50 | 83 | 123 | 146 | 123 | 83 | 77 | 97 | 201 | 35 | 56 | 43 | 46 |
| 60 | 95 | 158 | 178 | 189 | 82 | 88 | 100 | 211 | 46 | 60 | 52 | 50 |
| 70 | 113 | 166 | 190 | 234 | 89 | 98 | 107 | 216 | 61 | 66 | 68 | 57 |
| 80 | 92 | 122 | 172 | 130 | 95 | 96 | 117 | 122 | 63 | 71 | 73 | 66 |
| 90 | 81 | 123 | 138 | 87 | 112 | 92 | 123 | 136 | 70 | 79 | 76 | 72 |

A, NVP + Cu²⁺ + H⁺; B, TPGDA + Cu²⁺ + H⁺; C, TMPTA + Cu²⁺ + H⁺; D, UA + Cu²⁺ + H⁺; E, EA + Cu²⁺ + H⁺; F, PEA + Cu²⁺ + H⁺. All additives and coadditives were used by 1% v/v or w/v.

Table XII Effect of Copper (Cu²⁺) and Acid (H⁺) on TS of WPC with the Highest PL

| Additives and Cu ²⁺ + H ⁺ | AM | | BMA | | ST | |
|--|-----|----------------|-----|----------------|-----|----------------|
| | PL | T _f | PL | T _f | PL | T _f |
| Cu ²⁺ + H ⁺ | 113 | 0.89 | 112 | 0.74 | 70 | 0.96 |
| NVP + Cu ²⁺ + H ⁺ | 201 | 1.16 | 207 | 1.11 | 108 | 1.23 |
| TPGDA + Cu ²⁺ + H ⁺ | 195 | 0.76 | 169 | 0.65 | 92 | 0.94 |
| TMPTA + Cu ²⁺ + H ⁺ | 211 | 0.88 | 275 | 0.90 | 143 | 1.14 |
| UA + Cu ²⁺ + H ⁺ | 166 | 0.87 | 98 | 0.63 | 79 | 1.08 |
| EA + Cu ²⁺ + H ⁺ | 190 | 1.02 | 123 | 0.98 | 76 | 1.10 |
| PEA + Cu ²⁺ + H ⁺ | 234 | 1.06 | 211 | 1.00 | 72 | 1.06 |

Table XIII Effect of Coadditives Copper (Cu²⁺) and Lithium (Li⁺) on PL in Presence of Additives at Different Monomer/Methanol Compositions

| Monomer | | | | | | | | | | | | |
|---------------------------------|------------------------------------|-----|-----|-----|------------------------------------|-----|-----|-----|------------------------------------|----|----|-----|
| Polymer Loading (%) | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | |
| | Cu ²⁺ + Li ⁺ | A | B | C | Cu ²⁺ + Li ⁺ | A | B | C | Cu ²⁺ + Li ⁺ | A | B | C |
| 10 | 8 | 8 | 9 | 15 | 6 | 6 | 14 | 34 | 0 | 7 | 8 | 12 |
| 20 | 10 | 12 | 21 | 37 | 21 | 12 | 24 | 167 | 8 | 17 | 19 | 48 |
| 30 | 56 | 63 | 96 | 176 | 33 | 34 | 55 | 188 | 20 | 33 | 30 | 86 |
| 50 | 80 | 85 | 128 | 211 | 73 | 44 | 69 | 192 | 29 | 42 | 47 | 143 |
| 60 | 97 | 112 | 154 | 196 | 74 | 58 | 93 | 185 | 36 | 44 | 52 | 136 |
| 70 | 129 | 140 | 175 | 188 | 72 | 68 | 146 | 186 | 48 | 51 | 67 | 136 |
| 80 | 87 | 82 | 108 | 137 | 85 | 90 | 146 | 159 | 51 | 84 | 71 | 132 |
| 90 | 78 | 69 | 83 | 122 | 93 | 107 | 139 | 145 | 42 | 82 | 88 | 127 |

| Oligomer | | | | | | | | | | | | |
|---------------------------------|------------------------------------|-----|-----|-----|------------------------------------|-----|-----|-----|------------------------------------|----|----|----|
| Polymer Loading (%) | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | |
| | Cu ²⁺ + Li ⁺ | D | E | F | Cu ²⁺ + Li ⁺ | D | E | F | Cu ²⁺ + Li ⁺ | D | E | F |
| 10 | 8 | 9 | 11 | 14 | 6 | 5 | 10 | 16 | 0 | 3 | 8 | 10 |
| 20 | 10 | 22 | 28 | 38 | 21 | 18 | 23 | 26 | 8 | 16 | 18 | 24 |
| 30 | 56 | 60 | 81 | 96 | 33 | 62 | 52 | 55 | 20 | 23 | 38 | 33 |
| 50 | 80 | 86 | 107 | 111 | 73 | 74 | 68 | 82 | 29 | 33 | 47 | 62 |
| 60 | 97 | 102 | 113 | 125 | 74 | 85 | 83 | 103 | 36 | 36 | 52 | 75 |
| 70 | 129 | 110 | 125 | 147 | 72 | 98 | 96 | 115 | 48 | 38 | 66 | 91 |
| 80 | 87 | 109 | 118 | 130 | 85 | 105 | 112 | 129 | 51 | 60 | 71 | 87 |
| 90 | 78 | 89 | 103 | 112 | 93 | 106 | 119 | 133 | 42 | 72 | 92 | 92 |

A, NVP + Cu²⁺ + Li⁺; B, TPGDA + Cu²⁺ + Li⁺; C, TMPTA + Cu²⁺ + Li⁺; D, UA + Cu²⁺ + Li⁺; E, EA + Cu²⁺ + Li⁺; F, PEA + Cu²⁺ + Li⁺.

Table XIV Effect of Copper (Cu²⁺) and Lithium (Li⁺) on TS of WPC with the Highest PL

| Additives and Cu ²⁺ + Li ⁺ | AM | | BMA | | ST | |
|---|-----|----------------|-----|----------------|-----|----------------|
| | PL | T _f | PL | T _f | PL | T _f |
| Cu ²⁺ + Li ⁺ | 129 | 1.39 | 93 | 1.25 | 48 | 1.13 |
| NVP + Cu ²⁺ + Li ⁺ | 140 | 1.56 | 107 | 1.43 | 82 | 1.69 |
| TPGDA + Cu ²⁺ + Li ⁺ | 175 | 1.46 | 146 | 1.32 | 88 | 1.34 |
| TMPTA + Cu ²⁺ + Li ⁺ | 211 | 1.68 | 192 | 1.60 | 143 | 1.65 |
| UA + Cu ²⁺ + Li ⁺ | 110 | 1.27 | 106 | 1.26 | 72 | 1.16 |
| EA + Cu ²⁺ + Li ⁺ | 125 | 1.30 | 119 | 1.20 | 92 | 1.20 |
| PEA + Cu ²⁺ + Li ⁺ | 147 | 1.22 | 133 | 1.18 | 110 | 1.31 |

that both Cu^{2+} and Li^+ ions may have actively entered into the copolymerization process. But this needs more elaborate investigation for ascertaining its proper function at the equilibrium condition of the different components of the impregnating solution. It is already known that Li^+ ion is a good replacement of H^+ ions and Cu^{2+} ion is also known to act as protective and preservative purposes of the composite material. Thus, the combination of Cu^{2+} and Li^+ ions may be of good application in the composite formation when factors like preservation and strong tensile strength of the WPC are considered.

Cu^{2+} Ions + U

The high polymerizing capacity of urea for the bulk monomers in the presence of both the series of ad-

ditives (except AM + oligomers) is very slightly suppressed by the incorporation of Cu^{2+} ions with urea (Tables VII and XV). Tensile strengths (Table XVI) of the WPC are also high. That is the effect of Cu^{2+} ions not possibly reflected on the tensile property. Among the three sets of mixed coadditives ($\text{Cu}^{2+} + \text{H}^+$, $\text{Cu}^{2+} + \text{Li}^+$, and $\text{Cu}^{2+} + \text{U}$), $\text{Cu}^{2+} + \text{U}$ set seems to be the best so far considering polymer loading and tensile strength. Whatever may be the case, it is obvious that the combination of coadditives to the additives makes the copolymerizing process more complex. This is further complicated when the effect of radiation itself is taken into account.

Copolymerization of the bulk monomers (AM, BMA, and ST) reveals that styrene plays some hindering effect due to the fact that aromatic ring stays

Table XV Effect of Coadditives Copper (Cu^{2+}) and Urea (U) on PL in Presence of Additives at Different Monomer/Methanol Compositions

| Monomer | | | | | | | | | | | | | |
|---------------------------------|-----------------------------|-----|-----|-----|-----------------------------|-----|-----|-----|-----------------------------|----|----|-----|----|
| Polymer Loading (%) | | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | | |
| | $\text{Cu}^{2+} + \text{U}$ | A | B | C | $\text{Cu}^{2+} + \text{U}$ | A | B | C | $\text{Cu}^{2+} + \text{U}$ | A | B | C | |
| | 10 | 8 | 19 | 16 | 19 | 10 | 21 | 22 | 43 | 0 | 7 | 10 | 12 |
| 20 | 9 | 91 | 33 | 59 | 21 | 42 | 36 | 193 | 12 | 23 | 29 | 78 | |
| 30 | 52 | 178 | 142 | 253 | 40 | 71 | 87 | 230 | 22 | 51 | 43 | 109 | |
| 50 | 76 | 236 | 196 | 283 | 63 | 103 | 163 | 216 | 29 | 62 | 59 | 141 | |
| 60 | 99 | 208 | 252 | 236 | 76 | 153 | 183 | 211 | 35 | 74 | 73 | 140 | |
| 70 | 133 | 143 | 101 | 182 | 88 | 193 | 198 | 215 | 42 | 91 | 92 | 136 | |
| 80 | 81 | 117 | 132 | 179 | 98 | 196 | 230 | 209 | 52 | 86 | 96 | 136 | |
| 90 | 78 | 81 | 106 | 133 | 122 | 196 | 235 | 208 | 56 | 86 | 98 | 122 | |

| Oligomer | | | | | | | | | | | | | |
|---------------------------------|-----------------------------|-----|-----|-----|-----------------------------|-----|-----|-----|-----------------------------|----|----|----|---|
| Polymer Loading (%) | | | | | | | | | | | | | |
| Monomer (%) in MeOH (v/v) | AM | | | | BMA | | | | ST | | | | |
| | $\text{Cu}^{2+} + \text{U}$ | D | E | F | $\text{Cu}^{2+} + \text{U}$ | D | E | F | $\text{Cu}^{2+} + \text{U}$ | D | E | F | |
| | 10 | 8 | 11 | 13 | 18 | 10 | 31 | 36 | 43 | 0 | 7 | 9 | 9 |
| 20 | 9 | 32 | 43 | 46 | 21 | 45 | 71 | 92 | 12 | 14 | 19 | 22 | |
| 30 | 52 | 70 | 82 | 88 | 40 | 56 | 83 | 135 | 22 | 28 | 34 | 36 | |
| 50 | 76 | 93 | 121 | 129 | 63 | 85 | 99 | 270 | 29 | 36 | 45 | 52 | |
| 60 | 99 | 129 | 130 | 140 | 76 | 88 | 162 | 281 | 35 | 43 | 51 | 63 | |
| 70 | 133 | 147 | 156 | 151 | 88 | 92 | 218 | 287 | 42 | 50 | 62 | 77 | |
| 80 | 81 | 115 | 143 | 142 | 98 | 111 | 201 | 193 | 52 | 58 | 80 | 73 | |
| 90 | 78 | 96 | 138 | 129 | 122 | 113 | 197 | 278 | 56 | 63 | 82 | 72 | |

A, NVP + Cu^{2+} + U; B, TPGDA + Cu^{2+} + U; C, TMPTA + Cu^{2+} + U; D, UA + Cu^{2+} + U; E, EA + Cu^{2+} + U; F, PEA + Cu^{2+} + U.

Table XVI Effect of Copper (Cu²⁺) and Urea (U) on TS of WPC with the Highest PL

| Additives and Cu ²⁺ + U | AM | | BMA | | ST | |
|---------------------------------------|-----|----------------|-----|----------------|-----|----------------|
| | PL | T _f | PL | T _f | PL | T _f |
| Cu ²⁺ + U | 133 | 1.44 | 122 | 1.35 | 56 | 1.20 |
| NVP + Cu ²⁺ + U | 236 | 1.92 | 196 | 1.80 | 91 | 1.78 |
| TPGDA + Cu ²⁺ + U | 252 | 1.58 | 225 | 1.46 | 98 | 1.46 |
| TMPTA + Cu ²⁺ + U | 283 | 1.66 | 230 | 1.70 | 141 | 1.72 |
| UA + Cu ²⁺ + U | 147 | 1.71 | 113 | 1.65 | 63 | 1.26 |
| EA + Cu ²⁺ + U | 156 | 1.25 | 218 | 1.28 | 82 | 1.30 |
| PEA + Cu ²⁺ + U | 151 | 1.10 | 287 | 1.33 | 77 | 1.44 |

outside the vinyl plane, and, thus, the partitioning/diffusion of the styrene molecule is relatively slow than AM and BMA molecules. This is one of the reasons which yields low polymer loading with styrene. Acrylamide (AM), on the other hand, has the impact due to —CONH₂ group and BMA has the long chain backbone effect on the copolymerization process. These effects are well demonstrated in their results. H⁺ ions increase the polymer loading synergistically but reduce tensile strength substantially. Li⁺ ions maintain the enhanced polymer loading with moderate change of tensile property whereas Cu²⁺ ions reduce PL slightly with little effect on TS values.

Use of inorganic salts (Cu²⁺ and Li⁺) and urea is important in the sense that this is a new area for preparing composites (WPC) of different valuable properties like color, preservation, protection, etc. The composites formed in the presence of such additives and coadditives may serve some specific purposes.

The authors acknowledge the International Atomic Energy Agency (IAEA) for granting them financial support under the Technical Assistance Program BGD/8/008.

REFERENCES

1. M. A. Khan, K. M. Idriss Ali, and M. U. Ahmad, *J. Appl. Polym. Sci.*, **45**, 2113 (1992).
2. M. A. Khan and K. M. Idriss Ali, *Radiat. Phys. Chem.*, **38**, 537 (1991).
3. M. A. Khan and K. M. Idriss Ali, *Radiat. Phys. Chem.*, **40**, 69 (1992).
4. P. A. Dworjanyn and J. L. Garnett, *Radiat. Phys. Chem.*, **33**(5), 429 (1989).
5. M. A. Khan, K. M. Idriss Ali, and W. Wang, *Radiat. Phys. Chem.*, **38**(3), 303 (1991).
6. G. Scholes, *Annu. Rep. Chem. Soc. (U.K.)*, 170 (1970).
7. M. A. Khan and K. M. Idriss Ali, *Radiat. Phys. Chem.*, **40**, 421 (1992).

Received October 20, 1992

Accepted January 13, 1993