

Green Synthesis for Lignin Plasticization: Aqueous Graft Copolymerization with Methyl Methacrylate

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ABSTRACT: This study investigated the use of potassium persulfate (KPS) as an initiator for the grafting of methyl methacrylate (MMA) onto softwood kraft lignin. Ammonium iron (II) sulfate hexahydrate was used as a catalyst to overcome the inherent inhibition of lignin to free radical grafting and to make lignin copolymer under mild conditions using an aqueous medium. The influence of temperature, initiator concentration, time of reaction and monomer concentration on percentage of grafting were studied. A maximum of 31% grafting was achieved at 55°C. Graft copolymer was identified from the Fourier transform infrared (FTIR) spectrum by the new absorption peak at 1723 cm⁻¹ and the reduction of intensity of the band around 3350 cm⁻¹. The reduction of glass transition temperature (T_g), surface morphology and higher decomposition temperature of grafted lignin support the grafting of MMA on lignin. The grafted chains increased the surface area of lignin.

KEYWORDS: Lignin, graft copolymerization, methyl methacrylate, potassium persulfate, FTIR

1 INTRODUCTION

Lignin, the second richest natural polymeric material on earth, is considered to be a low value material with limited commercial applications. The growing bio-fuel industry and the existing pulp and paper industries are generating large amounts of lignin as waste product. Currently more than 50 million tons of lignin per year is produced from pulp and paper industries [1–2]. The major part of it is used as lower value fuel for pulping boilers or directly discarded to landfill as waste [3]. Reduction of fossil fuel and ecological concerns has caused the scientific world to focus more on the exploitation of this renewable and sustainable material.

Lignin is a very complex natural macromolecular material having various types of linkages and functionalities [4]. It is formed by the enzymatic polymerization of three monomeric units: coniferyl alcohol, synapyl alcohol and p-coumaryl alcohol (Figure 1). These monomeric units lead to formation of phenylpropanoid units of syringyl (S), guaiacyl (G), and p-hydroxyphenyl propane units (p-H) [5–8]. The

chemical as well as physical characteristics of lignin depend on the source of origin and method of extraction [2, 9–10].

Lignin can be utilized by surface modification, crosslinking, blending with polymers or degrading into monomeric blocks to make chemicals [11–12]. The use of lignin as a starting substance to prepare organic compounds like vanillin [13–14], quinones, aliphatic acids, hydroxylated aromatic compounds, aldehydes, etc., are also being studied. The function of lignin as a compatibilizing agent for making thermoplastic natural fiber composites was also studied [15–17]. The blending of lignin with thermoplastic polymers was found to have a promising effect on mechanical and thermal properties [18–20]. The structural similarity between lignin and phenol attracts researchers to exploit it for use as an alternative to phenol for the preparation of lignin-phenol-formaldehyde resins [21–26].

Properties of lignin can be modified and tailored to different degrees by various chemical modifications. Grafting is an effective method to give special functionality to materials. Selection of initiator and catalyst systems for graft copolymerization reactions is critical to achieve a good degree of grafting. Initiation method, monomer reactivity and availability of hydroxyl group also affect the grafting efficiency [27]. The grafted products are found to have application in a number

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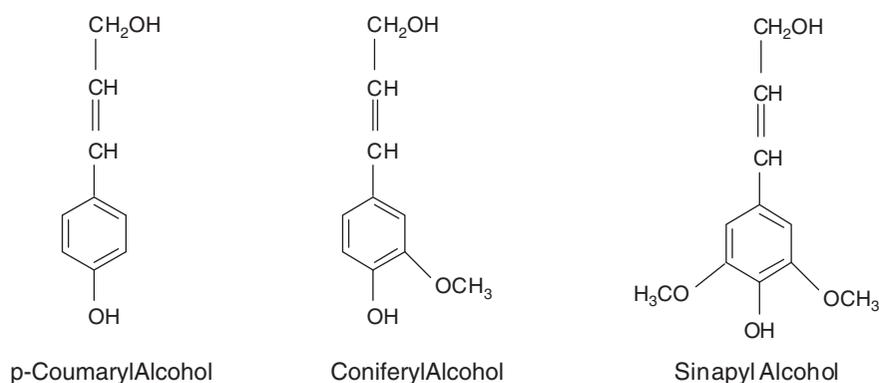


Figure 1 Monomeric units of lignin.

of areas ranging from emulsifiers, adhesives, coatings and paints; to biomedical instruments and molding substances. Their major use may be as materials for compatibilizing the polymer blends during chemical modification of cellulose and lignin by vinyl monomers which can enhance their flexibility, thermal stability, ion-exchange ability, and microbiological resistance [28]. Various vinyl monomers like styrene, acrylic acid, and acrylic amide have been used for grafting onto lignin [29–34]. The graft copolymerization can be commenced by irradiation [34–35], chemical initiators [4, 30, 33] or chemo-enzymatic agents [31] in appropriate solvents. Lignin-based graft copolymer materials like drilling mud thinner [36], thickening agent [33] and dispersing agent [37] were also prepared.

Grafting reactions are used to add new molecules onto lignin for increasing the interaction, absorption and reactivity of lignin with other materials. This will give a uniform surface property to lignin. Usually, monomer and lignin dissolve in organic chemicals to carry out reactions in homogeneous media. Solvents facilitate the monomers to move towards the active site of lignin molecules without difficulty and thus help the copolymer formation. Organic solvent usage for the graft copolymerization reaction is not likely to be environmentally friendly or price competitive. An alternative is to use an aqueous medium where the initiator and catalyst play a significant role in carrying the monomers to the active sites of the lignin. In this study, MMA, which is capable of making good interaction with synthetic polymers, was selected as monomer and grafted onto lignin using potassium persulfate (KPS) as an initiator with ammonium iron (II) sulfate as a catalyst. Low cost, easy control and low reaction temperature (45–80°C) are the advantages of this method. The effect of several interdependent parameters such as temperature of reaction, concentration of monomer, reaction time and concentration of initiator on the copolymer formation were examined, and changes such as thermal stability, morphology, surface

area, and hydrophobicity were used to evaluate the new copolymer.

2 EXPERIMENTAL

2.1 Materials

Kraft lignin under the trade name of Indulin AT (from the paper industry) was purchased from MeadWestvaco, USA. AR grade methyl methacrylate monomer (99%) was purchased from Sigma-Aldrich, Canada. The inhibitor present in monomer was removed by washing with 2% NaOH (Fisher scientific) solution, followed by water (till pH of the filtrate become neutral) to remove sodium ions. ACS grades of potassium persulfate and ammonium iron (II) sulfate hexahydrate were purchased from Sigma-Aldrich, Canada.

2.2 Surface Modification

Grafting reaction was conducted in a 250 ml round-bottom flask provided with reflux condenser. 5 ml methyl methacrylate monomer was added into 5 g of lignin in the reactor. The mixture was kept for 15 min to allow the adsorption of the monomer molecules on the lignin. Forty ml of distilled water was added to this mixture at a specific temperature (as in Table 1) with constant stirring. A predetermined quantity of ammonium iron (II) sulfate and potassium persulfate were added to the above mixture to induce the grafting reactions. Table 1 provides the details of the reaction conditions. The reaction products were filtered and washed till the pH of washings were neutralized. This was done to remove the remaining initiator and catalyst from the mixture. The filtrate was dried at 100°C in a convection oven for 12 hours, after which the dried sample was extracted by soxhlet extraction (with toluene) for 1 day to remove the poly(methyl methacrylate) homopolymer. The

Table 1 Experimental conditions for the graft copolymer synthesis*.

Sample	Methyl methacrylate (ml)	Potassium persulfate ($\times 10^{-2}$ mol/L)	Temperature ($^{\circ}\text{C}$)	Time (hrs)
1	5	9.25	45	8
2	5	9.25	55	8
3	5	9.25	65	8
4	5	9.25	75	8
5	2.5	9.25	55	8
6	5	9.25	55	8
7	7.5	9.25	55	8
8	10	9.25	55	8
9	5	2.31	55	8
10	5	4.62	55	8
11	5	9.25	55	8
12	5	11.56	55	8
13	5	9.25	55	4
14	5	9.25	55	8
15	5	9.25	55	12
16	5	9.25	55	16

* 5g lignin kept as constant throughout the reaction

grafted copolymer was dried for 6 hours in a vacuum oven (80°C) to remove toluene. The increased weight of the lignin was believed to be due to grafted methyl methacrylate chains.

Percentage of grafting (G_p), efficiency of graft (G_e), and homopolymer percentage (H_p) for the reactions were determined by the gravimetric method using equations 1 to 3 [38–39].

$$G_p = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

$$G_e = \frac{W_2 - W_1}{M} \times 100 \quad (2)$$

$$H_p = \frac{W_3 - W_2}{W_3} \times 100 \quad (3)$$

where, W_1 = weight of initial lignin, W_2 = weight of the grafted product, W_3 = weight of the product before soxhlet extraction, and M = monomer weight.

A blank lignin was made to identify the changes suffered by the lignin due to chemical modification and loss of material during the filtration and extraction process. This was prepared using the exact conditions used for the experiments without monomer.

Poly(methyl methacrylate) was also prepared in the same way under the same experimental conditions.

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra of lignin and modified lignin were analyzed using a NICOLET 6700 ATR-FTIR machine. A frequency range of $4000\text{--}400\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} was used for the analysis.

2.4 Surface Area

Surface area of lignin samples was measured by the Brunauer-Emmet-Teller (BET) method using NOVA station-C, Quantachrome instruments in nitrogen gas sorption analysis at 77.3 K . The samples were degassed by passing nitrogen gas at 55°C for 8–16 hours to remove the volatiles. BET surface areas were taken from a multipoint plot over a P/P_0 range of 0.05–0.35. Nitrogen is used as an adsorbent gas due to its easy availability and strong interaction with solid substances.

2.5 Scanning Electron Microscopy (SEM)

Morphological characterization of lignin and modified lignin was done using a scanning electron microscope (SEM) (model FEI S50). Fifteen kV accelerating

voltage was used for the characterization of gold-coated samples.

2.6 Hydrophobicity

Lignin and modified lignin were dried at 100°C for 48 hours. From this 2 g of samples were accurately weighed and kept in a desiccator provided with water at the bottom instead of moisture adsorbent. The humidity level inside the chamber was continuously monitored using a digital hygrometer and was a constant value of 95% throughout the experiment. Weight of the samples was monitored on alternate days.

2.7 Differential Scanning Calorimetry (DSC)

TA Instruments DSC Q200 Differential Scanning Calorimeter was used to measure glass transition temperature. A sample weight of 5–8 mg in an aluminium pan under nitrogen atmosphere was used for the run. The samples were heated from 30–180°C (first heating run) and held for 1 min to remove the remaining moisture and thermal history, cooled to 30°C, and again heated (second heating run) to 200°C. The heating and cooling was conducted at 10°C/min.

2.8 Thermogravimetric Analysis (TGA)

This analysis was used to find out the thermal stability and degradation temperature of lignin, modified lignin and homopolymer (PMMA). TA Instruments Q500 machine was used to heat the samples from 30°C to 800°C at a 20°C/min heating rate under nitrogen atmosphere (flow rate – 60 ml/min).

3 RESULTS AND DISCUSSION

3.1 Graft Copolymerization

The grafting reaction was conducted using 1:1 (W/V) ratio of lignin:methyl methacrylate with 9.25×10^{-2} mol/L initiator in the absence of the catalyst, ammonium iron (II) sulfate hexahydrate. It was found that the copolymer formation did not happen without the catalyst. Hence we increased the concentration of catalyst from 0.318×10^{-2} mol/L to 1.275×10^{-2} mol/L, and a higher graft copolymer yield was observed at 0.6375×10^{-2} mol/L concentration. So we have kept this concentration constant for the remainder of the study.

3.1.1 Effect of Temperature

Variation of grafting efficiency, grafting percentage and homopolymer formation with temperature is shown in Figure 2a. The grafting percentage improved when the temperature increased from 45 to 55°C. Further increase of temperature decreased the percentage of grafting. Increase of grafting percentage with the rise in temperature may be due to the improved decomposition rate of KPS and diffusion rate of monomer. Maximum percentage of grafting (25%) was observed at 55°C. The percentage of homopolymer formed during the reaction increased with the rise in temperature. The decreased percentages of grafting due to the increase of temperature to higher than 55°C can be attributed to the increased homopolymer formation and favored chain termination or transfer reactions.

3.1.2 Effect of Monomer Concentration

The observations for the influence of monomer concentration on G_p , G_e and H_p are shown in Figure 2b. From the figure we can observe that both the grafting and homopolymer formation increased with the increase of monomer concentration; 31% grafting and 51% homopolymer formation was observed with a reaction ratio of 1:1.5 (W/V) (Lignin:monomer). As the monomer concentration increases, more monomers can diffuse and can react with lignin free radicals thus improving the grafting level. The chance of reaction between monomer radicals will also increase with an increase of monomer concentration leading to the formation of a higher amount of homopolymer.

3.1.3 Effect of Initiator

The initiator plays a vital role in controlling the grafting percentage. As illustrated in Figure 2c, the percentage of grafting increased with an increase in $K_2S_2O_8$ concentration up to 9.25×10^{-2} mol/L, further than this value, it decreased. The maximum percentage of grafting was 25% when KPS concentration was 9.25×10^{-2} mol/L. The increase of initial grafting can be attributed to the creation of a higher amount of sulfate and -OH* radicals that are capable of creating more active sites on lignin [40]. More free radicals are formed at higher initiator concentration that can come in contact with more monomers and thus increase the formation of poly(methyl methacrylate). Due to this the percentage of grafting was not further improved.

3.1.4 Effect of Time

The variation of the percentage grafting with reaction time is shown in Figure 2d. The grafting percentage improved steadily by raising the reaction time up to

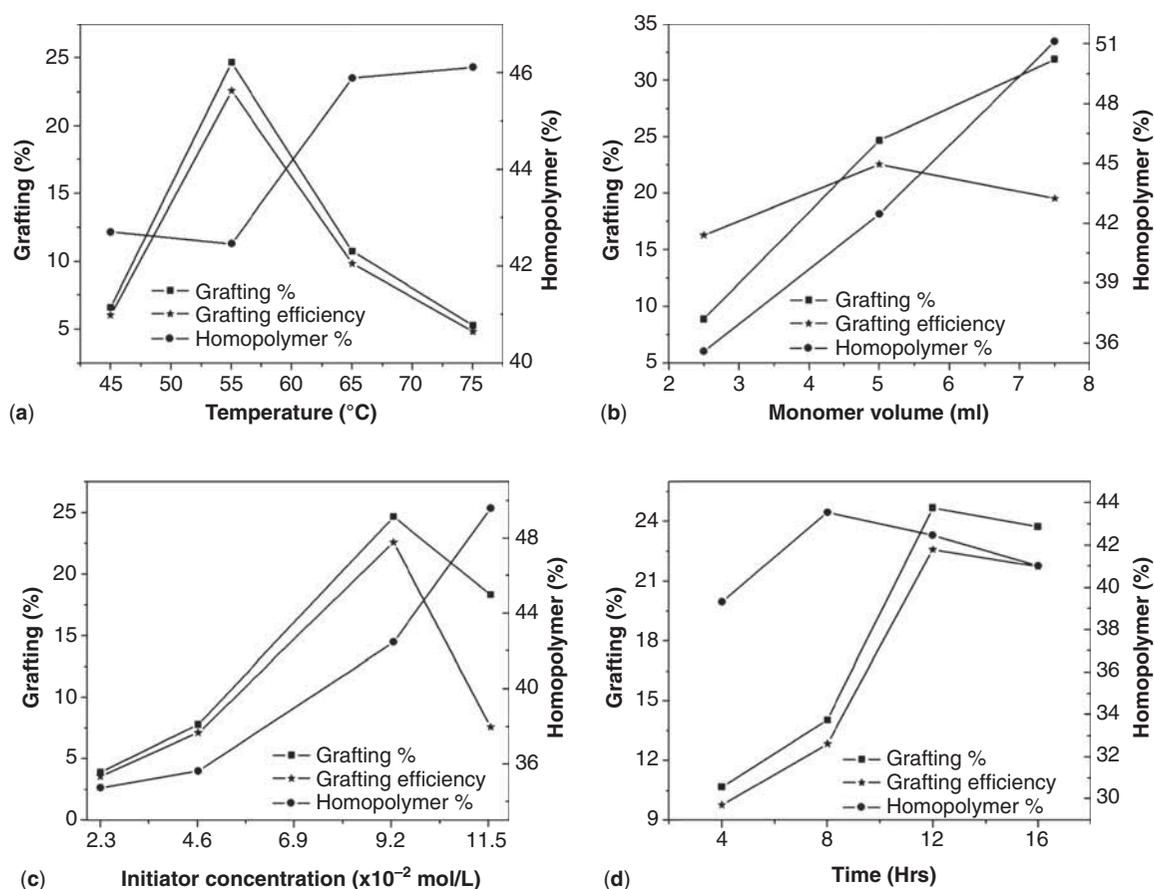


Figure 2 Effect of reaction conditions on graft copolymerization (a) Temperature (b) Monomer concentration (c) Initiator concentration and (d) reaction time.

8h. The improvement in the grafting may be caused by the availability of a higher amount of reaction sites on the lignin. A further increase of reaction time may cause mutual annihilation and the termination reactions between growing grafted chains and lignin macroradicals. This may decrease the grafting percentage with higher time [41].

3.2 Mechanism of Grafting

The ability of sulfate radicals to generate free radicals from the materials with $-OH$ functionality is already established [42–43]. Use of potassium persulfate as an initiator for the graft copolymerization of acrylic compounds at lower temperatures onto compounds with hydroxyl groups has been reported by several authors [27, 44]. Based on these observations it was hypothesized that the sulfate free radicals generated by the decomposition of potassium persulfate can abstract hydrogen from the hydroxyl groups on lignin backbone and can form oxygen free radicals. These active macromolecular radicals react with the double-bonded carbon of methyl methacrylate molecules and

form sigma bonds. This will create a new active site on the newly added molecule.

The possible reactions during the graft copolymerization are given in Figure 3. The initiator system consists of potassium persulfate and Fe^{2+} ions from ammonium iron (II) sulfate. Sulfate radicals formation is catalyzed by the reduction of KPS by Fe^{2+} ions (reaction 3) [45]. Since the reaction is in aqueous medium these sulfate free radicals can generate hydroxyl free radicals by reaction with water (reaction 2). Sulfate radicals and hydroxyl radicals abstract hydrogen from the $-OH$ group of lignin to create active sites on the lignin macromolecule (reaction 5) and thus accelerate the formation of graft copolymer (reaction 6) [44, 46–49]. In addition, the sulfate and hydroxyl radicals can also start the homopolymerization of MMA monomer to poly(methyl methacrylate) (reaction 7) [41]. Initially, the addition of monomer accelerates the grafting process, this was supported by our experiment results and was also the observation for the softwood lignin grafting reported by Ye *et al.* [41]. Compared to the relatively short life span of sulfate and hydroxyl radicals, the phenoxy radicals lifetime in lignin might be longer

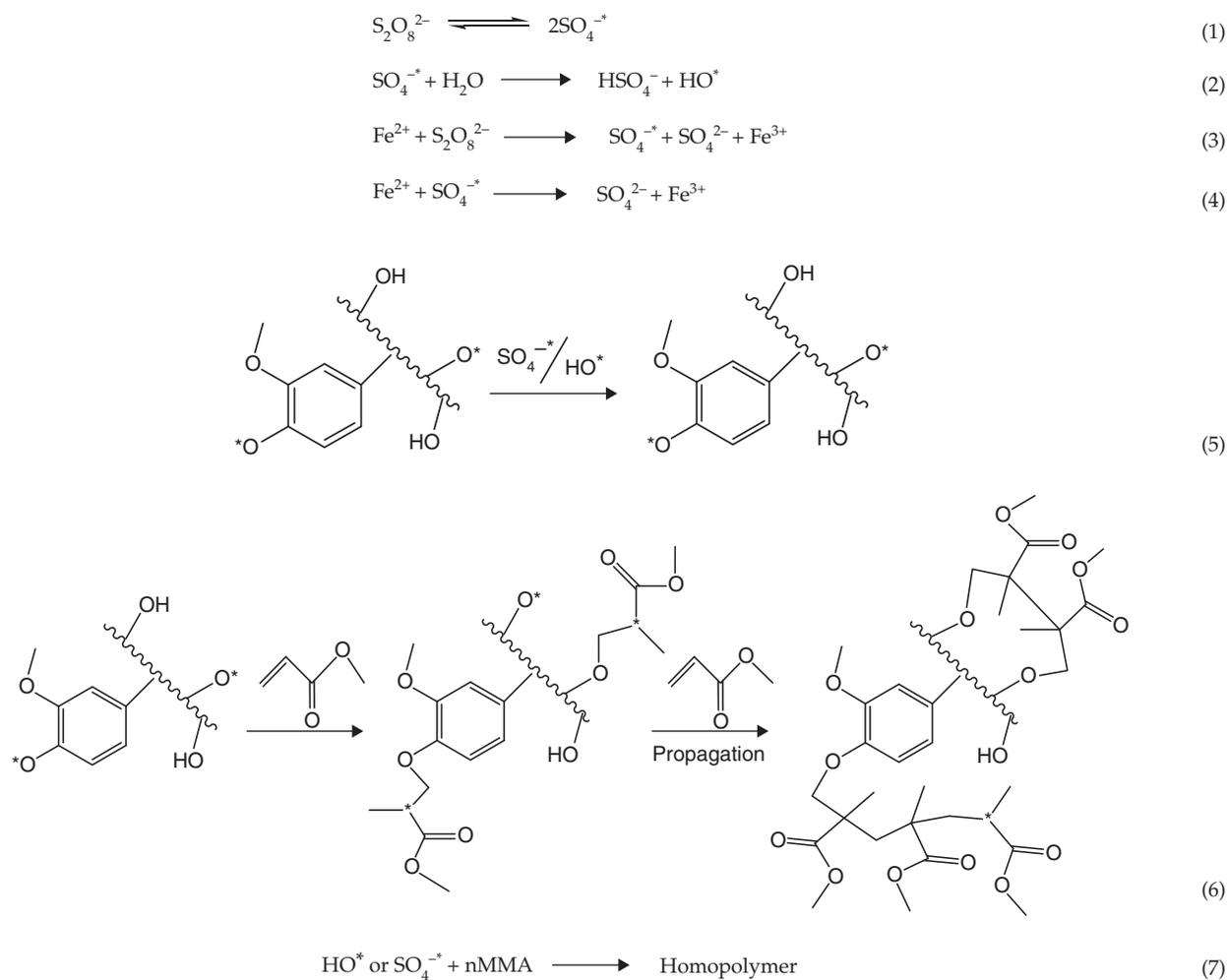


Figure 3 Proposed reaction mechanism.

[41]. This may be because of the resonance stabilization of phenoxy radical and larger steric hindrance of lignin macromolecule compared to sulfate and hydroxyl radicals. Hence the possibility of quenching reactions between living free radicals is very low [41]. Thus in the reaction system, the concentration of living macro free radicals may be higher when compared to MMA homopolymer radicals. This may be the reason for the acceleration of initial grafting reactions [41]. These grafting reactions can be terminated by chain transfer, coupling, or disproportionation reactions between lignin macromolecules and living free radicals. Homopolymer also undergoes termination reaction in a similar manner.

3.3 FTIR Analysis

Figure 4 illustrates the FTIR spectra of lignin, MMA grafted lignin and PMMA. PMMA showed a sharp peak around 1723 cm^{-1} because of its carbonyl functional group. Figure 4 clearly illustrates that the typical carbonyl group peak around 1723 cm^{-1} is present

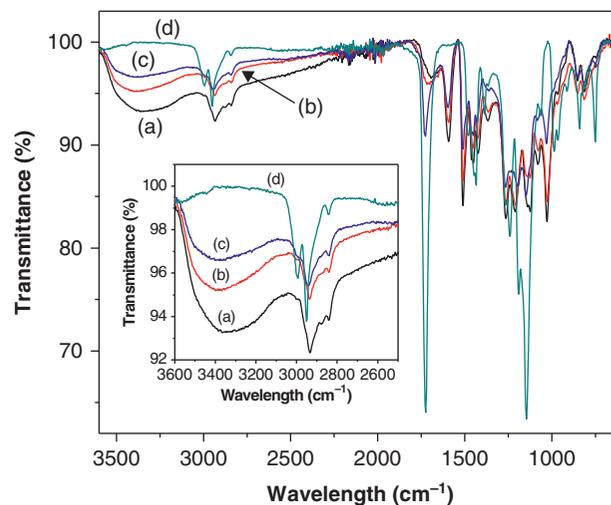


Figure 4 FTIR spectra of (a) lignin, (b) lignin from blank run, (c) modified lignin, and (d) poly(methyl methacrylate).

in the grafted sample [44, 48], whereas in lignin the absorption peak for the carbonyl group is absent. This is strong evidence for the grafting of methyl methacrylate on lignin. The presence of grafted polymer chains increased the carbonyl groups in the modified lignin. The broad band around 3420–3300 cm^{-1} in lignin and grafted lignin is due to the presence of -OH in aliphatic and phenolic chains [50]. The broadness and the intensity of this peak in the grafted sample are very low compared to the unmodified sample. The lower intensity for the modified lignin is caused by the replacement of hydrogen from the hydroxyl groups by grafted MMA chains. This further supports the grafting of MMA on lignin. FTIR spectra of lignin obtained from the blank run also showed broadened peak around 3350 cm^{-1} , a strong C-H peak at 2933 cm^{-1} , and an additional typical band of methyl groups at 2840 cm^{-1} as that of unmodified lignin [51]. It also showed aromatic skeletal vibration bands at 1592 cm^{-1} and 1510 cm^{-1} and -C-H deformations of asymmetric methyl and methylene groups at 1420 cm^{-1} and 1460 cm^{-1} . These observations indicate that the experimental conditions are not affected by the structure of lignin.

3.4 Surface Area

The surface area of lignin samples was measured by the BET adsorption method to find out the effect of grafting. The values showed that the surface area of MMA grafted lignin (7.102 m^2/g) is 6 times higher than the lignin (1.012 m^2/g). Generally, the surface area of a

material increases when it breaks down into smaller particles or new chains/molecules are attached on its surface. Creation of pores on the surface also increases the surface area of the material. Lignin obtained from blank preparation showed the surface area value of 1.462 m^2/g , which is almost similar to the value of the initial lignin. This indicates that the reaction conditions have no effect on the particle size, generation of pores or degradation of lignin. The presence of grafted PMMA chains on the surface of MMA-g-lignin improved the surface area of lignin as shown in Figure 5. The grafted polymeric chains increase the hydrophobic character of lignin and thus prevent the agglomeration of lignin particles. This may reduce the average particle size of lignin. So the higher surface area of MMA grafted lignin is due to the combined effect of grafted chains and reduction of particle size.

3.5 Surface Morphology

The morphologies of lignin and grafted lignin are shown in Figure 6. The morphologies of modified and unmodified lignin are found to be different. Particle size of unmodified lignin is higher than that of modified lignin. Lignin possesses a spherical shape with a rough surface. In addition, some random small and big pores are also dispersed on its surface, which can improve the interaction with initiator [41]. The morphological image of grafted sample showed that it has a smooth surface as well as uniform and smaller particle size. This may be due to the presence of

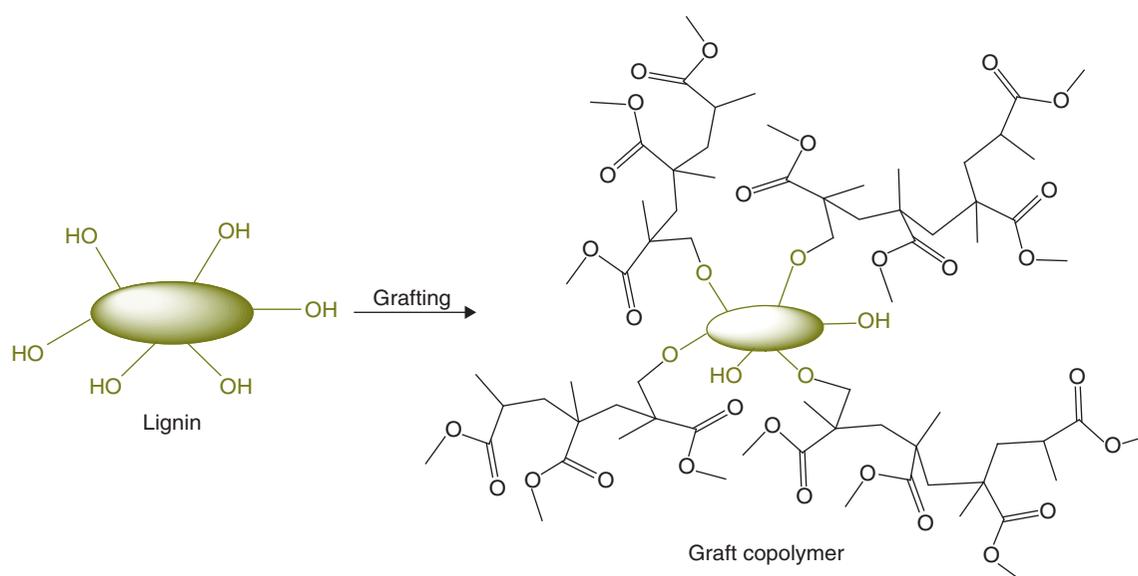


Figure 5 Schematic representation of grafting.

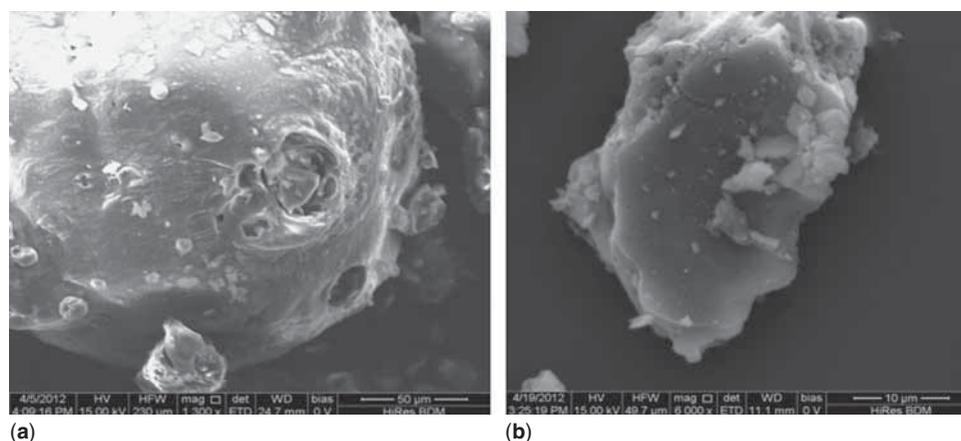


Figure 6 SEM micrograph of (a) lignin (b) modified lignin.

grafted PMMA chains on lignin particles. The grafting increased the hydrophobic character of lignin which prevents the agglomeration of lignin particles and leads to the reduction of particle size of graft copolymer. This increased the surface area of the grafted sample and confirmed the grafting of PMMA chains on lignin.

3.6 Hydrophobic Character

Lignin is traditionally considered as a class of hydrophobic natural biopolymer. Plenty of aliphatic and aromatic hydroxyl groups in lignin can easily absorb the atmospheric moisture. The replacement of hydroxyl groups further improves the hydrophobicity of lignin to the level similar to hydrocarbon-based polymers [29]. Enhanced hydrophobicity of modified lignin is desirable for many applications such as composite making, compatibilization, etc. The increase of hydrophobic character by the replacement of hydroxyl groups decreases the moisture absorption tendency. The percentage of moisture absorption of lignin and MMA-grafted lignin is shown in Figure 7. Rate of moisture absorption of lignin was very high compared to grafted lignin. Within 1 day lignin absorbed 6% moisture and then gradually increased to about 13% by 12 days. MMA-grafted lignin showed only 3% moisture absorption within the experiment period. This confirms the higher hydrophobic character of MMA-grafted lignin compared to unmodified lignin. Replacement of hydroxyl groups by polymer chains through grafting increases the hydrophobic character and thus reduces the moisture absorption tendency of lignin. Wang *et al.* observed higher hydrophobic character of lignin by grafting with rosin [2].

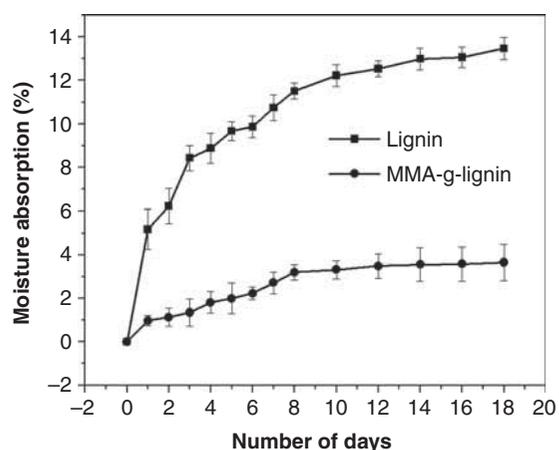


Figure 7 Moisture absorption of lignin and modified lignin.

3.7 DSC Analysis

T_g of lignin depends on various factors, such as inter-chain hydrogen bonding, moisture content, crosslinking, number of phenyl groups and its molecular mass [5, 52]. Hence the samples were heated to 180°C to remove the thermal history and to stabilize the interactions. T_g of the samples was determined from the second heating scan after cooling the samples from 180 to 30°C. T_g values of lignin derivatives found varied between 90 to 180°C [53]. DSC curves of various samples obtained from the second run are given in Figure 8. The T_g of lignin and lignin obtained from the blank run were found to be around 156°C and 169°C respectively. The increase in the T_g of the blank sample may be due to the reaction between the hydroxyl groups in the lignin chain in the presence of initiator. This may reduce the chain mobility and thus increase the T_g . The lowering of the intensity of the broad

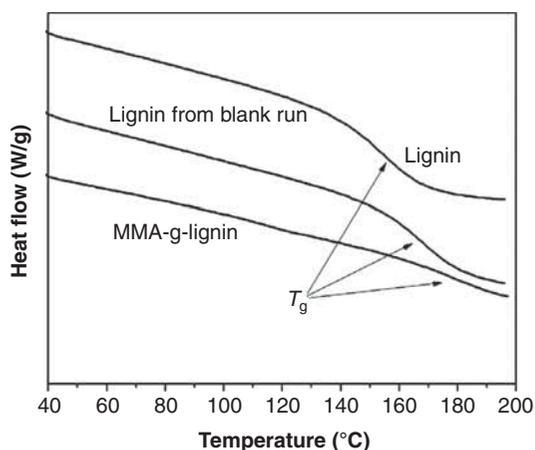


Figure 8 DSC curves of lignin, modified lignin and lignin from blank run.

band due to hydroxyl groups around 3400 cm^{-1} in the FTIR spectrum (Figure 4b) also supports the above. MMA-grafted lignin showed T_g value around 177°C . The increase in T_g may be attributed to the lowering of free volume [54]; the grafting of MMA on lignin may increase the bulkiness of lignin chains and thus decrease the chain mobility; thus the T_g value of grafted lignin increases. Grafting of acrylic acid on lignin also increased the T_g value [4]. The heat capacity change (ΔC_p) corresponding to the glass transition temperatures of lignin, lignin from blank run and MMA-g-lignin are found to be around 0.3026 J/g , 0.4155 J/g and 0.2456 J/g respectively. The reduction of ΔC_p with increasing T_g is due to decreased chain mobility and reduced number of thermally activated lignin chains as reported by Chung *et al.* [55].

3.8 Thermogravimetric Analysis

The mechanism of lignin degradation is very complex and crops up by a number of competing reactions. The bond fissions during these reactions within the lignin depend on various bond energy/strength [50, 56–57]. Thermogravimetric analysis was conducted to assess the consequence of the modification on the thermal properties of lignin and modified lignin. Figure 9 shows thermograms for lignin, lignin from blank run, modified lignin and PMMA. PMMA showed sharp degradation between $320\text{--}450^\circ\text{C}$, which is in the degradation temperature range of lignin. Hence the thermal stability of modified lignin is not increased. All lignins and PMMA showed weight reduction between $150\text{--}250^\circ\text{C}$. Degradation of lower molecular weight fragments in lignin and degradation of oligomeric PMMA molecules cause the weight reduction at this temperature range. The initial step of degradation of

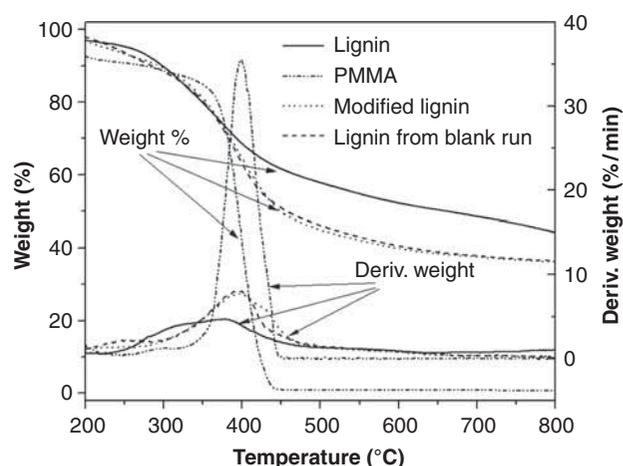


Figure 9 TGA thermograms of lignin, modified lignin and PMMA.

modified lignin around 200°C may be due to the degradation of lower molecular weight fractions of lignin and grafted oligomeric PMMA chains. Slightly higher initial thermal stability of modified lignin compared to unmodified lignin (Table 2) is due to the presence of grafted MMA chains.

Differential thermogram (DTG) peaks help to detect the difference of thermal behavior (Figure 9). Around 100°C lignins showed slight reduction in weight because of the adsorbed moisture [56, 58]. The major components of lignin degrade between the temperature ranges of $150\text{--}650^\circ\text{C}$. Hence decomposition from $150\text{--}650^\circ\text{C}$ was measured for the comparison of the thermal stability of lignin and modified lignin. At this temperature range lignins showed two degradation steps. The formation of char begins near 590°C by the removal of methane, and a considerable amount of residue remained without degradation after 800°C . For lignin about $40\text{--}45\%$ charred residue remained by the transformation of condensed matter [59]. Only $30\text{--}35\%$ charred residue was obtained for modified lignin. Formation of char is inversely related to the amount of methoxyl and $-\text{CO}$ groups [56]. Percent residue will be lower if the amounts of the above functional groups are higher. The amount of char (Table 2) confirmed that the MMA-g-lignin contains a high concentration of $-\text{CO}$ and methoxy groups due to the presence of grafted PMMA chains. Aguirre and co-workers observed two additional derivative peaks around 320 and 360°C due to the grafting of PMMA chain on wood fiber [42]. Since the lignin decomposition also happened in the same range of temperature we couldn't observe a distinct peak for PMMA-grafted lignin. The maximum degradation temperature shifted from 377.5°C in lignin to 397.3°C in MMA-g-lignin.

Table 2 Thermogravimetric analysis.

Sample	T_{O1} (°C)	T_1 (°C)	W_1 (%)	T_2 (°C)	W_2 (%)	T_{max} (°C)	% Residue at 700°C
Lignin	153.6	150–225	2.45	225–650	46.9	377.5	48.57
Lignin from blank run	157.6	150–250	5.75	250–650	50.96	393.8	38.4
MMA-g-Lignin	167.7	150–250	5.98	250–650	554.9	397.3	37.52
PMMA	150.9	150–250	7.89	320–450	86.54	399.2	0.814

T_{O1} - Onset of degradation of the first degradation step, T - degradation temperature range, T_{max} - Maximum degradation temperature, W - Weight change during degradation, 1, and 2 are the first and second degradation steps.

4 Conclusions

Methyl methacrylate can be successfully grafted onto lignin using potassium persulfate as an initiator. Use of an aqueous medium gives an added advantage of reducing environmental pollution and preparation cost. Percentage grafting, grafting efficiency and homopolymer formation appeared to vary with reaction conditions. A maximum of 31% grafting was achieved for 1:1.5(W/V) ratio (Lignin:MMA) at 55°C. Morphological characterization showed lower particle size and homogenized surface for MMA-grafted lignin copolymer compared to unmodified lignin. Maximum degradation temperature of lignin increased to 397°C after grafting with MMA. Surface area of lignin increased from 1.012m²/g to 7.102m²/g by grafting. The interaction of lignin with various polymer systems can be increased by functionalization with MMA. This will increase the direct utilization of lignin as compatibilizer, filler, reinforcing agent or as precursor for carbon fiber preparation.

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