



## Preparation and characterization of a newly water soluble lignin graft copolymer from oil palm lignocellulosic waste

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### ABSTRACT

Water soluble lignin graft copolymer (LGC) was synthesized using oil palm empty fruit bunch (OPEFB) fibre as a renewable biomass source. Initially, Kraft lignin (KL) was extracted by exploiting the OPEFB fibre Kraft pulping residue. KL was grafted with acrylic acid (AA) by using *p*-toluenesulfonic acid (PTS) as a catalyst in the condensation process via the bulk technique. The resulting copolymer was characterized by a Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetry–Fourier transform infrared (TG–FTIR) and carbon–hydrogen–nitrogen analyzer (CHN). The FTIR spectrum of the product showed absorption due to the presence of ester bonds as a proof of grafting. The DSC and TG–FTIR results showed significant improvements in the KL thermal properties at least 27.261% as well as a thermal degradation resistance. The elements percentages of KL compositions were changed as shown by the CHN data. SEM micrographs illustrated the grafting reaction homogenizing the KL morphological structure.

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### 1. Introduction

In recent years, oil palm empty fruit bunch (OPEFB) fibre, which is one of the lignocellulosic materials, showed great potential to be used as raw material in the Kraft pulping process, especially in Malaysia, which is considered a major palm oil producer in the world (Ibrahim et al., 2005). In conformity with that, Kraft black liquor remained as a waste after the completion of the pulping process. This aquatic colored and toxic effluent (Gupta, Ali, & Saini, 2007) i.e. black liquor, considered as a serious pollution source and caused costly disposal problems (Malaviya & Rathore, 2007). Nevertheless, Kraft black liquor consist of dissolved biomass materials such as lignin, hemicelluloses and degradation products of cellulose and hemicelluloses (sugar acids) (Wallberg, Linde, & Jönsson, 2006). Such biomass from industrial waste products could be a feasibly of cheap and commercially available raw material to produce; adsorbent, corrosion inhibitor and chemically modified biopolymer (Gupta, Ali, Suhas, & Mohan, 2003).

Kraft lignin (KL) is obtained from Kraft black liquor via the acidification process using sulfuric acid, hydrochloric acid or sulfur

dioxide (Wu, Zhang, Guo, & Huang, 2008). Generally, lignin is a highly stable and complex composite with a three-dimensional aromatic polymer structure formed from three phenylpropanoid alcohols units of *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol which are connected by ester groups (Amen-Chen, Pakdel, & Roy, 2001). Furthermore, lignin is the most abundant biopolymer on earth after cellulose and it naturally occurs in several types of plants such as hardwood, softwood and grasses (Pouteau, Dole, Cathala, Averous, & Boquillon, 2003). In spite of these large quantities, lignin has not yet been effectively utilized and this presents environmental problems (Ugartondo, Mitjans, & Vinardell, 2008).

Various studies have been conducted on lignin in order to overcome biomass environmental problems and produce new products with beneficial properties. One of these studies is graft copolymerization of lignin to produce a copolymer used as drilling mud thinner and viscosity reducer in high temperature (Wei, Liu, Yu, & Jiang, 2002). Another graft copolymerization reaction of lignin with 1-ethenylbenzene was used efficiently to enhance thermal stability as well as to change the hydrodynamic radius of poly (1-phenylethylene) (Chen et al., 1996). Graft copolymerization reaction of lignin by means of a specific monomers can be conducted either by the addition or condensation copolymerization. Apart from that, the addition copolymerization reaction is normally carried out using either free radicals or the ionic copolymerization process.

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Accordingly, a variety of vinyl monomers has been successfully grafted on the lignin using free radical copolymerization in appropriate aqueous or organic solvents. The grafting reaction can be initiated by calcium chloride with hydrogen peroxide as a redox initiator which induce the configuration of vinyl homopolymers on the lignin backbone (Chen & Meister, 1999), and then accelerate the formation of lignin graft copolymer (Bonini et al., 2001). In the same direction, ferrous ion with benzoyl peroxide is used as the initiator to create free radicals of acrylamide on the lignin structure (Mohamad Ibrahim, Nur Azreena, Nor Nadiah, & Mohd Saaid, 2006). These techniques are used to design lignin graft copolymer that had been well studied compared to the condensation technique. Remarkably, none of these studies has used *p*-toluenesulfonic acid (PTS) as a catalyst to accomplish the grafting lignin reaction. In general, the condensation technique can be conducted using a solvent as a reaction medium (i.e. solution copolymerization) and without a solvent (i.e. bulk copolymerization). The bulk condensation technique is conducted in the absence of any solvents that restrict possible a solvent effect. Moreover, the bulk technique only requires simple equipment to run the reaction and hence it is much preferred due to the economical aspect.

The present study demonstrates the grafting reaction of acrylic acid (AA) onto Kraft lignin (KL) using the bulk copolymerization technique. The lignin graft copolymer (LGC) is prepared under a condensation copolymerization type via the use of *p*-toluenesulfonic acid (PTS) as the catalyst. The graft copolymerization reaction was accomplished with a variation of reaction parameters such as temperature, time and the PTS concentration. The effects of the reaction conditions on the total conversion (TC) of LGC will be evaluated. The long term purpose of this study was to explore the possibility of using the bulk polymerization technique to produce chemically modified bio-polymer to be used as an additive in hydrocarbon drilling operations especially for high temperature and high pressure conditions.

## 2. Experimental

### 2.1. Materials

The raw material used in this study was the oil palm empty fruit bunch (OPEFB) long fibre supplied by Sabutek (M) Sdn. Bhd, a Malaysian company, that specializes in the recycling of OPEFB. The *p*-toluenesulfonic acid (PTS) was used as received from Merck (Merck, Germany). Acrylic acid (AA), with a 99% purity was purchased from Aldrich® (Sigma-Aldrich, USA). AA was purified under the vacuum distillation process to remove phenolic inhibitors, stored in the refrigerator and brought to room temperature before being used.

### 2.2. Characterizations

#### 2.2.1. Scanning electron microscopy (SEM)

The Kraft lignin (KL) and the lignin graft copolymer (LGC) surface layers morphologies were analyzed using a scanning electron microscope, (SEM) model LEO Supra 50 VP Field Emission. All samples were sputter-coated with a 20 nm gold layer before being subjected to a SEM analysis.

#### 2.2.2. Differential scanning calorimetry (DSC)

The glass transition temperature ( $T_g$ ) values of KL and LGC were estimated using the Perkin Elmer model Pyres 1 DSC. Approximately 10 mg of the sample were heated from  $-50$  to  $180$  °C at the heating rate of  $20$  °C/min in a nitrogen atmosphere at the flow rate of  $30$  ml/min.

#### 2.2.3. Thermogravimetry-Fourier transform infrared (TG-FTIR) analysis (TGA)

The thermal degradation behaviour of the KL and the LGC was studied using a Thermal Analyzer, model TGA/SDTA 851 fitted with Fourier Transform Infrared (Mettler Toledo). The samples were heated from  $30$  to  $900$  °C at the heating flow rate of  $20$  °C/min in nitrogen gas at the flow rate of  $30$  ml/min.

#### 2.2.4. Elemental analysis (CHN)

The percentages of carbon, hydrogen, nitrogen, sulfide and oxygen in KL and LGC structures were obtained using a CHNS/O Analyzer (Perkin Elmer, USA model) Series 2, 2400 using helium as the carrier gas. The heating temperature for the combustion column was maintained constant at  $925$  and  $640$  °C for the reduction column. Approximately  $2$  mg of the samples were used.

#### 2.2.5. Fourier transform infrared (FTIR)

The FTIR spectra of the ungrafted KL and LGC were recorded on the Perkin Elmer system 2000 FT-IR. All the samples were analyzed using the KBr pellet technique and scanned in the range from  $4000$  to  $400$   $\text{cm}^{-1}$ .

### 2.3. Extraction of Kraft lignin from OPEFB fibre

The extraction of KL from the black liquor was accomplished by employing an acidification method. The high alkali black liquor which was collected after the completion of the pulping process was then acidified using sulfuric acid in order to recover KL as precipitate. In particular,  $800$  ml of black liquor in  $1000$  ml beaker was gradually treated with few drops of  $20\%$  v/v sulfuric acid with simultaneously measuring the pH value until pH 2; thereby a precipitation of KL was formed. The precipitate was filtered and washed with pH 2 water, which was prepared using the same acid in the previous step. KL was then dried in a vacuum oven at  $45$  °C for  $72$  h. In order to avoid the moisture in the KL particles, it was grind to a powder form and dried again in a vacuum oven at  $45$  °C for  $72$  h.

### 2.4. Purification of Kraft lignin

The purification of KL was conducted by extracting KL in the soxhlet apparatus for  $6$  h with *n*-pentane to remove lipophilic non-lignin matters such as wax and lipids (Sun & Tomkinson, 2001). The precipitate was filtered and washed twice with pH 2 water to remove the excess *n*-pentane and non-lignin phenolic compounds which may remain after the pulping process. The purified KL was then dried further in the vacuum oven at  $45$  °C for another  $48$  h.

### 2.5. Graft copolymerization reaction

A grafting reaction was achieved in small test tubes equipped with magnetic stirrers. About  $0.75$  g of PTS was introduced into each tube with appropriate amounts of Kraft lignin (KL) and acrylic acid (AA). The tubes were deoxygenated by flushing them with nitrogen gas for  $10$  min, sealed with aluminum foil and then placed in a water bath at  $80$  °C for  $18$  h with vigorous stirring. After a specific reaction time, the tubes were immersed in an ice bath at  $0$  °C for  $1$  h with incessant stirring. The result was a highly turbid black liquid that was decanted into  $0.1$  M zinc sulfate aqueous solution at a ratio of  $1:10$  v/v with agitation and was allowed to stand at room temperature overnight. After this period, unreacted KL was precipitated and removed by filtration. The light brown liquid was evaporated to remove the aqueous solution and unreacted AA. The lignin graft copolymer (LGC) was obtained as light brown

fine particles. These particles were collected and dried in an oven at 100 °C for 72 h to remove moisture from the LGC. A possible reaction mechanism of grafting the AA chain onto the KL structure might comprise of two reaction steps as shown in Scheme 1(a and b). The suggested mechanism involved in the attachment of polyacrylic acid (PAA) chain onto the KL backbone via polycondensation process produced LGC and eliminated water. An ester bond was formed by the interaction i.e. the esterification between hydroxyl group in KL and carbonyl group of AA homopolymer chain. Furthermore, the ester bridge linked PAA as a pendant chain onto the KL main chain (Scheme 1a). The PAA polymeric chain was formed using a PTS inducement of AA monomers as shown in Scheme 1b.

### 2.6. Optimization of the reaction conditions

The graft copolymerization reaction was conducted with numerous batches consisting of different concentrations of KL and AA. In addition, the reactions were carried out under various conditions such as different reaction temperature ranging from 40 to 100 °C, different reaction time from 6 to 30 h and different concentration of the catalyst (0.25, 0.55, 0.75, and 0.95 g). The variation of the grafting conditions was performed at a constant weight of KL and AA. The percentage of total conversion (TC) was measured according to the following equation:

$$\%TC = \frac{W_t - W_k}{W_a} \times 100 \quad (1)$$

where  $W_t$  is the total weight of the product after the grafting reaction,  $W_k$  is the weight of crude KL and  $W_a$  is the weight of AA used in the graft copolymerization reaction (Jiang & Wilkie, 1998).

## 3. Results and discussion

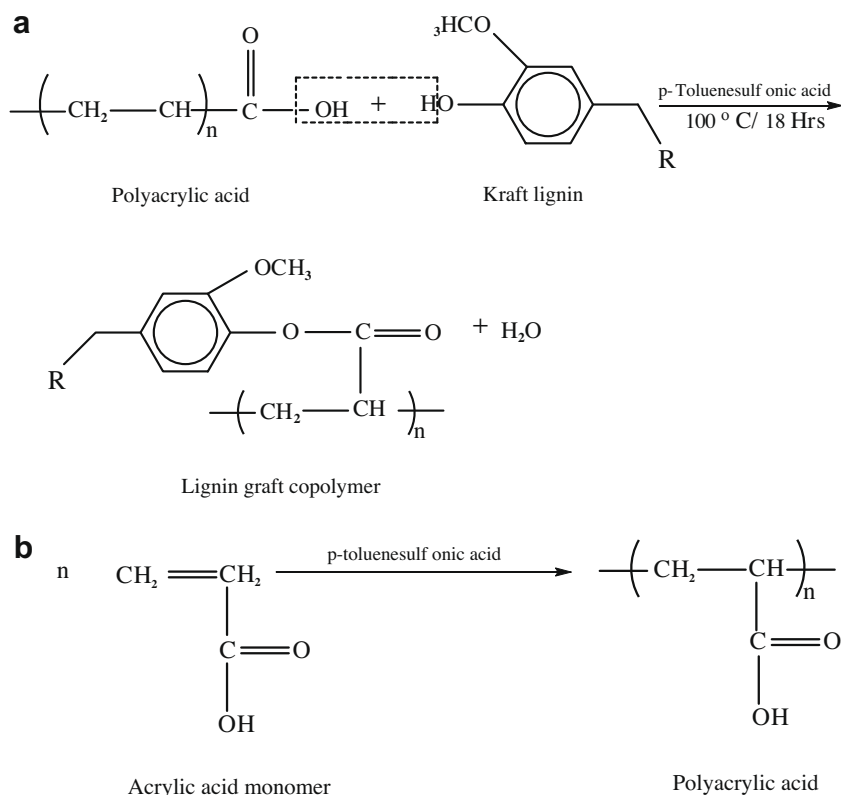
The KL extracted from the OPEFB fibre was insoluble in water. This insoluble property makes it a substance with constricted chemical reactivity which attributes to the complexity inside its structure due to its bulkiness and the reticulation of phenolic groups (Bonini, D'Auria, Ferri, Pucciariello & Sabia, 2003). The newly synthesized light brown colored copolymer (LGC) however, showed high solubility in water, methanol, ethanol, tetrahydrofuran (THF), sulfuric acid, hydrochloric acid, dimethyl sulfoxide (DMSO), dimethylformide (DMF) and acetone. In contrast with KL, LGC is insoluble in chloroform. The grafting reaction improved the solubility of KL; therefore, its chemical reactivity has been enhanced and that may attribute to grafted AA homopolymeric chains onto KL backbone via the condensation process as illustrated in Scheme 1(a and b).

### 3.1. Grafting verification

The Lignin graft copolymer and Kraft lignin were subjected to different characterizations in order to prove the grafting of AA onto KL. In addition, these characterizations were performed to study thermal behaviour, chemical properties and surface morphology of both KL and LGC. The characterized LGC was prepared via bulk copolymerization reaction under constant conditions as follows; 80 °C as reaction temperature, reaction period at 12 h, about 0.25 g of PTS as the catalyst, 0.4 g of KL and 3 ml of AA.

#### 3.1.1. DSC thermal analysis

The thermal properties of ungrafted KL and LGC were studied using the DSC thermal analysis. The KL is an amorphous compound with  $T_g$  at 58.03 °C as illustrated by DSC thermogram Fig. 1. The amorphousness of the KL may be due to the complication in its



**Scheme 1.** Suggested reaction mechanism of grafting AA chain onto KL main chain.

structure which somewhat impede the occurrence of an arrangement in its composition; therefore, no melting temperature  $T_m$  or crystallization temperature  $T_c$  has been recorded in the DSC thermogram. After the grafting reaction had been achieved, it was observed that the resulting LGC also occurred in an amorphous phase, verifying that the grafting reaction had not strongly adapted the complexity of KL starting material. LGC has two  $T_g$  values at 73.85 and 121.84 °C respectively as the DSC thermograms shown in Fig. 2. This illustrates the incompatibility in the LGC structure. The possible explanation of occurrence of these two  $T_g$  values is based on the free volume concept, which attributed a low  $T_g$  value to the large free volume in the graft copolymer chain while the highest  $T_g$  value refers to the chain with less free volume (Li et al., 2003). As free volume increase, the  $T_g$  temperature tends to decrease (Pticek, Hrnjak-Murgic, Jelencic, & Kovacic, 2005). The above-mentioned explanation investigated the correlation between the free volume property and the LGC chemical structure

that was suggested in Scheme 1(a and b). Therefore, the lower  $T_g$  value corresponds to AA homopolymer branched chain which is a hydrocarbon chain without bulky groups that gives PAA molecules enough space to move. This means, the mobility of PAA molecules tends to be more flexible, which may increase the free volume and decrease the  $T_g$ . On the contrary, the phenyl groups in KL may increase the bulkiness in the KL main chain and decrease its molecules mobility as well as its chain flexibility; thus, the free volume decrease and high  $T_g$  value obtained. Furthermore, the grafting reaction has enhanced the thermal properties of KL; whereas the two  $T_g$  temperatures of LGC are both more than the  $T_g$  temperature of KL.

### 3.1.2. TG-FTIR thermal analysis

The thermal behaviour of the ungrafted KL and LGC was distinguished by the TG-FTIR thermal analysis. The TG-FTIR curves detected volatile compounds which were volatilized during the

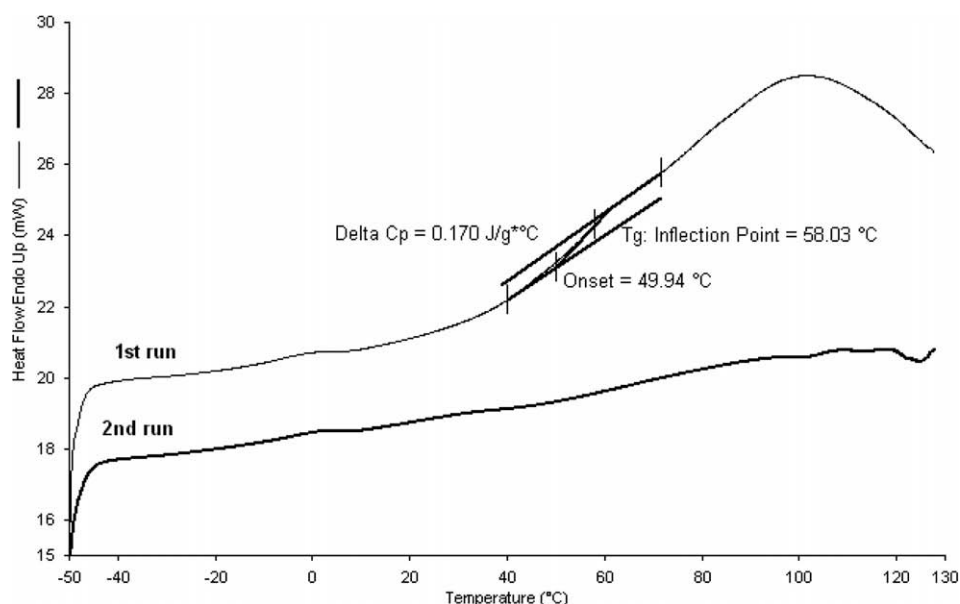


Fig. 1. DSC thermogram of KL,  $T_g$  at 58.03 °C.

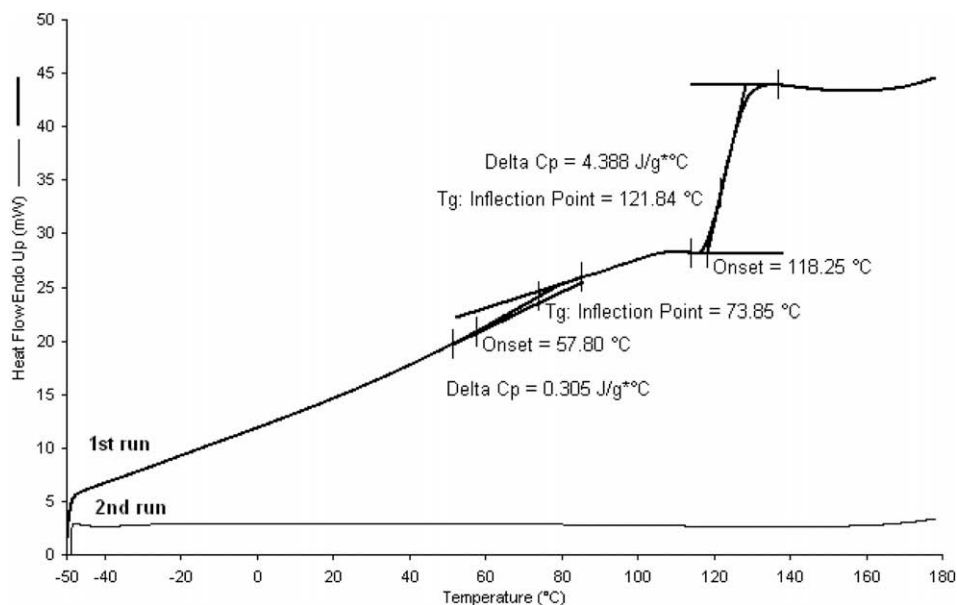


Fig. 2. DSC thermogram of LGC, two  $T_g$  temperatures at 73.85 and 121 °C.

degradation steps. Fig. 3 indicates the TG-FTIR thermogram of KL. The initial decomposition step of KL was recorded in the range of 35.38–114 °C with 2.2829% weight loss attributed to water removal (moisture) (Campanella, Tomassetti, & Tomellini, 1991). The second degradation occurred in the range of 114.36–288.65 °C with 17.1088% weight loss due to the elimination of water, nitrogen dioxide and sulfur dioxide. The appearance of sulfur dioxide during the KL pyrolysis attributed to the former effect of Na<sub>2</sub>S on the KL structure in the duration of Kraft pulping process (Fenner & Lephardt, 1981). The third decomposition step is in the range of 288.65–659.40 °C with 36.2974% weight loss due to volatilize water, carbon dioxide and ethyl isocyanate. The final degradation was detected in the range of 659.40–898.49 °C with 14.8965% weight loss referred to the release of carbon dioxide, ethyl isocyanate and *t*-butyl isocyanate. The volatilization of ethyl isocyanate and *t*-butyl isocyanate may suggest that the reaction of nitrogen gas with alkyl compounds which might have been generated during the KL thermal degradation (Liu, Wang, Zheng, Luo, & Cen, 2008). Fig. 4 highlights the TG-FTIR thermogram of LGC. The earlier degradation step of the LGC occurred in the range of 34.93–126.26 °C with 7.2148% weight loss due to the release water. The second decomposition step was recorded in the range of 126.26–288.04 °C with 20.2602% weight loss attributed to the elimination of acrylic acid, crotonic acid and methacrylic acid which may reveal the existence of PAA side chain in new product composition. The volatilization of acrylic acid and methacrylic acid might be due to the detachment of a number of AA monomeric chains which were weakly linked in PAA chain that were attached with KL backbone. The fragile ester bonds in the LGC

structure might simply be broken and liberate AA that changed into methacrylic acid at the thermal region at 126.26–288.04 °C. Water, sulfur dioxide, carbon dioxide and methyl sulfone were volatilized within the temperature range of 288.04–513.63 °C with 4.8728% weight loss. The volatilized sulfur dioxide and methyl sulfone is attributed to the effect of the previous Kraft pulping process (Fenner & Lephardt, 1981). At the range of 513.63–742.81 °C; sulfur dioxide, carbon dioxide and methyl sulfone were released with 29.6248% weight loss. The final decomposition step was observed in the range of 742.81–900.42 °C with 0.9318% weight loss due to the removal of: water, nitrogen dioxide and 2-methylpyridine. The (C–C) and (C=C) bonds in the LGC which may easily be broken at high temperature were combined and formed alkyl and vinyl compounds via decomposition and condensation reactions (Domínguez, Oliet, Alonso, Gilarranz, & Rodríguez, 2008). The alkyl and vinyl compounds may then configure with nitrogen gas resulting in 2-methylpyridine as a volatilized compound. The elimination of water and nitrogen dioxide is possibly attributed to the association between nitrogen gas and (OH) group released from LGC thermal decomposition. The appearance of water and carbon dioxide among the volatile compounds during the KL and LGC thermal degradation might be attributed to the reaction between the released (OH) group and (C–C) or (C=C) cleavage bonds (Baumlin et al., 2006). The TG-FTIR curves indicated that in the range between 35 and 898 °C, KL maintained 29.40% of its weight, while in the range between 34.9 and 900.42 °C the new product retained 37.075% of its weight. Therefore, the TG-FTIR thermogram demonstrates that the new product has better thermal stability.

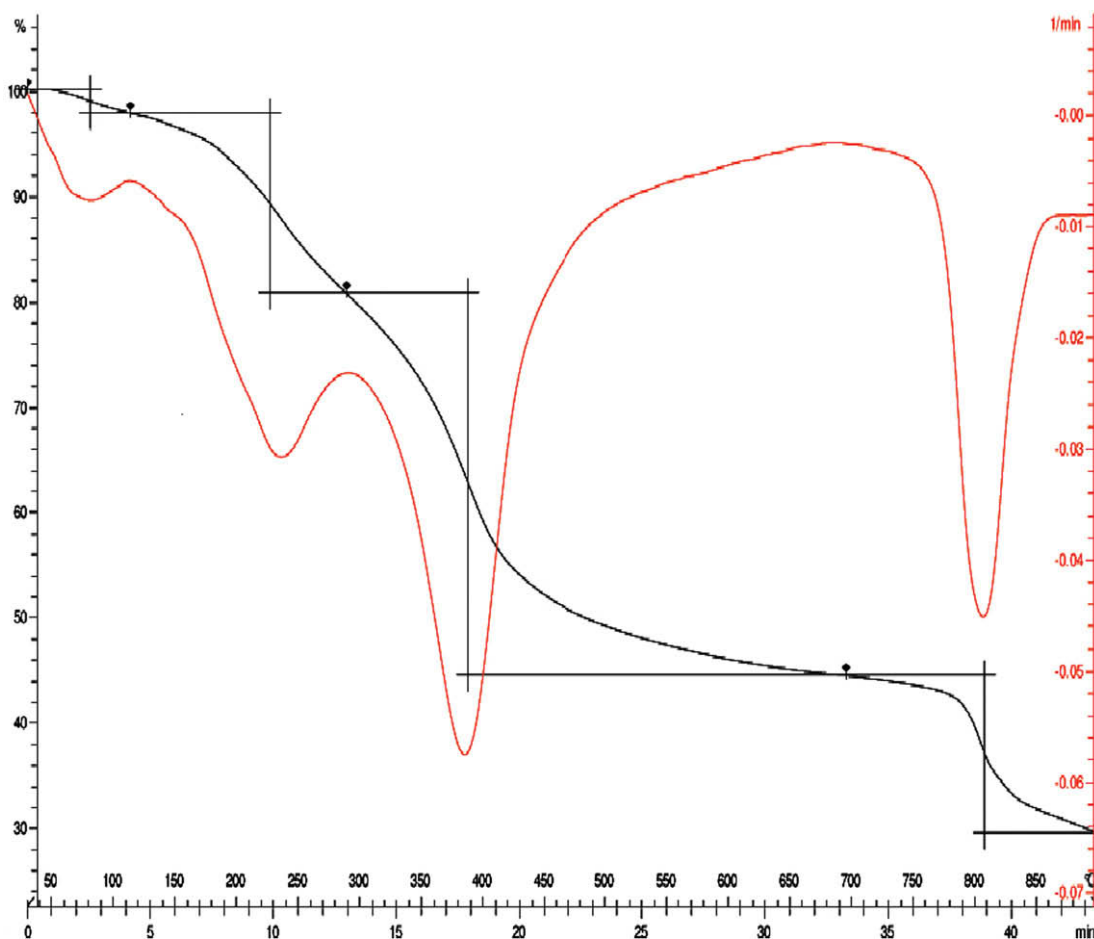


Fig. 3. TG-FTIR thermogram of KL.



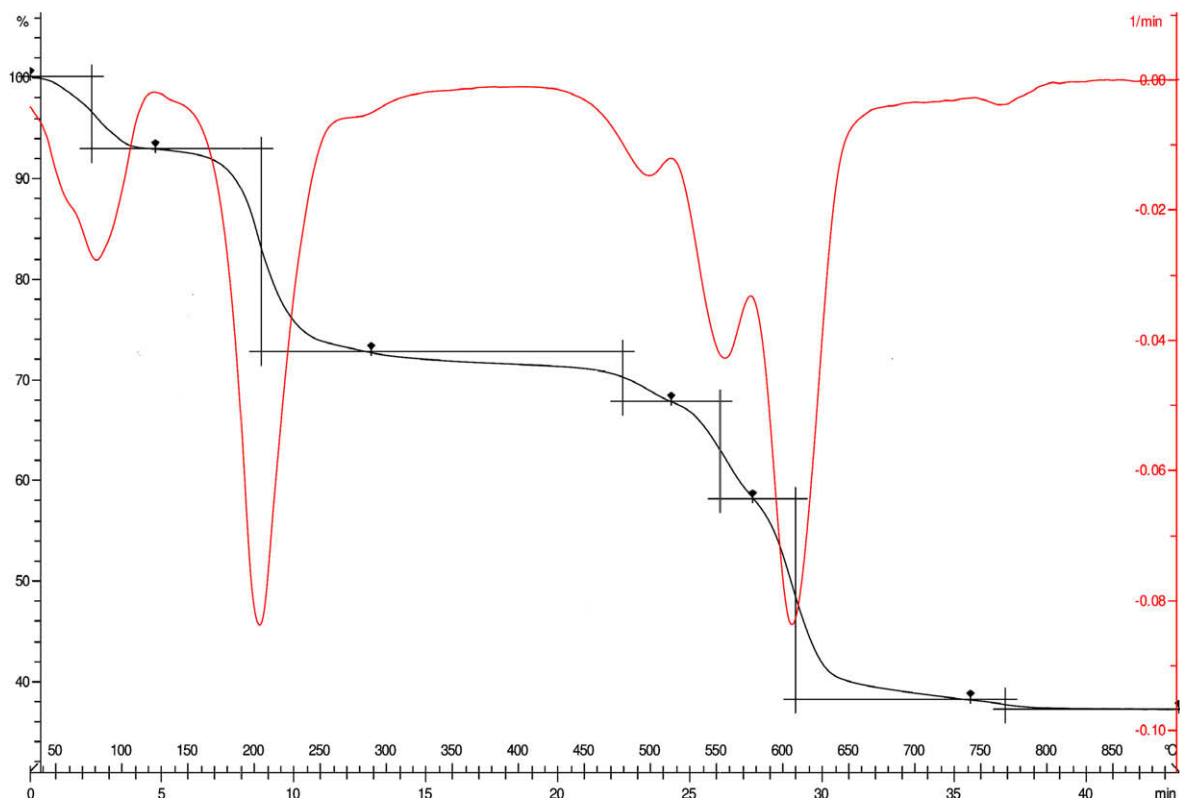


Fig. 4. TG-FTIR thermogram of LGC.

### 3.1.3. FTIR analysis

Fig. 5 illustrates the FTIR spectra of KL and LGC. The KL spectrum shows absorption at  $3415.52\text{ cm}^{-1}$  assigned to (OH) broaden band of either hydrogen bonded or hydroxyl group in the phenolic and aliphatic compounds. The absorption peak at  $2935.29\text{ cm}^{-1}$  was due to (C–H) stretch band of methyl group (Jin, Pu, Xie, Take-shi, & Liu, 2005). The vibration at  $1712.69\text{ cm}^{-1}$  exhibited (C=O) stretch band of carbonyl group (Ishimaru, Hata, Bronsveld, Meier, & Imamura, 2007). The stretching of (C=C) and (C–C) bands in the aromatic range were recorded at  $1616.20$  and  $1462.98\text{ cm}^{-1}$  respectively (Trinsoutrot et al., 2001). The peak at  $1143.11\text{ cm}^{-1}$  could be attributed to (C–O) bond in ethers. In the LGC spectrum, the presence of peak at  $3419.04\text{ cm}^{-1}$  was assigned to (OH) stretch bonds of hydroxyl group (Milstein et al., 1994). The frequency at  $2920.86\text{ cm}^{-1}$  was due to the stretching of (C–H) band of methyl group in lignin (Bonini et al., 2001). Peaks at  $2489.21$  and  $1919.17\text{ cm}^{-1}$  were considered aromatic overtones. The absorption at  $1723.07\text{ cm}^{-1}$  was due to (C=O) the stretch band in  $\alpha$  and  $\beta$ -unsaturated esters which verified the placement of ester bonds between aromatic rings in the KL structure and unsaturated polymeric chain of PAA and supported the expected grafting reaction mechanism in Scheme 1(a and b). The characteristic ester group in the spectrum substantiated that the LGC was formed by ester bonding between KL and PAA.  $1601.55$  and  $1497.10\text{ cm}^{-1}$  wave numbers were distinguished as C–C stretching bonds in aromatic rings in lignin components (Sreekala, Kumaran, Joseph, Jacob, & Thomas, 2000). Further evidence to the occurrence of the ester groups among LGC structure was provided by the absorption at  $1189.59\text{ cm}^{-1}$  which was assigned as an expanding (C–O) bond in the ester groups.

### 3.1.4. CHN elemental analysis

The percentages of KL elementals as recorded from the CHN analysis were: carbon: 38.46%, hydrogen: 4.18% and nitrogen:

0.45%, while the LGC results were: carbon at 11.90%, hydrogen at 2.48% and nitrogen at  $-0.11\%$ . It was observed that, the percentages of C, H and N in LGC were less than the percentages of the same KL elements. This variant between KL and LGC in the CHN dates could be attributed to the esterification process (Scheme 1a) which increased the number of ester bonds in LGC structure compared with KL. Since, the esterification process during the reaction leads to increase the solubility of the product (Zhang & Hayes, 1999). In this way, the increase might have enhance the LGC solubility.

### 3.1.5. SEM microscopy

Fig. 6 showed the SEM images of KL and LGC samples. From the SEM images, it showed that KL has a rough surface with shapeless configure and the granular structure can be observed (Bonini, D'Auria, Ferri, Pucciariello & Sabia, 2003). On the other hand, the morphological image of LGC indicates continues harmonized structure with wavy surface. In addition, it can be seen from Fig. 6 that the existence of pores in LGC. These pores could facilitate the penetration and enhanced the solubility of LGC. The morphology of KL was completely changed after grafting reaction.

## 3.2. Grafting optimization

The effects of KL, AA, PTS, time and temperature on the graft copolymerization reactions were estimated and the optimum conditions obtained for graft copolymerization are as mentioned and discussed in subsequent sections.

### 3.2.1. The effect of reaction time

The grafting reaction time varied from 6 to 30 h with constant concentration of KL, AA and PTS. The reaction was conducted through a steady heating temperature at  $80\text{ }^{\circ}\text{C}$ . Fig. 7a shows the effect of various reaction times on the percentage of total conver-

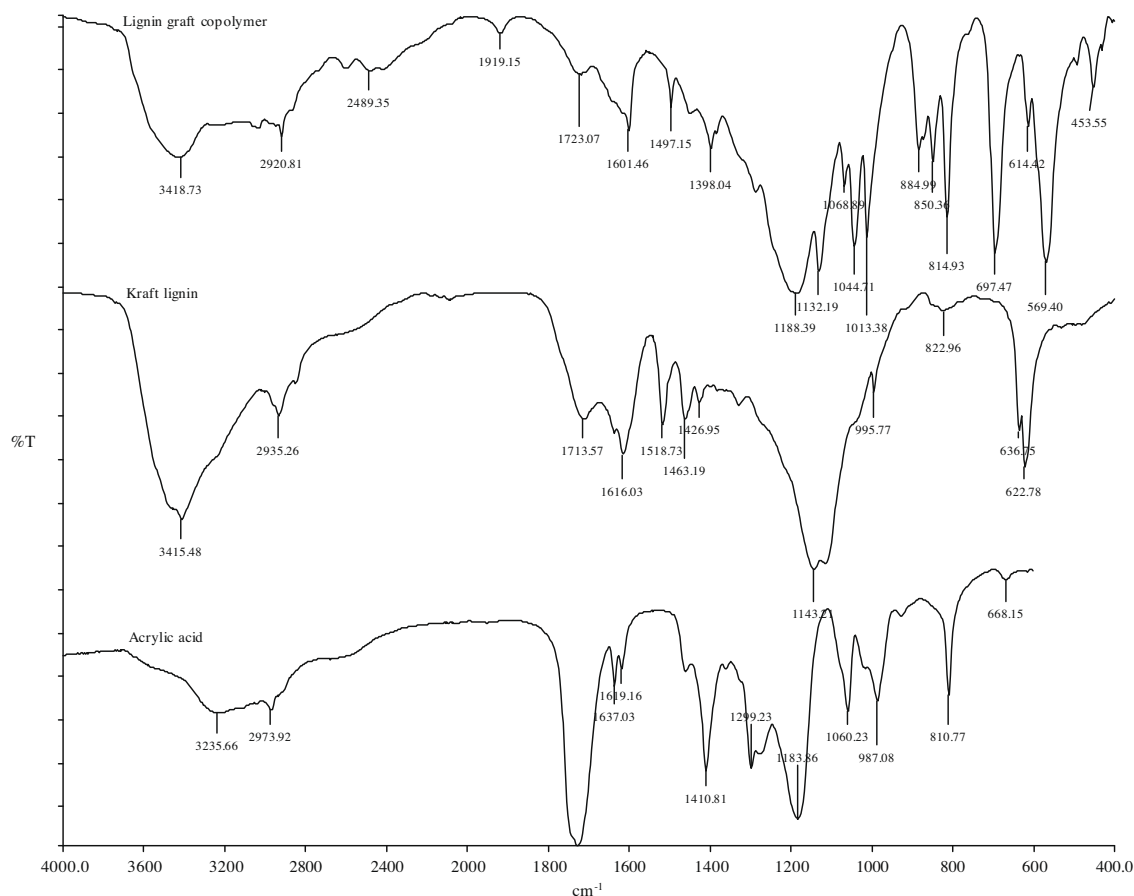


Fig. 5. FTIR spectra of LGC, KL and AA.

sion TC. When the grafting reaction was carried out at a period from 6 to 12 h, an increase in the percentage of TC was observed; which could be attributed to the inception of the propagation step. Therefore, ongoing connection of AA polymeric side chains with the main chain occurred during this period of time. The highest percentage of TC was observed when the reaction time was raised to 18 h. This increase may be due to the saturation of KL backbone chain with adequate branched PAA chain. Furthermore, the decrease in the percentage of TC with increasing reaction time from 24 to 30 h could be attributed to the decrease of the propagation velocity. This might have been due to reduce the ability of PTS to induce the condensation process in tandem with rising reaction time. Owing to the highest percentage of TC obtained with the grafting reaction that was achieved at 18 h, this is considered the optimum time period to graft AA onto KL.

### 3.2.2. The effect of reaction temperature

The temperature of graft copolymerization reaction also varied from 20 to 100 °C with different concentrations of KL, AA and PTS. The above mention reaction was performed at 12 h as the time period. Fig. 7b highlights the affect of different reaction temperatures on the percentage of TC. When the grafting reaction was conducted at 20 °C, the percentage of TC was 0%, and there was no significant change of viscosity in the reaction medium; indicating that the grafting reaction does not occur at that temperature. It was observed that, an increase of viscosity was observed with a high percentage of TC at 40 °C, which may be due to an increase of the reaction ratio when the reaction temperature was raised. The percentage of TC decreased with the increase in reaction temperature above 40 °C which could be attributed to the limitation of the reactant's ability due to the decrease reaction ratio. On the other hand,

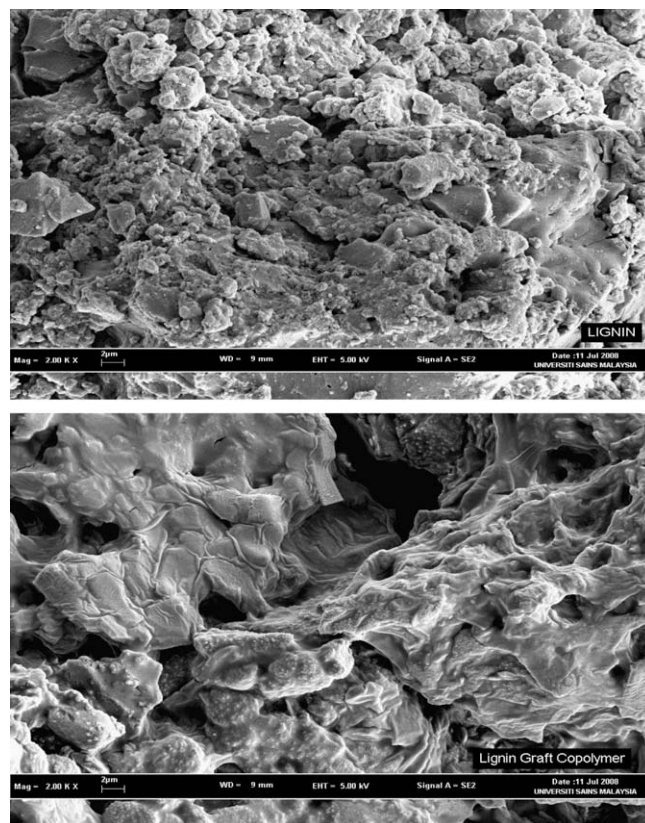
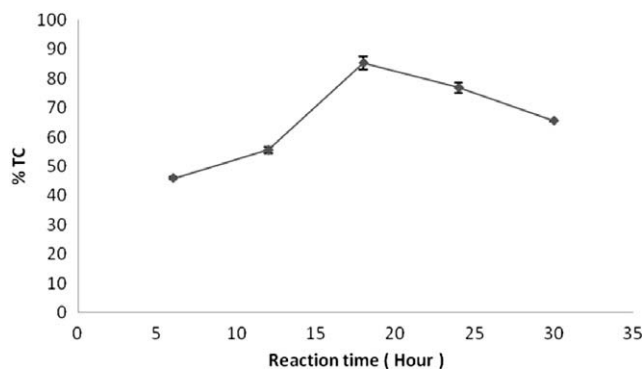
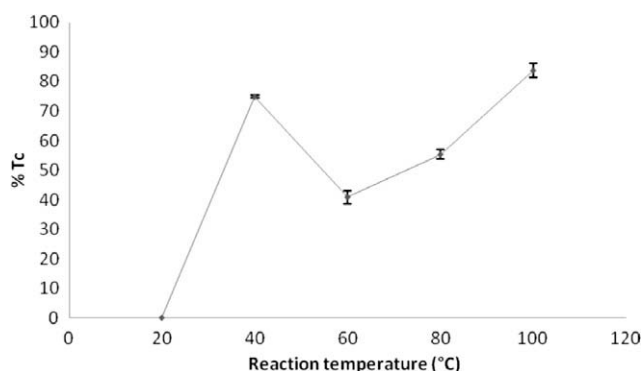


Fig. 6. SEM microphotographs of: KL (above) and LGC (below).



**Fig. 7a.** Effect of reaction time on the percentage of TC: KL, 0.2256 g; AA, 3.45 g; PTS, 0.75 g; reaction temperature 80 °C.

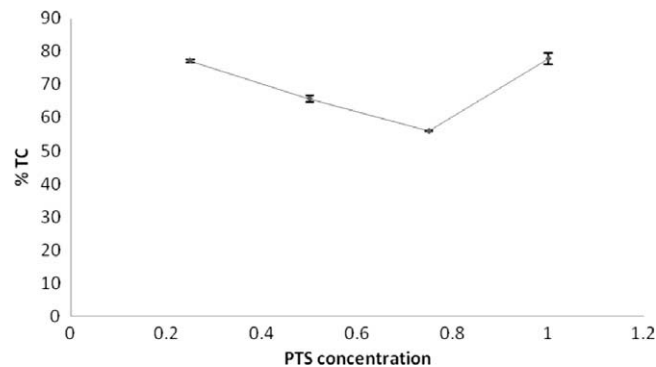


**Fig. 7b.** Effect of reaction temperature on the percentage of TC: KL, 0.2256 g; AA, 3.45 g; PTS, 0.75 g; reaction time, 12 h.

TC percentage started to increase in tandem with the elevation of reaction temperature until it reaches the maximum percentage (82.16%) at 100 °C. This can be explained by the high temperature that was provided the high energy to the polymeric side chain which facilitated branching onto the main chain. Thereby, the reaction ratio was increased and that might have resulted in the highest conversion.

### 3.2.3. The effect of PTS concentration

The concentration of PTS was used as the catalyst to motivate the condensation copolymerization of that KL was varied as follows; 0.25, 0.50, 0.75 and 1.00 g respectively with constant concentrations of KL and AA. The conditions of the grafting reaction used to study the affect of PTS concentration were; reaction time at 12 h and reaction temperature at 80 °C. Fig. 7c shows the effect of varied PTS concentration on the percentage of TC. The percentage of TC started with a high value when 0.25 g of PTS was used. This may be attributed to the high capability of PTS to induce the condensation reaction between the PAA polymeric chain and the KL backbone. This inducement facilitated the formation of ester bonds between PAA and KL. As the concentration of PTS in the grafting batched increased, a decrease in the percentage of TC was observed. A possible explanation could be that when the PTS was concentrated in the reaction medium, it might have decreased the reaction rate which in some way constricted the esterification process and resulted in the LGC with a low conversion rate. An increase of the TC percentage against the high concentration of PTS was observed, that may illustrate an increase in the PTS capability which resulted high conversion. The highest percentage of TC was obtained with 0.25 g of PTS; therefore, it is much preferable based on practical and economical aspects.



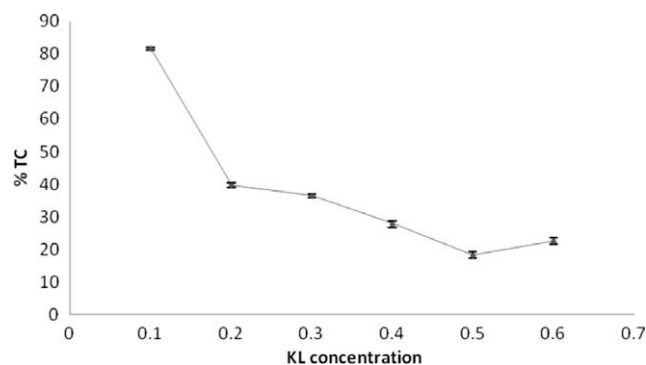
**Fig. 7c.** Effect of PTS concentration on TC percentage: KL, 0.2256 g; AA, 3.45 g; reaction time, 12 h; reaction temperature, 80 °C.

### 3.2.4. The effects of KL concentration

The graft copolymerization reaction was conducted using various batches consisting of different concentrations of KL (0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 g). The grafting reaction was carried out with a steady heating temperature at 80 °C and constant reaction time at 12 h using 0.75 g of PTS as a catalyst for each of the batches. Fig. 7d illustrates the effect of varying KL concentration on the percentage of TC. High percentages of TC were obtained when (0.1, 0.2, and 0.3) g of the KL was used in the grafting batches. This could be due to the increase of the tendency of the KL molecules at low concentration in comparison with high concentration. This permitted the branched points to form and extend along with the KL backbone and resulted LGC with high TC percentage. Conversely, high concentrations of KL in the grafting batches may increase the reticulation in the KL structure, which hindered the expansion of the grafting sites through the KL backbone. This gave low TC percentages relative to the increased KL in the concentration in the grafting batches.

### 3.2.5. The effect of AA concentration

The AA concentration used in the grafting batches were (2, 3, 4, 5, 6, and 7) ml. The grafting reaction was achieved under constant conditions of reaction time at 12 h and at the reaction temperature of 80 °C. When 0.75 g of PTS was introduced into each batch of the grafting batches. Fig. 7e shows the affect of variant concentrations of AA on the percentage of TC. The TC percentage was increased continuously with the decrease in the AA concentration in the grafting batches that was attributed to raising the affinity of PAA polymeric chain to attach onto the KL structure via ester bonds. The highest concentration of AA in the grafting batches may generate deficiency in some degree of distribution on the grafting sites



**Fig. 7d.** Effect of KL concentration on the percentage of TC: reaction temperature 80 °C; reaction time, 12 h; PTS amount, 0.75 g.



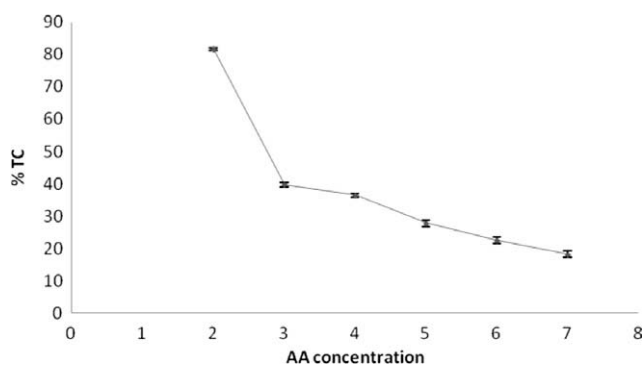


Fig. 7e. Effect of AA concentration on TC percentage: reaction time, 12 h; reaction temperature, 80 °C.

on the KL structure which restricted the formation of ester bonds and reduced TC percentage. As a consequence, the grafting reaction of KL appeared to be more functional with a low concentration of AA.

#### 4. Conclusions

In this experiment, the water soluble LGC was successfully prepared by the means of the bulk copolymerization technique using PTS as a catalyst. Apart from that, PTS could be a sufficient catalyst to induce KL grafting reactions for further studies. It can be concluded that the percentage of the TC was dependant upon the KL concentration, the AA concentration, the PTS concentration, the reaction time and the reaction temperature. Additionally, the graft copolymerization reaction produced LGC which had better thermal stability in comparison with KL as shown by DSC and TGA-FTIR thermograms. Moreover, the chemical structure of KL has changed as the CHN analysis illustrated. It is interesting to note that the morphological surface of the KL was homogenized by the grafting reaction as observed in SEM microphotographs. However, this study elucidated the possibility of applying the bulk technique to polymerize KL with a specific vinyl monomer. In this case and further studies, KL should be soluble in the vinyl monomer to avoid the need of any solvents to carry out the polymerization reaction.

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