PREPARATION AND APPLICATION OF DIMER ACID/LIGNIN GRAFT COPOLYMER

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Dimer acid (DA) was grafted onto lignin (EHL) to form a graft copolymer DA-g-EHL. The selection of the reaction type and the optimization of the reaction conditions for the grafting reaction were conducted through orthogonal and single factor experiments. FT-IR and thermal analysis were used to characterize the graft product. It was found that, compared with free radical grafting, DA can be grafted onto EHL more effectively by ester condensation with strongly acidic cation exchange resin as a catalyst. Under optimum reaction conditions, the increase of acid value and the yield of graft copolymer can reach about 9.3% and 83%, respectively. The application of DA-g-EHL in preparing modified phenolic aldehyde amine curing agent (PAA) was studied. Results showed that the flexibility of the epoxy resin cured by DA-g-EHL modified PAA is significant higher than that of the resin cured by EHL modified PAA. The graft of DA onto EHL may reduce the rigidity of EHL and the chain stiffness of the PAA modified by EHL.

Keywords: Lignin; Dimer acid; Grafting reaction; Curing agent

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INTRODUCTION

Lignin is the second most abundant organic resource on earth, exceeded only by cellulose. It is primarily a structural material to add strength and rigidity to cell walls and constitutes 15 to 40 wt% of the dry matter of woody plants. The lignin (EHL) used in this study was isolated from the residue of enzymatically hydrolyzed cornstalks as a by-product of bioethanol industry. Making use of this agro-based renewable biomass to replace common petroleum-based raw material in producing plastics will not only benefit the bio-industry but also diminish potential environmental pollutions. The applications of different kinds of lignin in the synthesis and modification of many valuable polymer materials, including polyurethane, polyethylene, phenolic, and epoxy resins, have been reported in recent years (Ciobanu et al. 2004; Sun et al. 2007; Jin et al. 2010; Sailaja and Deepthi 2010).

Lignin is a crosslinked macromolecular material based on a phenylpropanoid monomer structure. The structural units of lignin are shown in Fig. 1. Due to its network molecular structure, lignin is rigid and relatively bulky. It imposes stiffness and steric hindrance to any chain to which it is attached. Therefore, the resins modified by lignin usually have good thermal stability and high tensile strength. However, in most cases, the flexibility of the resins decreases significantly after modification, which limits the use of lignin in many potential applications (Alexy et al. 2000; El Raghi et al. 2000).

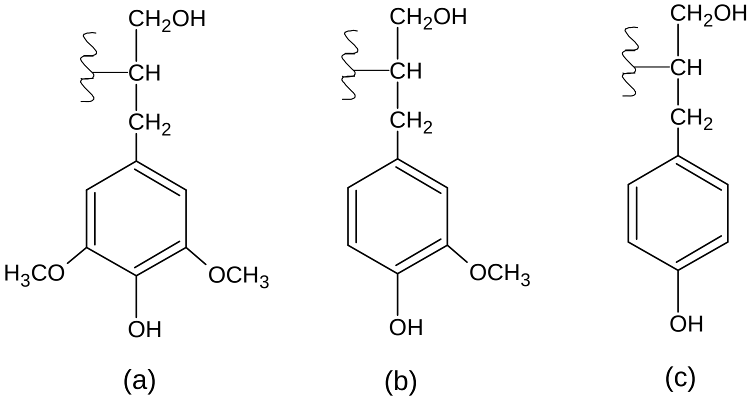


Fig. 1. The structural units of lignin (a) syringyl, S, (b) guaiacyl, G and (c) *p*-hydroxyphenyl propane, H

Dimer acid (DA) is a dicarboxylic acid prepared by dimerizing unsaturated fatty acids by a Diels-Alder reaction (Fig. 2). Since its main raw material is derived from natural oils such as tall oil, cottonseed oil, and soybean oil, DA is also an important renewable resource, and it is used primarily in the synthesis of polyamide resins, alkyd resins, and some functional copolymers (Guo and Huang 2004; Heidarian et al. 2004; Hablot et al. 2010; Matadi et al. 2011). Industrial DA usually contains predominantly a dimer of stearic acid. In contrast to lignin, the aliphatic carbon chains confer considerable flexibility to DA. The introduction of DA into EHL may increase the backbone flexibility of the graft copolymer, and thereafter reduce the chain stiffness of the polymers modified by EHL. The aim of this work was to (a) present an effective method for the preparation of a novel graft copolymer DA-g-EHL and (b) to give a preliminary evaluation of the potential application of DA-g-EHL in producing modified epoxy resin curing agents.

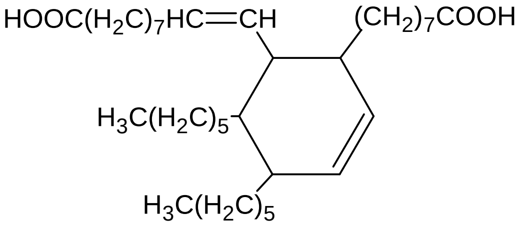


Fig. 2. Molecular structure of DA

EXPERIMENTAL

Materials

EHL was isolated from the residue of enzymatically hydrolyzed steam-exploded cornstalks that had been treated with sodium hydroxide solution (Chen and Cheng 2009; Zhou et al. 2011). Due to the unique isolation procedures used, the density of functional groups was very high in EHL. The weight-average molecular weight of the lignin was 2062 g/mol, the hydroxyl number was 124.6 mg KOH/g, and the content of phenolic hydroxyl and methoxy groups was 4.25 mmol/g and 9.3%, respectively. In addition, the content of impurities, such as residual sugar (0.7%) and ash (2.1%), was quite low. DA used in this study was supplied by Baixin Science and Technology Co., Ltd, China. It is a light-yellow, viscous liquid at room temperature with the dimer, trimer, and monomer content at >95, <5, and <1%, respectively.

A strongly acidic cation exchange resin (CER) and a SO_4^{2-}/ZrO_2 solid super acid (SSA) were used as catalysts in the grafting reaction. SSA was prepared in the laboratory using precipitation-impregnation method described by Wang et al. (2007). Cation exchange resin (CER) was purchased from Sinopharm Chemical Reagent Co., Ltd, China. It is based on crosslinked polystyrene and the crosslinking is achieved by adding 0.5-25% of divinylbenzene to styrene at the polymerization process. The sulfonic acid groups are introduced after polymerization. The total exchange capacity of CER is 4.5 mmol/g. Benzoyl peroxide (BPO), dioxane, and methanol were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. They were used as received.

Preparation of DA-g-EHL

In a typical grafting reaction, 10g of EHL and 0.09 g of catalyst were dissolved in 80 mL dioxane and added into a jacketed reactor flask equipped with a stirrer, a thermometer, and a reflux condenser with drying tube. The system was agitated and heated to 50°C, and 4.5 g of DA was thereafter dissolved in 20 mL dioxane and added dropwise into the reactor within 30 min. The grafting reaction was then carried out at solvent refluxing temperature with nitrogen sweep for 5 h.

After completing the reaction, the catalyst was immediately separated from the dark-brown solution by centrifuge. Then, the graft copolymer was precipitated by adding the solution into vigorously stirred methanol. The precipitate was filtered off, washed with methanol, and dried at 70°C under vacuum for 24 h. Finally, the dried product was extracted in a Soxhlet extractor with chloroform for 12 h and dried to a constant weight.

From Fig. 2 it can be observed that homopolymerization of DA in the grafting reaction is very difficult; this is because of steric hindrance by 1, 2-disubstitution of double bonds. Hence, homopolymerization of DA is negligible in the grafting copolymerizaton of DA onto EHL. The suggested mechanism of the grafting reaction is illustrated in Fig. 3.

Characterization of DA-g-EHL

The functional groups on EHL and DA-g-EHL were analyzed by a FT-IR2000 spectrometer (Perkin Elmer, U.S.). The thermal degradation behavior of EHL and DA-g-EHL was studied by a STA449F3 thermal analyzer (Netzsch, GER). The samples were heated from 30 to 800°C with a heating rate of 10°C/min in nitrogen atmosphere. The hydroxyl number of EHL and the acid number of the graft copolymer were measured by chemical titration according to Chinese National Standard GB 12008.3 and GB 12008.5, respectively. The end point of titration was determined by pH value for dark brown color of EHL. Each data point was taken as the average of three measurements.

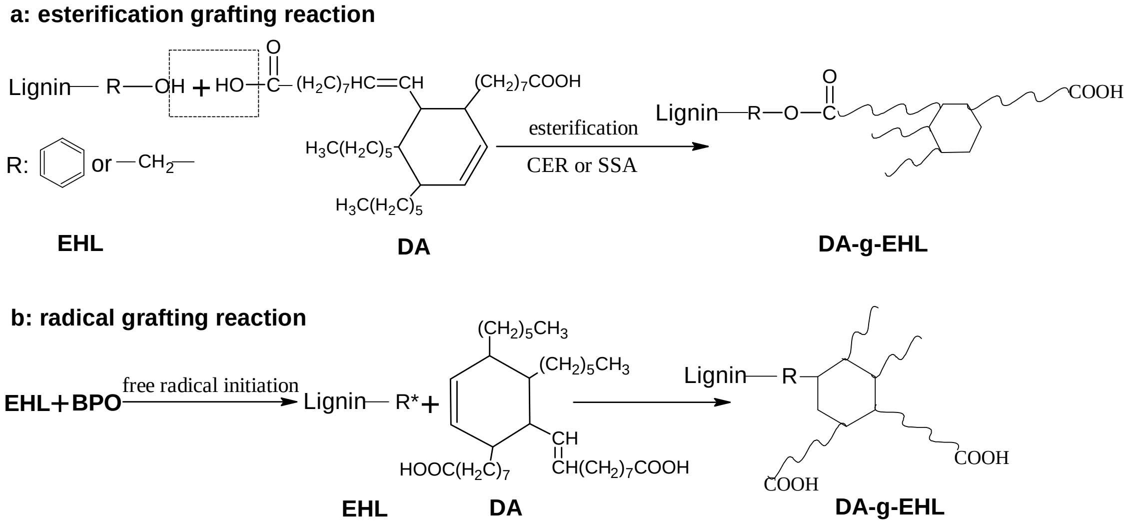


Fig. 3. Suggested reaction mechanism of grafting DA onto EHL

Since the graft of DA onto EHL will increase the acid value of copolymer DA-g-EHL, the “increase of acid value” and the “yield of graft copolymer” were used to evaluate the grafting effect in this study. The yield of graft copolymer refers to the amount of copolymer obtained in the grafting reaction. It was calculated according to the following equation (Ke et al. 2010),

$$\text{Yield of graft copolymer (\%)} = \frac{w_2}{w_0 + w_1} \times 100 \tag{1}$$

where w_0, w_1 and w_2 are the weight of crude EHL, DA and graft copolymer DA-g-EHL, respectively. The increase of acid value was defined as the increase rate of EHL acid value after grafting reaction,

$$\text{Increase of acid value (\%)} = \frac{p_2 - p_1}{p_1} \times 100 \tag{2}$$

where p_1 and p_2 are the acid value of EHL and DA-g-EHL, respectively.

Application of DA-g-EHL in Polymer Modification

To evaluate its potential application in polymer modification, DA-g-EHL was applied in the preparation of modified phenolic aldehyde amine (PAA) following the method described by Hu et al. (2007). In these reactions, 25 wt% of phenol was replaced by DA-g-EHL or pure EHL to give two modified PAA samples. Two modified and one commercial PAA samples were thereafter used as epoxy resin curing agents, and the curing conditions were as follows: the dosage of PPA was 20 wt% of epoxy resin; the curing temperature was 86^{o}C, and the curing time was 3 h. The tensile and the bending properties of the cured epoxy resin were measured according to Chinese National Standard GB/T 1040 and GB/T 9341, respectively.

RESULTS AND DISCUSSION

Selection of Catalyst or Initiator

DA is a kind of long-chain fatty acid with unsaturated bonds and carboxyl groups. Therefore, DA may be grafted onto EHL by radical grafting reaction or esterification. BPO is a radical initiator widely used in the synthesis of various types of polymers and graft copolymers. Because of the ease of application and separation, SSA and CER are both promising catalysts in esterification. In this study, BPO, SSA, and CER were used as initiators or catalysts and added to the reaction mixture in catalytic proportion under typical reaction conditions. The increase of acid value and the yield of the products catalyzed by BPO, SSA, and CER were 2.83%/74.1%, 7.11%/80.5%, and 9.21%/82.7%, respectively. These data indicated that the catalytic effect of radical initiator BPO is significant lower than that of esterification catalysts SSA and CER. This phenomenon suggests that although DA can be grafted onto EHL by radical reaction and esterification, esterification is a far more effective method for this process.

It can be seen in Fig. 2 that DA has a long aliphatic chain with many possible conformations and two terminal carboxyl groups. Through changes in the chain conformations, the functional group -COOH on DA may encounter and react with -OH on EHL easily. Contrary to carboxyl groups, two unsaturated double bonds on DA are at the middle of the molecule. Thus, the radical grafting reaction may be greatly hindered by the surrounding aliphatic chains because of the effect of steric hindrance. Moreover, the hindered phenolic structure on EHL will also inhibit the radical grafting reaction to some extent. Therefore, condensation grafting copolymerization is more likely to take place than radical grafting in this case. Although both SSA and CER can catalyze the grafting reaction between DA and EHL effectively, a better grafting effect was observed when CER was used in the reaction. Therefore, CER was used as the catalyst in the following studies.

Optimization of the Synthesis Conditions

In order to optimize the synthesis conditions, many factors that may have an effect on the grafting reaction were considered in the preliminary experiments. Based on the results of orthogonal analysis, the effect of some key factors, including the mass ratio of DA to EHL, the dosage of catalyst and the reaction time, on the grafting reaction were further studied by single factor experiments.

Effect of the mass ratio of DA to EHL

In the grafting reaction, DA was grafted onto EHL through ester condensation. The effect of the mass ratio of DA to EHL on the increase of acid value and the yield of graft product was investigated and shown in Fig. 4. It was found that the acid value of graft copolymer increased first with increasing mass ratio and then reached a plateau when the mass ratio exceeded 0.4:1. The maximum of the increase of acid value (9.25%) was reached at a mass ratio of 0.45:1. However, since the acid value of DA is 194 to 198 mgKOH/g and the hydroxyl value of EHL is 124.6 mgKOH/g, the theoretical mass ratio should be close to 0.64:1 in a typical ester condensation. This variation can be ascribed to the complex structure of lignin. During the grafting reaction, some hydroxyl groups were buried inside the network structure of EHL and cannot get access to the carboxyl groups on DA. Therefore, the active hydroxyl value of EHL was lower than 124.6 mgKOH/g and the optimum mass ratio decreased accordingly from 0.64 to 0.45:1 in the reaction.

As the mass ratio increased from 0.30 to 0.55:1, the yield of graft copolymer decreased constantly from 84.4% to 78.5%. When the increase of acid value reached the plateau (mass ratio at 0.4-0.45:1), a sharp decline of the yield was observed. This is because at this stage, all the accessible hydroxyl groups on EHL have been esterified. Further increasing amount of DA cannot improve the grafting effect any more, which thereafter results in the sharp decline of the yield. Thus, the ideal mass ratio of DA to EHL is 0.40:1 to 0.45:1.

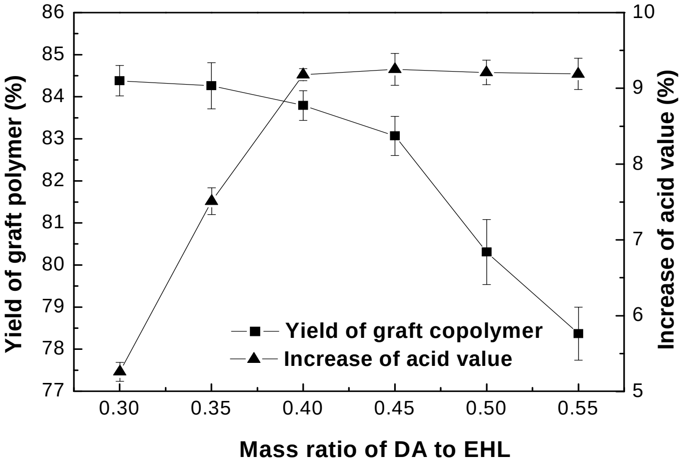


Fig. 4. Effect of the mass ratio of DA to EHL on the acid value and the yield of graft copolymer

Effect of the dosage of catalyst

The effect of the dosage of CER on the grafting reaction was studied and results are shown in Fig. 5. It can be seen in Fig. 5 that both of the increase of acid value and the yield of copolymer first increased and then decreased with increasing catalyst dosage.

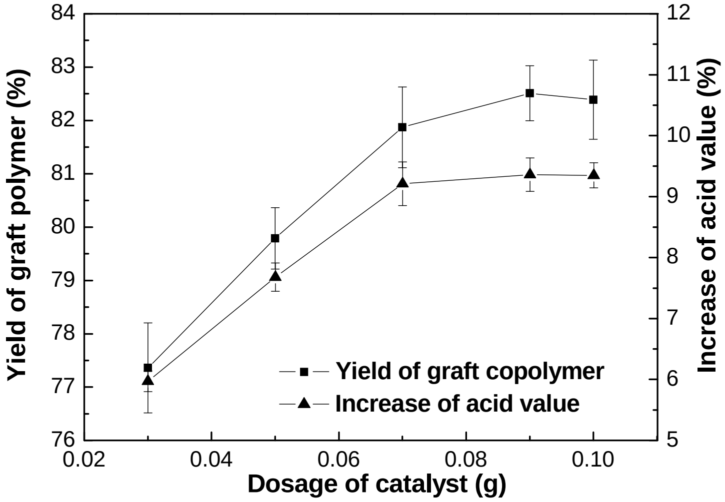


Fig. 5. Effect of the dosage of catalyst on the acid value and the yield of graft copolymer

The highest acid value and yield was achieved when the dosage of catalyst was 0.09 g, namely 0.6 wt% of the total monomer. The slight decrease of the grafting effect at 0.1 g may be attributed to the side reactions caused by the use of excessive catalyst. Therefore, 0.6 wt% of the total monomer was considered to be the suitable catalyst dosage for CER in this reaction.

Effect of reaction time

As can be seen from Fig. 6, both of the acid value and the yield of copolymer tended to increase with extending reaction time, which indicated that a longer reaction time will lead to a more complete grafting reaction. However, this increase slowed down dramatically or even stopped after 5 h of reaction. In Fig. 6, the increase of acid value and the yield of graft polymer did not improve significantly as the reaction time was extended from 5 to 7 h, indicating that the reaction rate was very slow during this reaction time. The grafting reaction can be roughly divided into two parts: the esterification between DA and EHL and the further condensation between some grafted EHLs. Both of the reactions will be made slower by the decrease of the density of active groups and the increase of system viscosity caused by the forming of graft copolymers with extending reaction time. Therefore, although a longer reaction time leads to a bit higher yield, 5 h is taken to be the optimum reaction time in this study because the grafting reaction rate is too slow thereafter.

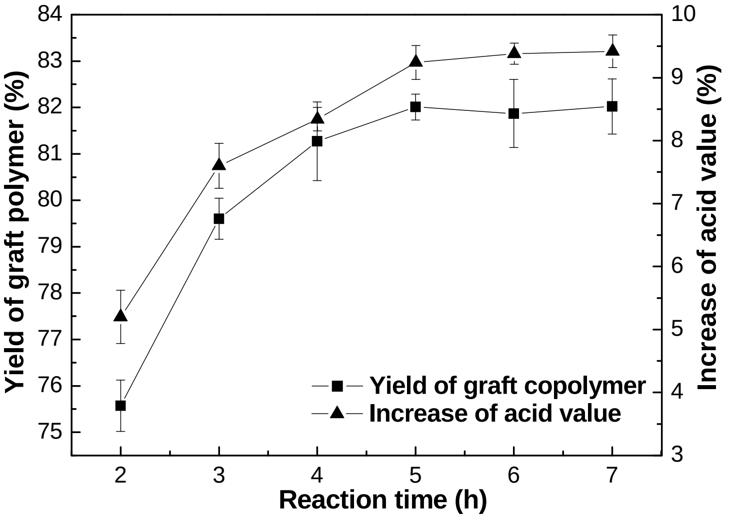


Fig. 6. Effect of reaction time on the acid value and the yield of graft copolymer

Characterization and application of DA-g-EHL

Based on a comparison between the IR spectrum of DA-g-EHL and that of pure EHL (Fig. 7), it was found that the relative intensity of the adsorption bands at 1690 cm^{-1} (assigned to C=O stretching vibration) and 1238 cm^{-1} (assigned to C-O stretching vibration of ester) increased significantly after the grafting reaction. Furthermore, the intensity of the adsorption band at 3420 to 3440 cm^{-1} (assigned to O-H stretching vibration of hydroxyl) decreased at the same time. These variations demonstrated that DA had been grafted onto EHL through ester condensation (Shen et al. 2008).

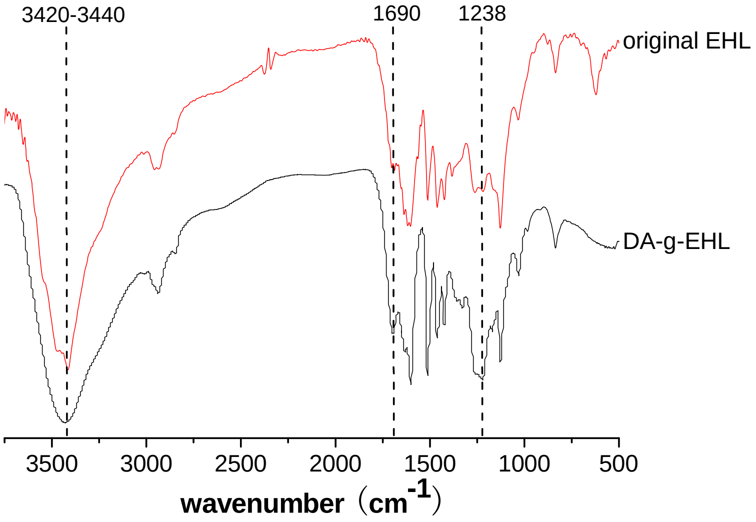


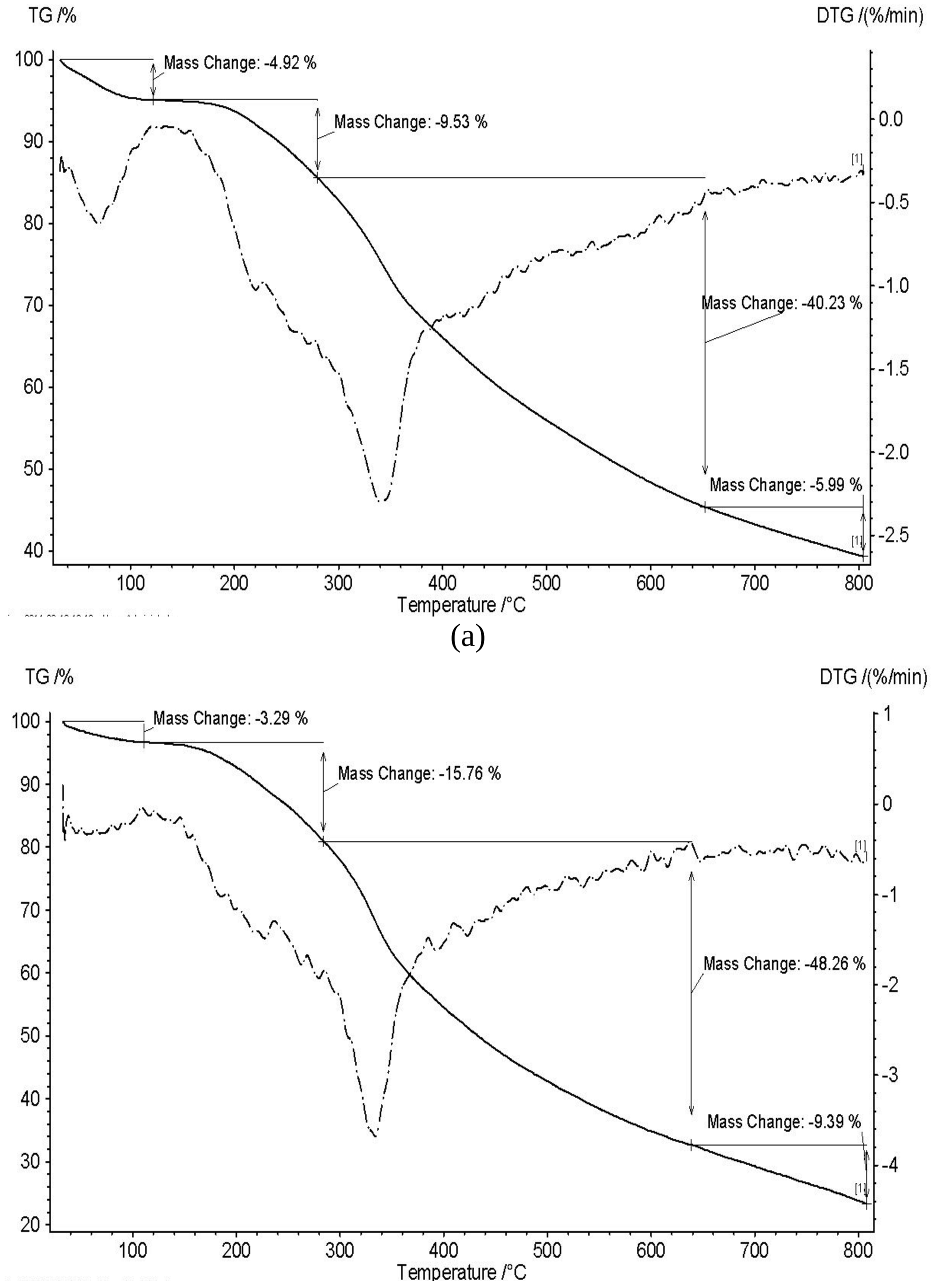
Fig. 7. FT-IR spectra of original EHL and DA-g-EHL

The thermal degradation behavior of original EHL and DA-g-EHL was studied by TG analysis. TG curves reveal the mass loss of samples with the rising of temperature, and its first derivative thermogravimetry (DTG) indicates the corresponding rate of mass loss. The TG and DTG thermogram of EHL and DA-g-EHL are shown in Fig. 8.

Four thermal decomposition steps can be observed during the heating process. The first decomposition step was recorded in the range of 30 to 115^{o}C, which corresponded to the evaporation of water contained in the samples. The second step covered the range of 115-280^{o}C. The mass loss in this step was attributed to the elimination of water, sulfur dioxide, nitrogen dioxide, and organic acids (Ibrahim et al. 2010). The third step was detected in the range of 280-650^{o}C. The mass loss in this step was due to the pyrolytic degradation of lignin backbone structure, which released carbon dioxide and monomeric phenols into vapor phase. When the samples were heated above 650^{o}C, some aromatic rings began to decompose (Mansouri et al. 2011).

The major difference between the TG curves of EHL and DA-g-EHL occurred in the second decomposition step. In the range of 115-280^{o}C, the mass loss of DA-g-EHL (15.76%) was significantly higher than that of EHL (9.53%). This is because most of the fragile ester bonds break down in this thermal region, which leads to the volatilization of DA from grafted EHL. The variation of the mass loss in the second step reveals the existence of DA side chain in the graft copolymer.

To evaluate its potential application in polymer modification, DA-g-EHL was applied in the preparation of modified phenolic aldehyde amine (PAA). The modified and commercial PAAs were thereafter used as epoxy resin curing agents. Some mechanical properties of E-44 epoxy resins cured by different PAAs are listed in Table 1. It was found that the overall mechanical properties of the epoxy resin cured by DA-g-EHL modified PAA was very close to that of the resin cured by commercial PAA. The higher hardness of the epoxy resins cured by modified PAA may be attributed to addition of EHL into the curing agents. Since EHL is a rigid and heavily crosslinked polymer, the introduction of EHL or DA-g-EHL into the curing agent may enhance the crosslink density and the structural rigidity of the cured epoxy resins.



(a)

(b)

Fig. 8. TG and DTG thermogram of (a) EHL and (b) DA-g-EHL

Compared with the resin cured by EHL modified PAA, the bending strength and the elongation at break of the resin cured by DA-g-EHL modified PAA were significantly higher. Figure 2 shows that DA has a long aliphatic chain with many possible conformations. The graft of DA onto EHL will reduce the rigidity of EHL, which subsequently reduces the chain stiffness of the PAA modified by EHL. Therefore, compared with EHL modified PAA, the use of DA-g-EHL modified PAA as curing agent may improve the flexibility of the cured epoxy resin.

Table 1. Some Properties of the Epoxy Resins Cured by Different Curing Agents

Curing agents	Commercial PAA*	EHL modified PAA	DA-g-EHL modified PAA
Bending strength at break (MPa)	90.46	73.87	89.18
Elongation at break (%)	6.62	5.77	7.75
Tensile strength (MPa)	39.55	34.41	36.22
Vickers hardness (HV)	15.43	18.13	18.04
* PAA: phenolic aldehyde amine curing agent			

CONCLUSIONS

1. Dimer acid (DA) can be grafted onto enzymatic hydrolysis lignin (EHL) by ester condensation with dioxane as solution. Strongly acidic cation exchange resin is an efficacious catalyst for the grafting reaction. Under optimum reaction conditions, the increase of acid value and the yield of graft copolymer can reach about 9.3% and 83%, respectively.
2. The graft of DA onto EHL will reduce the rigidity of EHL and the chain stiffness of the PAA modified by EHL. Compared with EHL modified PAA, the use of DA-g-EHL modified PAA as curing agent may improve the flexibility of the cured epoxy resin.

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