

Thermal Degradation of Modified Phenol-Formaldehyde Resin with Sodium Silicate

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Abstract

Phenol formaldehyde (PF) is thermosetting polymer that is widely used in many applications, including as an adhesive in wood industry. Modification using sodium silicate has been successfully improving the curing temperature and bonding strength. But, it's important to studies phenol formaldehyde thermal stability, since its main application were using high temperature. In this work, the thermal stability of modified phenol formaldehyde was studied using thermogravimetric analysis (TG/DTA) at heating rate of 10°C/min to understand the step of the degradation process. In addition, the ash content was determined at 1000°C in order to compare the thermal stability of the PF resin samples. The amount of sodium silicate was varied in the range of 0% to 25% (w/w) in terms of sodium silicate to phenol. The experimental results indicate that modified PF resin has improved thermal stability in comparison with conventional PF resin. The thermogravimetric curves showed four stage of the phenol formaldehyde thermal decomposition. The presence of sodium silicate can increase the crosslink density that improves the thermal stability at temperature lower than 700°C. However, at temperature higher than 700°C the Si-O bonding were easier to break than the methylene and methylene ether bond that lead to faster decomposition in phenol formaldehyde for higher sodium silicate concentration.

Keywords: phenolic resin; thermal stability; wood; adhesive; sodium silicate

1. Introduction

Phenol formaldehyde (PF) is one of the most common synthetic resins that used in a wide area of application. This resin known as an important adhesive in wood panel industry [1,22] and also used in coatings and advanced composite matrix in aerospace and electronic industries [2]. The resin offer some advantages such as high temperature resistance, high char yield and solven resistant [3,20]. PF resin with improved thermal and pyrolysis characteristic are desirable in composite for thermo-structural application [21]. But, this resin also has some disadvantageous nature, such as moderate brittleness and evolution of volatile substances in condensation-cure reaction [20]. Therefore, thermal degradation are important topic to be researched, including here is their heat resistance and thermal stabilisation. The making process of this resin has remained unchanged for some times. For example, wood adhesive is usually made of resol-type phenol formaldehyde with F/P molar ratio higher than one and in basic condition. The most common basic catalyst used for the resin preparation is sodium hydroxide [4]. Several studies have been done to investigate modified resin thermal degradation using thermogravimetric analysis (TG). TG measures weight change as a function of temperature and/or time [23]. For instance, the thermal degradation of lignin-modified resin [2], the influence of titanium and silicon on the resin oxidative degradation [5], non isothermal degradation of phenolic triazine [16] and the thermal stability of natural fibre and phenolic resol [6]. The decomposition process of phenolic resin is usually accelerated by the number of dihydroxy phenyl methylene group [17] and also the high oxygen content of phenol [16].

In the recent years, phenol formaldehyde modification using silicon-containing chemical has been studied in order to modify the thermal properties [19]. Polymerization of phenol formaldehyde using SiO₂ nanocomposite gives better thermal stability and flame retardant [7] and also increasing the hardness [8]. Other works reported that silicon carbide [9] and vinyl triethoxysilane [10] can also be used as phenol formaldehyde modifiers. Another alternative of silicon-containing chemicals that has potential as modifier is sodium silicate. In our previous study, the addition of sodium silicate into phenol formaldehyde gives higher crosslink density, thus gave improvement in lowering the curing temperature, activation energy and increasing the bonding strength. However, the effect of sodium silicate dosage on the thermal degradation which is important in the application that needs high thermal resistance has not been reported. For instance, for wood based composite, this information is useful in determining the temperature in which wood structure no longer have structural integrity [23].

This paper presents the study to gives better thermal resistance of PF resin using sodium silicate as modifier. The resin was made of 37% formaldehyde, phenol and sodium silicate. The effect of sodium silicate dosage on the thermal degradation was investigated using Thermogravimetric/Differential Thermal Analysis.

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2. Method

2.1. Materials

The Phenol (Merck), sodium hydroxide (Merck), 37% aqueous formaldehyde (Merck), aquadest and sodium silicate (Sigma-Aldrich) were analytical pure purchased from commercial resources.

2.2. Preparation of PF resin

The resin was synthesized by batch polymerization with a molar ratio of phenol to formaldehyde of 1:1.5, following Wang's methods [11]. Phenol, aquadest and sodium silicate were mixed and stirred in a flask. After heated to 80°C, formaldehyde was added dropwisely into the mixture, then the mixing was continued for 4 hours. The resulting resin was then dehydrated for 2 hours at 60°C in vacuum condition resulting in a viscous solution. The amount of sodium silicate to phenol was varied at certain value.

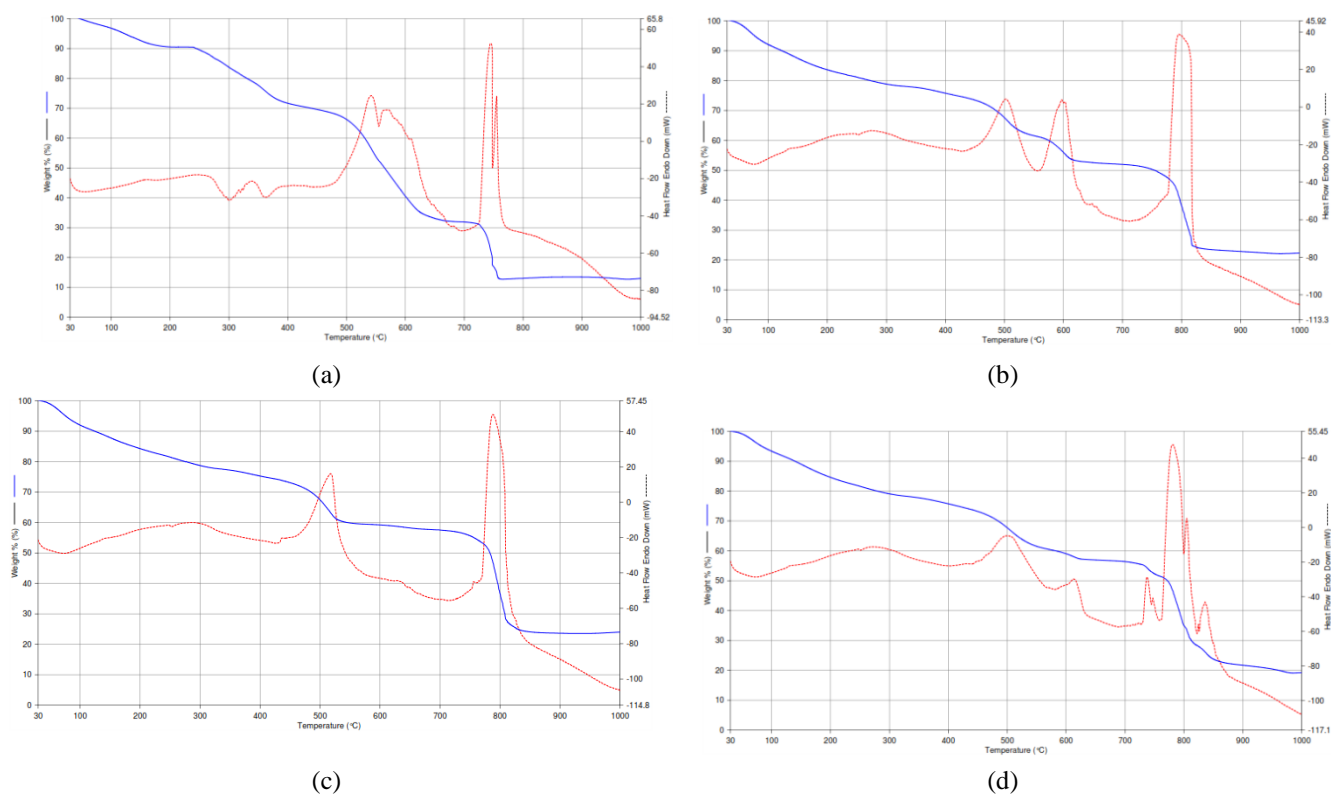
Each sample for thermal analysis was dried for 30 minutes in an oven at 100°C and then crushed using mortar. The sampel was weighed 5.0 mg then placed onto the sample pan. Thermogravimetric/Differential Thermal Analysis (Perkins TG/DTA Diamond Series) was used to characterize the heat flow and mass loss during heating. The Perkins PYRIS software was used for data collection and analysis. The program was set to a heating rate of 10°C/min in atmospheric condition. In order to confirm the repeatability and authenticity of the generated data for all considered cases, the experiments were repeated two times at every sample. The observed deviation were very little.

2.3. Research Variables

The research variables consists of dependent variables and independent variables. The dependent variables included the polymerization temperature 80°C, initial pH 11 and F/P ratio 1.5. The independent variable is sodium silicate concentration. Resin modification were done using sodium silicate as modifier with a variation of 0%, 6.25%, 12.5%, 18.75% and 25% (w/w) of sodium silicate to phenol mass ratio.

3. Results and Discussion

In this research, we focused on the thermal stability of the PF resol resins under oxidative atmosphere. The measurement of the amount and the velocity of the sample mass loss as function of the temperature in controlled atmosphere are used primarily to determine the oxidative stabilities of materials as well as their compositional properties [2]. The thermogravimetric methods can analyze materials that exhibit mass loss due to decomposition, oxidation and volatile materials losses (such as small particle and moisture) [2,24]. Therefore this methods are very often used to analyze materials that applied or processed in high temperature. The TG/DTA curve for each sample are presented in fig. 1.



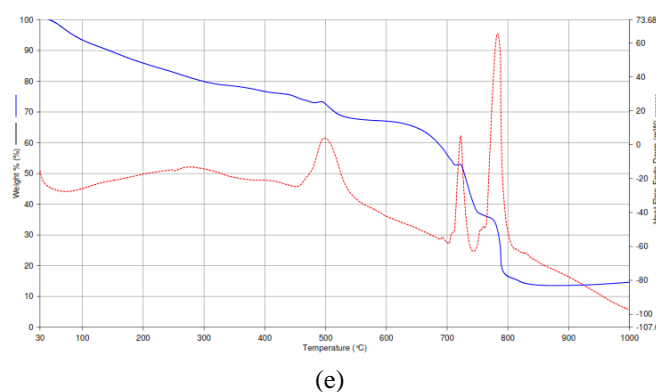


Fig.1. TG curve of the PF with variation 0; 6.25; 12.5; 18.75; 25 % (w/w) respectively

The degradation of resol resin was shown in the TG curve obtained with a heating rate of 10 °C/min. Fig.1 shows that in general there are 4 steps of the phenolic resin weighted loss. In the first steps, heating a pre-cured resin to curing temperature gives us steady loss of the volatile and low molecular weight materials such as phenol and solven [23] and also some monomers [2], followed by water and formaldehyde loss evolving from the resin during processing [13,24]. The substances will be liberated at lower temperatures due to the results of the methylol groups condensation reaction [12, 17]. The small exothermic up peak that emerged in the range of 90-180°C are the curing temperature [23,24]. Since the exothermic heatflow of the curing process is lower than the endothermic evaporation, the overall curve would show the endothermic down peak. For the PF resin without sodium silicate addition, this step occurs in temperature up to 220°C. But, the PF resin with sodium silicate addition the range is slightly higher, up to 300°C. It is clearly shown that all the modified phenolic resins possess better thermal stability in comparison to the conventional resol resin. The mass loss of the modified PF resin (20-22%) is higher than the conventional (10%) since the water and formaldehyde released in condensation reaction are also higher.

The second stage resulted from the degradation of the polymer. The lower molecular weight component of the polymer degrades faster to the higher molecular weight polymer component [23]. We found from the TG curve, that more sodium silicate added, the mass loss was lesser. This fact indicates that the resin with 25% (w/w) sodium silicate addition has oligomers and polymers with higher molecular weight. The higher molecular weight probably occurs because of sodium silicate's ability to make a network structure [14]. Therefore, sodium silicate can easily make a bond with the phenol formaldehyde [13] thus giving more complex polymer with higher molecular weight. It is well known that the mass loss of phenolic resin during post curing is 15% on average [2], the analyzed PF resins showed mass losses in the range of 12-17%, which is still in accordance with the literature on thermal degradation of phenolic resins.

The third stage of degradation is due to the thermo oxidation of the resin [2]. There is always a thermo-oxidative process during degradation of the system in both air and inert atmosphere [16,18]. It is obvious since the source of the oxygen is not only from the atmosphere, but also from the phenol itself. This step takes place at 550 up to 700°C, during this step the modified PF resin was degraded with mass loss less than 15% compared to conventional PF resin that has 37% losses. The main reaction is the breakage of the aromatic rings that releases gaseous substances, i.e. CH₄, H₂, CO, CO₂ and other low molecular weight chemicals [13,15]. TG curve in Fig. 1 shows that higher sodium silicate added gives better thermal stability because of crosslink density and probably conductive resistances. The sodium silicate could block the heat conduction thus prevent the thermal degradation [13].

Table 1. Ash content of the PF resin

Sodium silicate addition (% (w/w))	Ash content (%)
0	12.65
6.25	22.20
12.50	24.27
18.75	19.43
25.00	14.05

The last step occurs at temperature higher than 700°C, where it gives the highest weight loss for the modified PF resins. Lower sodium silicates added give lower weight loss, because the crosslink made by sodium silicate is not as strong as the methylene and methylene ether crosslink. Other works suggest that the -Si-O- bond energy was higher than the -C-C- bond energy [13], thus the thermal degradation was faster. Initially, the degradation of silica network structure was restricted by intermolecular hydrogen bonding at lower temperature [19], but the restriction will disappear when the phenolic resin starts to degrade at higher temperature. Finally, overall thermal stability can be indicated from the ash content, which is a higher value indicates that a polymer is more thermally stable [2]. From Table 1, the ash content at 1000°C of the modified PF resin is higher than the conventional PF resin.

4. Conclusion

The mass loss during thermal decomposition of modified phenol formaldehyde resol resin have been studied in oxidative atmosphere using thermogravimetry. The TG curve shows that the addition of sodium silicate has significant effect into thermal stability. It was established that with the increase in sodium silicate percentage the PF resin exhibits high thermal stability on temperature below 700°C since sodium silicate easy to make network bond. It was also conclude that for temperature higher than 700°C, modified PF resin decompose faster because the crosslink made by sodium silicate are weaker than the methylene bridge. While this study provides important insight into the degradation mechanism of the resin, it would useful to made further study in kinetics method in their degradation.

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