

ACIDITY AND SOLUBILITY OF RUBBERWOOD AND THEIR IMPACTS ON THE CURING BEHAVIOUR OF UREA-FORMALDEHYDE RESIN

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CHAOWANA P. 2016. Acidity and solubility of rubberwood and their impacts on the curing behaviour of urea-formaldehyde resin. In this study, effects of rubberwood acidity and catalyst content on curing behaviour of urea-formaldehyde (UF) resin were investigated. Various types of rubberwood raw materials, namely, wood without bark, wood with bark, bark and pressure-refined fibres were measured for pH and buffer capacity. Their solubility extractives were also determined. There were significant differences between raw materials. Bark had the highest pH and buffer capacity. Bark also had the highest extractive content. Hot water solubility, cold water solubility, 1% NaOH solubility, alcohol-benzene solubility and ash content were significantly correlated with buffer capacity, while only ash content was correlated with pH. Addition of catalyst decreased peak temperature but increased the reaction enthalpy of UF resin. This influence was not evident in higher level of added catalyst because further increase had little effects.

Keywords: Extractives, reaction enthalpy, peak temperature

INTRODUCTION

Rubber tree (*Hevea brasiliensis*) belongs to the family Euphorbiaceae. It is one of the most economically important species because the milky latex from the tree is the primary source of natural rubber. More than 80% of total rubber plantation areas are in Asia, with Malaysia, Indonesia and Thailand covering almost 70% (Shigematsu et al. 2011). Thailand has a total rubber area of 2.67 mil ha distributed in the south, east and north-east regions (Chantuma et al. 2012).

From 25 till 30 years, latex yield from rubber trees significantly decreases. The trees are then felled and new ones, generally planted. Large logs are used for furniture and furniture parts, household items and miscellaneous products. Residues from plantations and sawmills such as branches, small logs, off-cuts, edges and slabs are used as raw material for wood composite products, e.g. particleboard, medium density fibreboard (MDF) and oriented strand board. In recent years, the number of particleboard and MDF plants using rubberwood as raw material has rapidly increased. This decreases

wood supply and raises cost of raw material. Consequently, some plants have now focused on non-traditional raw materials such as bark, tops and residues. Bark usage has been reported to improve thickness swelling and formaldehyde emission of particleboard and MDF (Chen & Paulitsch 1974, Roffael 1982, Prasetya & Roffael 1991, Lelis & Roffael 1995, Blanchet et al. 2000). However, mechanical properties such as modulus of rupture, modulus of elasticity and internal bond strength decreased. A change in raw material may affect board properties and requires additional adjustment of some processing parameters. Hence, the information on pH and buffer capacity of these raw materials is fundamental to determine the optimum adhesive formulation and hot pressing parameters for board manufacturer.

Urea-formaldehyde (UF) resin is formed from the reaction of urea and formaldehyde. It is widely used for particleboard and MDF because of low cost, ease of use under a wide variety of curing conditions, low curing temperatures, water solubility, resistance to microorganisms,

excellent thermal properties and lack of colour, especially of cured resin. Moreover, UF resin is known as an acid-catalysed-curing resin. The use of acid catalysts can significantly improve the curing process, providing better curing rate and product properties. Ammonium salts such as ammonium sulphate and ammonium chloride are most widely used as catalysts. A variety of other acids can be used as catalyst, including formic acid, boric acid, phosphoric acid, oxalic acid and acid salts of hexamethylenetetramine (Pizzi 1994). Research has been geared towards investigating the acidity and solubility of raw materials as well as understanding their impacts on UF resin curing rate, degradation reactions and panel properties (Johns & Niazi 1980, Slay et al. 1980, Guo et al. 1998, Park et al. 2001, Zanetti & Pizzi 2003).

The aim of this work was to investigate the acidity and solubility of different rubberwood raw materials. The curing behaviour of UF resin as affected by catalyst content as well as pH and buffer capacity of raw materials was also studied.

MATERIALS AND METHODS

Raw materials

Four kinds of rubberwood raw materials obtained from particleboard and MDF plants were used, namely, rubberwood chips without bark from MDF plant, rubberwood particles with bark from particleboard plant, rubberwood bark from MDF plant and pressure-refined rubber fibres from MDF plant. Each raw material was ground into small particles and screened with -40/+60 mesh sieve. Furnish remaining on the 60# mesh screen was used for the study.

Table 1 presents the working properties of the commercial UF resin (E1 type)

used. Ammonium sulphate was used as the catalyst for differential scanning calorimeter (DSC) measurements.

pH value and buffer capacity measurements

The measurement of pH value was modified from TAPPI T 509 (TAPPI 1983). One gram of dry specimen was soaked in 70 ml of distilled water. The solution was stirred for 1 hour at room temperature. pH meter was used to determine the pH. The value was recorded when there was no more drift in the measurement for 30s.

The buffer capacity measurement procedure was adapted from the method described by Maloney (1993). A total of 30 g of dry specimen were soaked in 400 ml of distilled water at room temperature for 30 min. The mixture was stirred and filtered through filter paper using vacuum. A total of 150 g of the liquid were titrated with 0.01 N sulphuric acid. The liquid was mixed by magnetic stirrer and the pH measured after acid addition, until pH 3.5. The buffer capacity value was calculated from normality and the volume of acid needed to change the pH to 3.5.

Raw material extractive solubility

The extractive solubilities, namely, hot–cold water solubility, 1% sodium hydroxide solubility, alcohol and alcohol–benzene solubility as well as ash content were determined according to TAPPI T 207 (TAPPI 1999), T 212 (TAPPI 2007a), T 204 (TAPPI 2007b) and T 211 (TAPPI 2002) standard methods respectively.

Differential scanning calorimeter analysis

DSC was used to determine the exothermic curing of UF resin blended with different raw

Table 1 Working properties of urea–formaldehyde resin used in this study

Property	Result
Appearance	White-coloured liquid
Viscosity at 20 °C	208 cps
Solid content 3 hours at 105 °C	65.20%
pH at 20 °C	8.86
Density at 20 °C	1.27 g cm ⁻³

materials and catalyst contents. About 1 g of each dry sample was blended with UF resin content of 14% weight (based on oven-dry wood) and catalyst contents of 0, 1, 2, 3 and 4% weight (based on resin solids content). The prepared sample was weighed in a sealed aluminium capsule pan. Each test was done under nitrogen at heating rate of 10 °C min⁻¹ between 30 and 300 °C.

RESULTS AND DISCUSSION

Rubberwood raw materials had pH and buffer capacity in the range of 5.4–6.1 and 0.3–0.6 respectively (Table 2). Bark showed the highest pH and buffer capacity, which might result from its abundant extractives (Table 2). The pH and buffer capacity of wood with bark were higher than those without bark.

The pH of refined fibres prepared from rubberwood chips without bark by thermo-mechanical refining process was lowest. The result showed that the pH of pressure-refined fibre was reduced after refining. This suggests that the refining process with high pressure and temperature causes wood degradation, whereby acetic and formic acids are released, contributing to decreased pH (Wu et al. 2002, Zhang et al. 2003, Pan et al. 2008). The buffer capacity of pressure-refined fibres significantly increased compared with that of wood without bark. This might result from increasing extractive solubility (Table 2). The extractive contents of pressure-refined fibres such as hot water solubility, cold water solubility, 1% NaOH solubility and alcohol–benzene solubility increased after thermo-mechanical refining process. These results confirmed that there was relationship between wood acidity properties and their extractive solubility.

There were positive linear correlations between acidity and extractive solubility (Table 3). The pH value strongly correlated with ash content, while buffer capacity significantly correlated with hot water solubility, cold water solubility, 1% NaOH solubility, alcohol–benzene solubility and ash. The results of Balaban and Uçar (2001) supported this finding. They reported that hot water solubility and 1% NaOH solubility were correlated with wood acidity properties.

Table 3 indicates that pH and buffering capacity of wood are strongly affected by the type and amount of extractives. Normally, pH of wood species is on the acid side. Most species fall in the pH range of 3–7 (Gray 1958, Fengel & Wegener 1984). These researchers reported that wood acidity arose from extraneous mineral substances (such as ash) and organic substances (such as cold and hot water solubilities alcohol solubility and benzene solubility). Many other researchers have found that the setting or curing reaction of some adhesives is sensitive to these factors. The extractives of teak that are soluble in alcohol/benzene were found to adversely affect the setting of UF resin (Narayanamurti et al. 1962). Wood with varying types and amounts of extractives was found to affect the activation energy of UF resin curing reaction (Mizumachi 1973). Extractives obtained from pressure-refined wood fibres were reported to decrease the gel time of UF resin (Slay et al. 1980).

Figure 1 shows decreasing exothermic peak temperature of curing reaction of UF resin with increasing catalyst content. The effect of ammonium sulphate on UF resin curing is to release sulphuric acid by reacting with free formaldehyde. For higher ammonium sulphate content, the more sulphuric acid is released. This increases UF resin acidity and results in a higher curing rate and lower exothermic peak temperature. Interestingly, peak temperatures distinctly decreased when the catalyst content increased to 1%. With further increased in catalyst content (> 1%), peak temperatures slightly decreased. This could be due to the pH of UF resin decreasing to the critical point when catalyst was added, which consequently increased the curing speed of UF resin. With further catalyst addition, no more hydronium ion could be released because there was no available free formaldehyde to react with ammonium sulphate. The peak temperatures then became very limited. It appeared that the optimum content was around 1% of catalyst based on the solid content in the resin.

Compared with pure UF resin, resins mixed with rubberwood raw materials showed lower peak temperatures at 0%. However, the peak temperature of pure resin decreased more rapidly than those of mixed resin with increasing catalyst content to 1%. Yet the reduction of pure

Table 2 Acidity and extractive solubility of the rubberwood raw materials

Raw material	pH	Buffer capacity (milliequivalents)	Hot water solubility (%)	Cold water solubility (%)	1% NaOH solubility (%)	Alcohol solubility (%)	Alcohol– benzene solubility (%)	Ash (%)
Wood without bark	5.59 (0.03)	0.31 (0.01)	1.44 (1.31)	3.89 (0.79)	20.68 (0.42)	1.65 (0.44)	7.00 (0.47)	1.32 (0.56)
Wood with bark	5.83 (0.07)	0.40 (0.02)	4.60 (0.41)	4.06 (0.31)	26.96 (0.36)	1.65 (0.44)	11.44 (0.46)	4.23 (0.54)
Bark	6.07 (0.02)	0.58 (0.03)	6.22 (2.86)	12.49 (1.06)	29.37 (0.47)	5.84 (0.92)	15.89 (1.87)	7.92 (0.96)
Refined fibre	5.44 (0.05)	0.40 (0.02)	4.51 (0.45)	4.22 (0.91)	26.36 (0.24)	5.25 (0.02)	12.53 (2.74)	1.32 (0.57)

Values in parentheses are standard deviations

Table 3 Correlation values between acidity properties and extractives of rubberwood raw materials

Raw material property	pH	Buffer capacity	Hot water solubility	Cold water solubility	1% NaOH solubility	Alcohol solubility	Alcohol– benzene solubility	Ash
pH	1	0.626	0.391	0.662	0.389	0.042	0.366	0.941
Buffer capacity	0.626	1	0.816	0.879	0.774	0.568	0.889	0.838

and mixed resins was similar with higher catalyst contents. This might be caused by the effect of raw material acidity. At lower catalyst contents, the main source of acid catalyst of resin mixture was raw material acidity, while at higher catalyst content, ammonium sulphate. Bark had the highest pH and buffer capacity, which reduced the effect of acid catalyst and resulted in highest peak temperature. Therefore, wood with bark showed higher peak temperature than wood without bark. Moreover, refined fibre revealed higher peak temperature than wood without bark because of the higher buffer capacity of refined fibre.

Another interesting observation is the influence of catalyst addition on reaction enthalpy (Figure 2). The curing reactions of UF resins are typically exothermic. Thus, it could be assumed that the reaction enthalpy, ΔH , would be proportional to the degree of conversion during the curing process. The increase of ΔH with increase of catalyst content was noticed in previous research on UF adhesive cure and was explained by the catalyst effect on decreasing pH resulting in increased adhesive reactivity.

Our results showed similar behaviour to previous investigations (Xing et al. 2005, Popović et al. 2011). The results suggested that the addition of catalyst above 1% was less effective, which probably resulted in conditions when most of the reactive groups of the adhesive were activated and when further addition of ammonium sulphate only slightly affected the reaction enthalpy.

Figure 2 also shows that resin mixed with bark had the highest value of reaction enthalpy for all levels of catalyst content. This is probably due to the highest pH and buffer capacity of rubberwood bark.

From the practical point of view, bark should be separated from wood and separately used in particleboard manufacturing. Unfortunately, many plants cannot completely remove bark from wood. Moreover, it is difficult to determine which raw material types are coming into the plant. This problem can be solved by sorting the various types of raw materials before they can be metered into the production line.

Catalyst content, hot-pressing time and temperature should be given special consideration to accelerate the resin-curing rate.

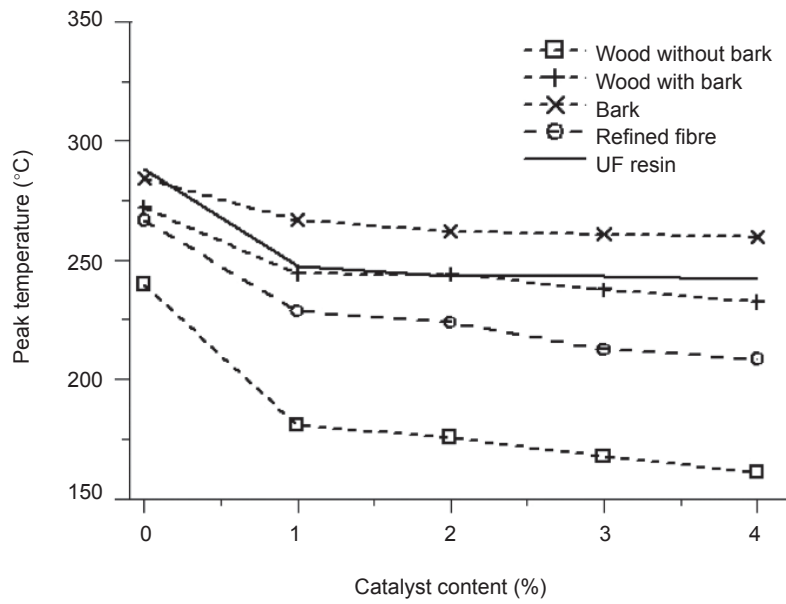


Figure 1 Effects of catalyst content and raw material type on peak temperature during cure of urea–formaldehyde (UF) resin obtained from differential scanning calorimeter runs at heating rate of 10 °C min⁻¹

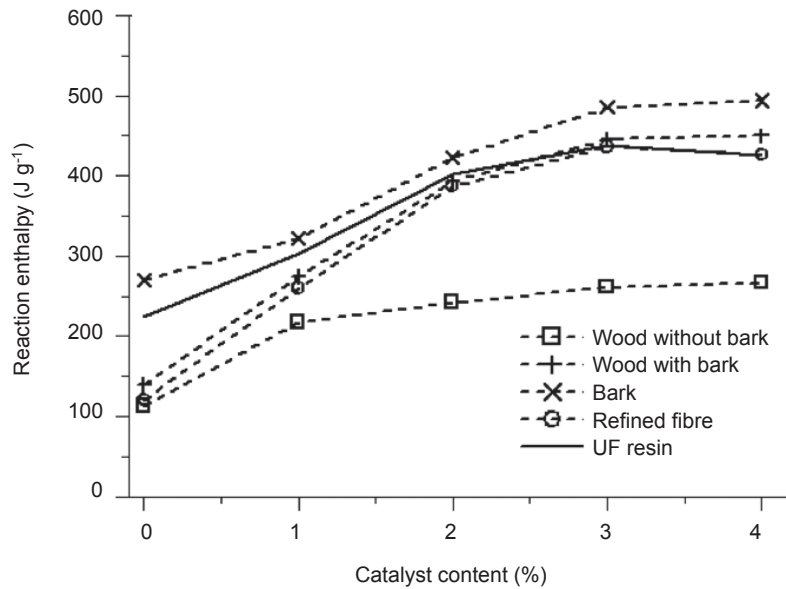


Figure 2 Effects of catalyst content and raw material type on reaction enthalpy during cure of urea–formaldehyde (UF) resin obtained from differential scanning calorimeter runs at heating rate of 10 °C min⁻¹

CONCLUSIONS

Rubberwood bark had the highest pH, buffer capacity and extractive content. Linear relationships between extractive content and pH and buffering capacity existed. Hot water, cold water, 1% NaOH, alcohol–benzene and ash contents were significantly correlated with buffer capacity, while only ash content was correlated with pH in the case of rubberwood raw material. The curing behaviour of UF resin was affected by raw material and catalyst content. Generally, the peak temperature of cure of UF resin decreased mainly because of decreasing wood acidity and catalyst content. The curing enthalpy of UF resin increased due to increasing wood acidity and catalyst content. However, the effect of raw material acidity on curing behavior of UF resin was significant at lower levels of catalyst content (< 1%) but insignificant at higher levels of catalyst content (> 1%).

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