Thermal Properties of Isocyanate as Particleboard’s Adhesive

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Abstract. The objective of this study was to evaluate the thermal properties of isocyanate as particleboard adhesives. In this study, thermal properties of the isocyanate was investigated particularly its curing behavior either using water or wood with a temperature range from 25 to 500°C using thermal analyzer (Mettler Toledo). When isocyanate is used as the binder in particleboard system, the reactive –NCO group reacted with water (because wood is a hygroscopic material and contains free water and bound water) and also with the –OH group from wood. Sample of isocyanate was H3M purchased from PT. Polichemie Asia Pacific and wood particle was Eucalyptus sp. taken from PT. Toba Pulp Lestari. About 10 mg of the mixture either isocyanate with water or wood in various weight ratios were scanned at four different heating rates (2.5; 5; 10; and 20°C/min). Results of this study showed isocyanate cured either using water or moisture wood particle indicated by the \( T_p \) or peak temperature on the thermograms of differential scanning calorimetry (DSC). However when isocyanate reacted with wood particle, the \( T_p \) emerged more than two which indicated isocyanate also reacted with wood components. Furthermore, values of enthalpy seemed irregular probably due to different structures and compositions of wood particle. This influence, however, was masked by the moisture present in the wood (free and bound water), because water was much easier to react with isocyanate than were the –OH within the wood particle. It was suggested to calculate activation energy since the heating rates used up to four and to understand whether water, wood particle, or both affected the main reaction mechanism among isocyanate, water within the wood (free and bound water), or wood components.

1. Introduction

A significant market was born for particleboard bonded by isocyanate in the late 1960s and early 1970 after the proven that isocyanate was effective for bonding particleboard [1]. Data from [2] strengthen that isocyanate has been placed third rank in worldwide market adhesive for wood after urea-formaldehyde (UF) and melamine-urea-formaldehyde (MUF) resin, respectively. Up to now, isocyanates have been applied for gluing in engineered wood products especially wood-laminating industry as the urethane prepolymer originated from isocyanate-polyol reaction products and as the isocyanate have been served in the particleboard industry [3]. In other words, the type of isocyanate generally used for the first is the water-based emulsion adhesives with isocyanate as the cross-linker [4] while the type of isocyanate generally used for the latter is MDI or 4-4’-diphenylmethane diisocyanate [3]. The methods of mass production for particleboard using this adhesive have been patented in Europe.
since 2013 [5]. A comprehensive review describes the development of these both adhesives in Indonesia has been published recently [6].

In this following study will be limited to particleboard isocyanates, since world production of particleboard reaches up to 93 million m$^3$ per year nowadays [7]. Further, some tremendous application researches have been emerged in relation with particleboard bonded isocyanate, for example Papadapolous [8] compared between conventional particleboard bonded UF resins and the one bonded isocyanate. The latter gave superior properties even though there was addition of wax around 1%. Modification UF resin with isocyanate for bonding particleboard has been done by Dziurka & Mirski [9] and Nuryawan et al. [10]. The similar results have been obtained that physical and mechanical properties of the particleboard were enhanced with the increase of isocyanate loading to the UF resin. The reason for the excellent performance of isocyanate compared to another wood adhesive is still a matter of debate. Zhou and Frazier [11] showed that isocyanate is able to form covalent urethane bonds with hydroxyl groups of wood components, which was interpreted as a contribution to strong bondline behavior. However, the major reaction of isocyanate takes place with water situated in the wood substrate to form polyurea/biuret networks [12-13]. In this respect, infra red spectroscopy was employed to investigate the evidence of the interaction between isocyanate with water or wood [14-15]. Further, because manufacturing of particleboard involved hotpressing, some thermal analytical methods have been applied for investigating the thermal properties of wood particle-isocyanate adhesive system. For example Umemura et al. [16-17] reported the durability of unique sample of isocyanate assessed by DMA (dynamic mechanical analysis). He and Yan [18] stated that curing kinetics of isocyanate have been influenced by moisture in wood as well as wood species in limited moisture therein. Recently, the authors presented thermal stability of isocyanate when exposed to water or hygroscopic wood particle assessed by TGA (thermogravimetric analysis) to investigate the resistance to heat including its degradation [19].

Excess water or moisture in the particleboard system resulted in blister or blowing particleboard. On the contrary, starve water or moisture in the particleboard resulted in less strength. In other words, wood particle-isocyanate adhesive system is exposed rapidly changing conditions of pressure, steam and heat during manufacture. Therefore, we evaluate thermal properties of isocyanate as particleboard’s adhesive, including curing characteristics of isocyanate using water or moisture wood particle. The objective of this work is to study the fundamental aspect of thermal properties of the isocyanate, particularly its transformation temperature and enthalpy when isocyanate exposed to water or hygroscopic wood particle. Therefore, in this contribution, isocyanate was mixed with either water or wood particle and scanned under differential scanning calorimeter (DSC) because a little report available related to the nature of free and bound water within the wood particle.

2. Materials and methods
Isocyanate used was product of PT. Polichemie Asia Pacific (Medan branch, North Sumatera, Indonesia) with trademark of H3M having 98% solid content. Eucalyptus sp. wood particles with 20-mesh in size were taken from PT. Toba Pulp Lestari (Porsea, North Sumatera, Indonesia). For accurate analysis, measurement of moisture content was conducted using gravimetric analysis prior to mix with isocyanate, resulted in 6.20%.

2.1. Formulation mixture
Simple mixing isocyanate with either water or wood particle at various proportions based on weight (w/w) was applied in order to develop the mixture. Isocyanate was placed into a beaker glass and either water (1%; 3%; 5%; and 7%) or wood particle (5%; 10%; 12%; and 15%) was added. Both components were thoroughly stirred by glass spatula about 5 minutes or until they looked physically mixed. Addition of water was much less than wood particle with considering wood contains water therein (free and bound water).

2.2. Differential scanning calorimetry (DSC)
Differential scanning calorimetry (DSC) measurements were performed on TGA/DSC1 Star system Mettler Toledo, operating at Institute of Advance Materials-University Putra Malaysia (Selangor, Malaysia). For each measurement, about 10 mg of the mixture either isocyanate with water or wood in various weight ratios were scanned to a temperature gradient ranging from 25 to 500 °C with four different heating rates ($\beta$) of 2.5; 5; 10 and 20°C/mins using nitrogen gas 50.0 ml/mins. The enthalpy changes were recorded and analyzed for the enthalpy integral ($\Delta H$) and the peak maximum ($T_p$) using a software package of STARe 15.00. For the control, prior scanning the mixtures, each component (isocyanate/ IC and wood particle/ WP) was scanned at normal heating rate of 10°C/mins.

3. Results and Discussions

3.1. DSC measurements of the isocyanate and wood particle in normal heating rate

Figure 1 showed typical DSC’s thermograms of main components of the mixture, namely IC and WP at heating rate of 10°C/minutes.

![Figure 1. Typical thermograms of DSC’s isocyanate (a) and wood particle (b) at $\beta$=10°C/mins.](image)

There were two $T_p$ of the IC’s thermogram (Figure 1.a.) presumably because of the difference in the molecular weight of the composition as well as the chemical species [6]. According to [20], MDI is available in three broad types of compositions, namely polymeric MDI (PMDI), monomeric MDI (MMDI), and modified MDI which have different characteristics as well, such as functionality, odor, -NCO content, viscosity, freeze point, boiling point, and density. The distinct characteristics of the compositions may result in different $T_p$. An endothermic $T_p$ of the WP’s thermogram (Figure 1.b) related to water vapor. Water originated from free water in the lumen and bound water within cell-walls. In fact, the moisture content of the WP was 6.20%. Detail DSC data measurements, including onset and endset temperature, $T_o$ and $T_e$, and enthalpy ($\Delta H$) presented in Table 1.

| Sample | $\beta$ (°C/mins) | $T_o$ (°C) | $T_p$ (°C) | $T_e$ (°C) | $\Delta H$ (J/g) |
|--------|------------------|------------|------------|------------|-----------------|
| IC     | 10               | 312        | 335        | 384        | 185             |
| WP     | 10               | 393        | 442        | 482        | 179             |

3.2. Influence of amount water and heating rate to the DSC measurement

Figure 2 showed a representative DSC’s thermograms of mixture of IC and water at two different $\beta$. Mixture of IC and water, less amount of water (Figure 2.a) or much amount of water (Figure 2.b), resulted in consistent number of $T_p$, for each measurement yielded two $T_p$. 

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Figure 2. Typical representative thermograms of DSC’s mixture of low ratio of water (IC and 3% water (w/w) at slow $\beta = 5^\circ\text{C/mins}$ (a) and high ratio of water (IC and 7% water (w/w) at fast $\beta = 20^\circ\text{C/mins}$ (b).

As shown in presented data in Table 2, $T_o$, $T_p$, and $T_e$ occurred at high temperature. IC reacts with water and the rate of the reaction is very slow at temperature below $50^\circ\text{C}$ [20]. The first $T_p$ around $300^\circ\text{C}$ represented the early stage of curing and the second $T_p$ around $400^\circ\text{C}$ represented the latter stage of curing. Therefore in this present study, the early part of cure is dominated by chain extension of IC pre-polymer and little is contributed to strength development. The latter stages of cure are dominated by the development of a polymer network. During the development of the three-dimensional network adhesives strength grows as well [21]. Unfortunately the reaction of IC with water liberates $\text{CO}_2$ gas and forms insoluble polyureas as shown in the equation (1)

$$\begin{align*}
\text{R-N=C=O} + \text{H}_2\text{O} & \rightarrow \text{R-N-C-N-R} + \text{CO}_2 \quad \text{(1)}
\end{align*}$$

$\beta$ as the rate of temperature increase in a response to a temperature program [22] seemed affected the $T_p$ in isocyanate-water system. Fast $\beta$ ($20^\circ\text{C/mins}$) resulted in higher $T_p$ and slow $\beta$ ($2.5^\circ\text{C/mins}$) yielded lower $T_p$ except for less amount of water ($\leq 3\%$). This phenomenon can be explained using kinetic modelling for achieving a better understanding of the curing occurrence. In case of IC-water system, the cure reaction always involves the consumption of $-\text{NCO}$ group. Kinetic parameters can be estimated from multiple ramps with different $\beta$ at least four and the calculation will be published in upcoming publications. By monitoring the kinetics modelling of IC cured with water, the insight can be gained even though further analysis is needed to ensure the mechanism of the reaction between IC and water.

Table 2. Data obtained from DSC thermograms including $T_o$, $T_p$, $T_e$ and $\Delta H$ at different $\beta$ from measurement of sample made of mixture IC and water at various ratios.

| Sample     | $\beta$ ($^\circ\text{C/mins}$) | $T_o$ ($^\circ\text{C}$) | $T_p$ ($^\circ\text{C}$) | $T_e$ ($^\circ\text{C}$) | $\Delta H$ (J/g) |
|------------|-------------------------------|--------------------------|--------------------------|--------------------------|------------------|
| IC+1% water | 2.5                           | 349                      | 419                      | 433                      | 327              |
|            | 5                             | 263                      | 312                      | 366                      | 144              |
3.3. DSC of the mixture (isocyanate and wood particle) at various composition and different heating rates

Figure 3 showed a representative DSC’s thermogram of mixture of IC and WP at two different $\beta$. The mixture of IC and WP, with less amount of WP (Figure 3.a) or much amount of WP (Figure 3.b) using slow $\beta$ and fast $\beta$, respectively. Unexpectedly, slow $\beta$ (2.5 and 5°C/mins) resulted in three up to four $T_p$ consistently for each measurement as shown in detail in Table 3. On the contrary, normal $\beta$ (10°C/mins) and fast $\beta$ (20°C/mins) resulted in only two $T_p$. This results indicated that $\beta$ influenced the resulted $T_p$. Most of early heat generation prior to the maximum is likely IC consumption contributing to increase in the molecular weight of the polymer, the exothermic peak doesnot represent structures or reaction products that form late in cure. The variation in peak conversion with the $\beta$ can reflect the transition of the reaction features [18].
Figure 3. Typical representative thermograms of DSC’s mixture of low ratio of WP (IC and 5% WP (w/w) at slow $\beta=2.5^\circ$C/mins (a) and high ratio of WP (IC and 15% WP (w/w) at fast $\beta=20^\circ$C/mins (b)

Indeed, isocyanate reacted with either free or bound water from WP but if the water is present in the wood materials, -NCO group within the IC would react with water in preference [15]. Equation (2) confirmed that -NCO group within IC reacted with -OH from wood provided set of combination and variety of polymer containing ester, ether, urea, alkyl or aryl units that affect thermal stability of the material [23].

$$\text{R} \text{N} \text{C} \text{O} + \text{HO-wood} \rightarrow \text{R} \text{N} \text{C} \text{O} \text{H} \text{wood} \quad \ldots\ldots(2)$$

There was some controversy on the various reactions during IC reacting with wood, based on the chemistry of IC, that the main reaction of IC with WP in the presence of moisture may include primary and secondary reactions. First, IC reacts with primary and secondary hydroxyl groups (-OH) within the wood to form urethane and with water absorbed in the wood to form urea. Second, urethane and urea then react with IC, as the secondary reaction to form allophanate and biuret. Studies of [24,25] on IC/wood bondline by nuclear magnetic resonance spectroscopy that the curing chemistry of IC with dried wood resulted predominantly in biuret-type structures from the IC reaction with a small amount of moisture. When the pre-cure moisture content of wood was increased to 4.5%, the end products of curing were predominantly polyurea-type structures with less biuret formation and residual isocyanate. In other words, the -OH groups in wood may react with IC to form polyurethane, providing direct covalent linkages between the adhesive and wood. However, the reaction of IC with water absorbed in wood to form polyurea and biuret-type structures can compete strongly with the urethane formation.

In this case, IC reacted with either free or bound water from WP first, then continued by wood components; whether cellulose, hemicelluloses, or lignin, which was indicated by the 2$^{nd}$, 3$^{rd}$, and 4$^{th}$ $T_p$ as shown in Table 3 on low $\beta$. Results experiment of [18] strengthened this phenomenon that the reactions of IC with WP without moisture are diffusion-controlled, because the reactants of wood, including cellulose, hemicelluloses and lignin, are macromolecules. Moreover, some cellulose regions are highly crystalline, resulting in a lower mobility of these reactants.
Table 3. Data obtained from DSC thermograms including $T_o$, $T_p$, $T_e$ and $\Delta H$ at different $\beta$ from measurement of sample made of mixture IC and WP at various ratios

| Sample   | $\beta$ (°C/mins) | $T_o$ (°C) | $T_p$ (°C) | $T_e$ (°C) | $\Delta H$ (J/g) |
|----------|-------------------|------------|------------|------------|------------------|
| IC+5% WP | 2.5               | 225        | 279        | 291        | 80               |
|          |                   | 288        | 304        | 311        | 47               |
|          |                   | 311        | 324        | 350        | 102              |
|          |                   | 350        | 409        | 446        | 168              |
|          | 5                 | 277        | 297        | 332        | 209              |
|          |                   | 255        | 338        | 366        | 66               |
|          |                   | 366        | 411        | 444        | 95               |
|          | 10                | 292        | 327        | 384        | 189              |
|          |                   | 361        | 421        | 464        | 97               |
|          | 20                | 317        | 350        | 396        | 190              |
|          |                   | 381        | 441        | 500        | 152              |
| IC+10% WP| 2.5               | 252        | 280        | 292        | 55               |
|          |                   | 259        | 331        | 360        | 148              |
|          |                   | 360        | 386        | 426        | 84               |
|          | 5                 | 294        | 305        | 325        | 121              |
|          |                   | 278        | 325        | 365        | 67               |
|          |                   | 365        | 411        | 447        | 103              |
|          | 10                | 300        | 329        | 378        | 183              |
|          |                   | 376        | 431        | 471        | 152              |
|          | 20                | 314        | 351        | 397        | 190              |
|          |                   | 374        | 436        | 493        | 137              |
| IC+12% WP| 2.5               | 252        | 280        | 292        | 57               |
|          |                   | 329        | 331        | 364        | 156              |
|          |                   | 364        | 390        | 430        | 86               |
|          | 5                 | 294        | 299        | 326        | 111              |
|          |                   | 307        | 343        | 365        | 59               |
|          |                   | 365        | 410        | 447        | 99               |
|          | 10                | 284        | 326        | 376        | 188              |
|          |                   | 340        | 416        | 472        | 124              |
|          | 20                | 299        | 354        | 396        | 165              |
|          |                   | 378        | 426        | 473        | 69               |
| IC+15% WP| 2.5               | 243        | 273        | 292        | 71               |
|          |                   | 306        | 317        | 353        | 101              |
|          |                   | 367        | 371        | 414        | 41               |
|          | 5                 | 289        | 302        | 316        | 90               |
|          |                   | 316        | 330        | 364        | 43               |
|          |                   | 376        | 393        | 425        | 21               |
|          | 10                | 219        | 344        | 379        | 287              |
|          |                   | 310        | 403        | 469        | 111              |
|          | 20                | 285        | 355        | 394        | 216              |

For conclusions, $T_p$ on the thermograms DSC indicated IC cured either using water or moisture WP. However when IC reacted with WP, the $T_p$ emerged more than 2 which indicated IC also reacted with wood components. The reaction enthalpy and reaction rate were lower for WP than for the water indicated IC reacts with water in preference. Value of enthalpy seemed irregular and varies probably due to different structures and compositions of WP. This influence, however, was masked by the
moisture present in the wood (free and bound water), because water is much easier to react with IC than were the –OH within the WP because of the low mobility of the hydroxyls in WP. In other words, IC may react with both –OH and water in IC/WP mixture. This led to the significant influence of the moisture content in WP on the curing kinetics, in terms of DSC thermograms and reaction enthalpy. It was suggested to calculate activation energy since the heating rates used up to 4 and to understand whether water, WP, or both affected the main reaction mechanism among IC, water within the wood (free and bound water), or wood components.

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