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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 prepolymers 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 m³ 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 (β) 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 (ΔH) 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.

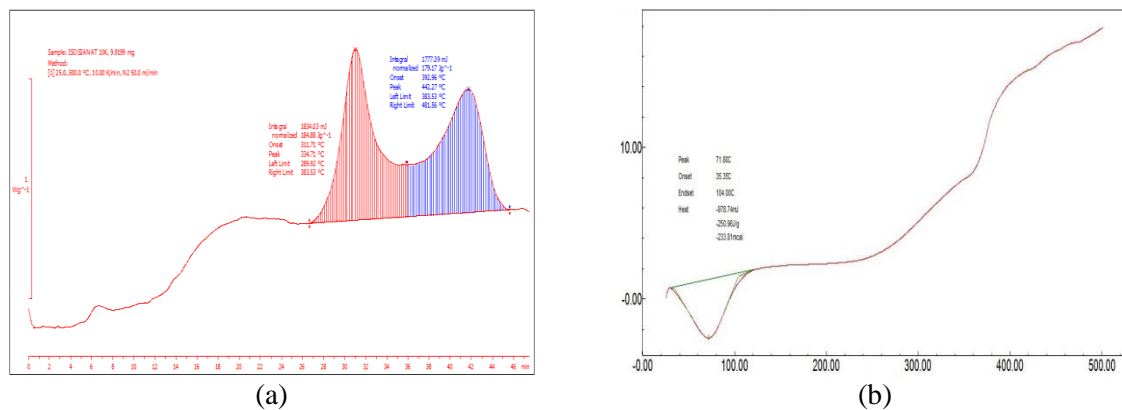


Figure 1. Typical thermograms of DSC's isocyanate (a) and wood particle (b) at $\beta=10^\circ\text{C}/\text{mins}$.

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 (ΔH) presented in Table 1.

Table 1. Comparison of DSC data of the IC and WP at $\beta=10^\circ\text{C}/\text{mins}$.

Sample	β ($^\circ\text{C}/\text{mins}$)	Temperature ($^\circ\text{C}$)			ΔH (J/g)
		T_o	T_p	T_e	
IC	10	312	335	384	185
		393	442	482	179
WP	10	35	72	104	251

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 β . 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 .

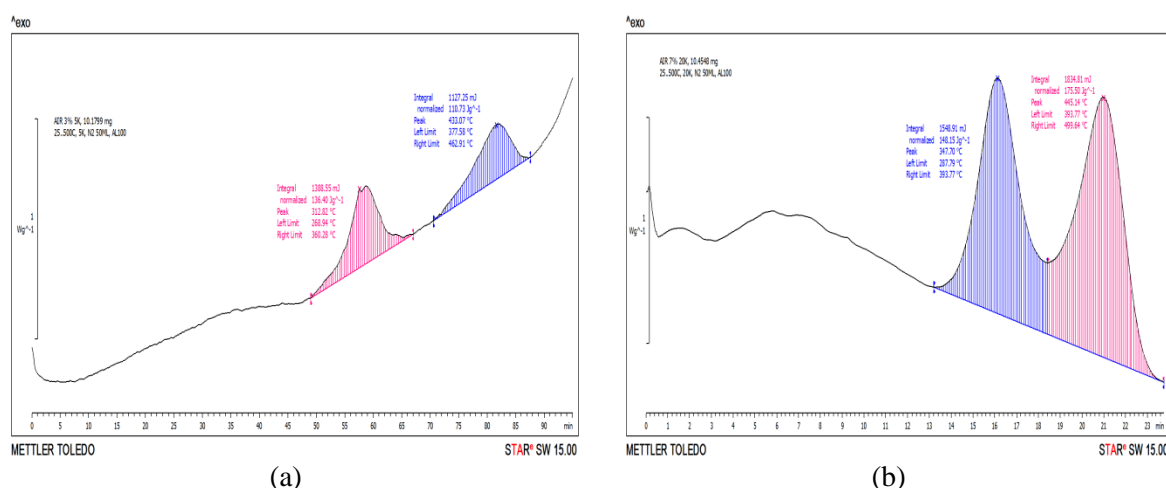
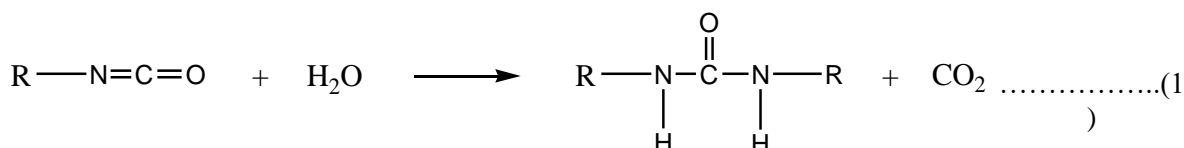


Figure 2. Typical representative thermograms of DSC's mixture of low ratio of water (IC and 3% water (w/w) at slow $\beta=5^\circ\text{C}/\text{mins}$ (a) and high ratio of water (IC and 7% water (w/w) at fast $\beta=20^\circ\text{C}/\text{mins}$ (b).

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°C [20]. The first T_p around 300°C represented the early stage of curing and the second T_p around 400°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 CO_2 gas and forms insoluble polyureas as shown in the equation (1)



β as the rate of temperature increase in a response to a temperature program [22] seemed affected the T_p in isocyanate-water system. Fast β ($20^\circ\text{C}/\text{mins}$) resulted in higher T_p and slow β ($2.5^\circ\text{C}/\text{mins}$) 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 β 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 ΔH at different β from measurement of sample made of mixture IC and water at various ratios.

Sample	β ($^\circ\text{C}/\text{mins}$)	Temperature ($^\circ\text{C}$)			ΔH (J/g)
		T_o	T_p	T_e	
IC+1% water	2.5	349	419	433	327
		433	454	499	336
	5	263	312	366	144

IC+3% water	10	366	431	463	140
		282	331	377	160
		377	437	477	168
	20	291	350	388	134
		388	448	501	143
	2.5	350	412	438	204
		438	451	498	185
	5	269	313	360	136
		378	433	463	111
	10	267	328	378	173
		378	435	477	201
	20	289	349	387	135
387		445	493	154	
IC+5% water	2.5	261	305	345	281
		345	420	499	849
	5	273	317	361	124
		373	431	463	118
	10	291	339	384	165
		384	443	488	157
	20	285	350	390	154
		389	449	494	173
	2.5	259	289	353	115
		363	413	442	124
	5	269	312	365	134
		365	432	466	145
IC+7% water	10	283	337	367	155
		367	442	491	202
	20	288	348	394	148
		394	445	500	176

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 β . The mixture of IC and WP, with less amount of WP (Figure 3.a) or much amount of WP (Figure 3.b) using slow β and fast β , respectively. Unexpectedly, slow β (2.5 and 5°C/min) resulted in three up to four T_p consistently for each measurement as shown in detail in Table 3. On the contrary, normal β (10°C/min) and fast β (20°C/min) resulted in only two T_p . This results indicated that β 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 β can reflect the transition of the reaction features [18].

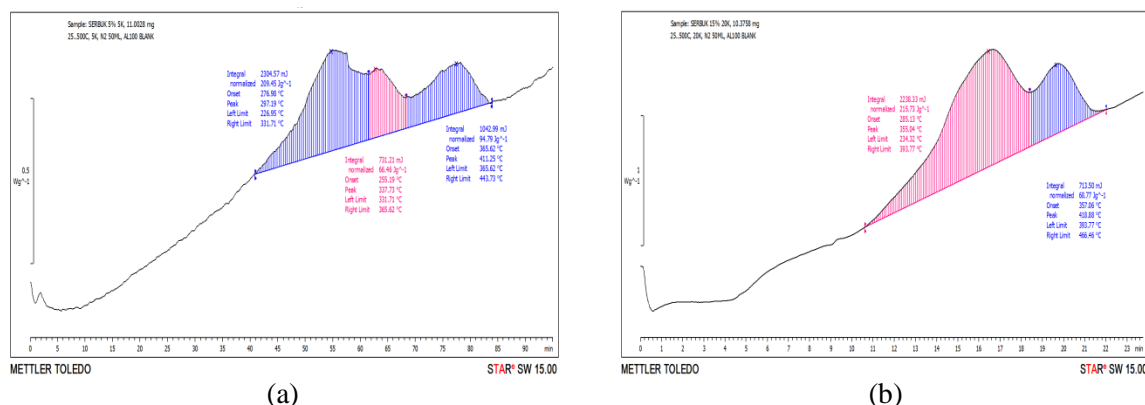
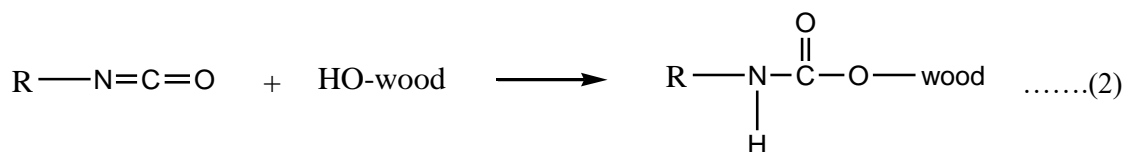


Figure 3. Typical representative thermograms of DSC's mixture of low ratio of WP (IC and 5% WP (w/w) at slow $\beta=2.5^\circ\text{C/min}$ (a) and high ratio of WP (IC and 15% WP (w/w) at fast $\beta=20^\circ\text{C/min}$ (b)

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].



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 2nd, 3rd, and 4th T_p as shown in Table 3 on low β . 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 ΔH at different β from measurement of sample made of mixture IC and WP at various ratios

Sample	β (°C/mins)	Temperature (°C)			ΔH (J/g)
		T_o	T_p	T_e	
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
		329	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
		357	419	466	69

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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