Thermal stability of isocyanate as particleboard’s adhesive investigated by TGA (Thermogravimetric Analysis)

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Abstract. The objective of this study was to evaluate the thermal stability of isocyanate as particleboard adhesives by means of TGA (thermogravimetric analysis). In this study, thermal properties particularly thermal stability of isocyanate-water/wood system was studied up to a temperature of 500 °C using thermal analyzer (Mettler Toledo). When isocyanate was used as the binder in particleboard system; the reactive –NCO group reacted with water (because wood is a hygroscopic material and contains free and bound water) and also with the –OH group from wood. The isocyanate was H3M purchased from PT. Polichemie Asia Pacific and the 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 two different heating rates (slow and fast; 2.5 and 20 °C/min, respectively) with a temperature range from 25 to 500 °C. Results of this study indicate there were more resistant segments to heat in the mixture of isocyanate and water shown from the residual weights about 61 -71% compared to in the mixture of isocyanate and wood particle (only 54-62%). Furthermore, there were fewer steps to degrade in the mixture of isocyanate and water shown from the number of peak temperatures about 1-2 peaks than that in the mixture of isocyanate and wood particle (2-4 peaks). New evidence also emerges that isocyanate reacted with water first shown from the weight loss from the low temperature in the mixture of isocyanate and wood particle.

1. Introduction
Amino resins, phenolic resins, and isocyanates are the three most used thermosetting resins for wood-adhesive systems in forest products industry [1]. The first two have been made based on reactions of formaldehyde with urea, melamine, phenol, resorcinol, or mixtures thereof; thus both in the production process and in the application on the wood products, they are bonded by these adhesives or in the life-service and release formaldehyde emission. The latter up till now has been produced at least using 25 methods for the preparation [2] which reaction between an amine or its salt and phosgene is the most familiar and described elsewhere in detail [3].

In relation with the application, isocyanates have been mainly used for binding in engineered wood products manufacturers as a urethane prepolymer originated from isocyanate-polyol reaction products recently being used in wood-laminating industry and as the isocyanate currently being used in the particleboard industry [4]. In other words, the type of isocyanate generally used for bonding wood laminated-based products is water-based emulsion adhesives with isocyanate as the cross-linker [5]
while the type of isocyanate generally used for particleboard manufacture is MDI or 4-4’-diphenylmethane diisocyanate [4]. Further, fiberboard mills had been adopted particleboard manufacture in applying MDI as the binder [6, 7]. The methods of mass production for both particleboard and fiberboard using isocyanate adhesive have been patented in Europe since 2013 [8]. A comprehensive review describing the development of these both adhesives in Indonesia has been published recently [9].

So this following study will be limited to particleboard isocyanates, since some tremendous fundamental research have emerged, such as evidences of the interaction between isocyanate with water or wood [10, 11] and thermal properties of this adhesive including curing kinetics [12], the durability [13, 14], and effect of wood species to the curing behaviour of this adhesive [15]. However, there is still an information gap of understanding in thermal stability of this resin, particularly after exposed to water or wood particle. Therefore, in this contribution, isocyanate was mixed with either water or wood particle and scanned under thermogravimetric analysis (TGA) to study the resistance to heat including its degradation. The objective of this work is to assess the fundamental aspect of thermal properties of the isocyanate, particularly its thermal stability when the isocyanate is exposed to water or hygroscopic wood particle.

2. Materials and methods
Isocyanate was H3M purchased from PT. Polichemie Asia Pacific (Medan branch, North Sumatera, Indonesia) having 98% solid content. Wood particles with 20-mesh in size were Eucalyptus sp. taken from PT. Toba Pulp Lestari (Porsea, North Sumatera, Indonesia) having 6.20% moisture content.

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 and either water (1%; 2%; 3%; and 5%) or wood particle (5%; 7%; 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. Thermogravimetric analysis (TGA)
Thermogravimetric analysis (TGA) was carried out by employing TGA/DSC1 Star system Mettler Toledo, operating at Institute of Advance Materials-University Putra Malaysia (Selangor, Malaysia). About 10 mg of the mixture either isocyanate with water or wood in various weight ratios was scanned at two different heating rates (slow and fast; 2.5 and 20 °C/minutes, respectively) with a thermally degraded in the temperature ranging from 25 to 500 °C and using nitrogen gas 50.0 mL/mins. For the control, prior scanning the mixtures, each component (isocyanate and wood particle) was scanned at a normal heating rate of 10 °C/minutes.

3. Results and discussions
3.1. TGA of the isocyanate and wood particle in the normal heating rate
Figure 1 shows typical TGA’s (top) and derivative weight (bottom) curve of main components of the mixture, namely isocyanate and wood particle at a heating rate of 10 °C/minutes. There were three peak temperatures of the isocyanate’s curve (figure 1.a) and two peak temperatures of the wood particle’s curve (figure 1.b). Further, the peak temperature of the isocyanate’s curve shows lower temperature than wood particle as presented in table 1. This indicates that isocyanate was degraded first at low temperature (64-83 °C) and needed more steps to decompose until higher temperature (194-388 °C) presumably because of the difference in the molecular weight of the composition of the isocyanate as confirmed by gas chromatography-mass spectroscopy (GCMS) data [9].
Figure 1. Typical curve of TGA’s and derivative weight of isocyanate (a) and wood particle (b) at a heating rate of 10 °C/mins.

Even though in this case isocyanate was degraded first compared to wood particle and the degradation temperature was lower than wood temperature’s, data of residue sample confirmed that isocyanate was more resistant than wood particle. Residue sample of the isocyanate was more than 50% while wood particle’s was only about 30%.

Table 1. Comparison of TGA data of the isocyanates and wood particle at heating rates of 10 °C/min.

| Sample            | Heating rate \(^\circ\)C/mins) | Temperature \(^\circ\)C | Residue sample (%) |
|-------------------|-------------------------------|------------------------|-------------------|
|                   |                               | Range                  | Peak              | Actual | Calculated |
| Isocyanate (IC)   | 10                            | 64-83                  | 74                | 53.91  | 53.93      |
|                   |                               | 133-194                | 176               | 53.91  | 53.93      |
|                   |                               | 194-388                | 315               | 31.72  | 31.67      |
| Wood particle (WP)| 10                            | 24-169                 | 86                | 31.72  | 31.67      |
|                   |                               | 169-499                | 362               |        |            |

3.2. Influence of composition and heating rate to the TGA assessment

Figure 2 shows a representative TGA’s curve of a mixture of isocyanate and water/wood particle at two different heating rates. A mixture of isocyanate and water (figure 2.a) resulted in less number of peak temperatures than a mixture of isocyanate and wood particle (figure 2.b), indicating that mixture has influenced in the thermal properties. Further, the addition of water or wood particle within isocyanate resulted in low temperature peak consistently as shown in table 2 and table 3.

In this present study, heating rate as the rate of temperature increase in response to a temperature program [16] seemed affected the peak temperature in the isocyanate-water system. Fast heating rate (20 °C/mins) resulted in higher peak temperature and slow heating rate (2.5 °C/mins) yielded lower peak temperature. In the case of high heating rate, sample seemed become dense packing. Such free diffusion is inhibited and the decomposition temperature increases. At low heating rate, the sample temperature is more uniform, and diffusion of products gases can occur within the sample, lowering the decomposition temperature [16].

In isocyanate-wood particle system, heating rate affects not only the value of peak temperature but also its number. Generally, when slow heating rate (2.5 °C/mins) was applied, the number of peak temperature increased. Slow heating rate might the extent of sample decomposition was greater at a lower heating rate [16].
Figure 2. Typical representative curve of TGA’s mixture of isocyanate and 3% water (w/w) at slow heating rate of 2.5 °C/mins (a) and isocyanate and 12% wood particle (w/w) at fast heating rate of 20 °C/mins (b).

3.3. TGA of the mixture (isocyanate and water/wood particle) at various composition and two different heating rates

Table 2 compared data of the mixture of isocyanate-water system at various compositions. Two main regions of mass loss were observed (see IC+1% water and IC+5% water); the first region with the peak 66, 86, 49, and 78 °C were due mainly to loss of absorbed water and trace formation of volatile compounds such as CO$_2$ release as the equation (1).

$$R - N = C = O + H_2O \rightarrow R - N-C-N-R + CO_2$$ (1)

Table 2. TGA data of the mixtures of isocyanate and water at two different heating rates.

| Sample          | Heating rate (°C/mins) | Temperature (°C) | Residue sample (%) |
|-----------------|------------------------|------------------|--------------------|
|                 |                        | Range            | Peak               |
|                 |                        | Actual           | Calculated         |
| IC+1% water     | 2.5                    | 24-104           | 66                 | 64.46  | 64.46 |
|                 |                        | 136-337          | 266                |         |       |
|                 |                        | 38-139           | 86                 |         |       |
|                 | 20                     | 166-400          | 319                | 68.11  | 68.11 |
| IC+2% water     | 2.5                    | 154-335          | 271                | 64.75  | 64.75 |
|                 |                        | 169-405          | 321                | 68.80  | 68.80 |
|                 | 2.5                    | 175-341          | 276                | 65.43  | 65.43 |
| IC+3% water     | 20                     | 42-174           | 137                | 69.30  | 69.30 |
|                 |                        | 181-405          | 315                |         |       |
|                 | 182-409                | 25-65            | 49                 | 60.76  | 60.75 |
| IC+5% water     | 2.5                    | 156-342          | 286                | 70.56  | 70.56 |
|                 |                        | 40-111           | 78                 |         |       |

The second region with the peak 266, 319, 286, and 321 °C was due to the degradation of lateral chains of the cured resin [17, 18]. NCO group within isocyanate can react with a compound having active hydrogen such as water [1, 19, 20]. Therefore, when the addition of water therein, it will react as shown in equation (1) [21], cure and degrade with the ramp of heating rate temperature applied.
Thermal degradation of a polyurethane including isocyanate went through two or three stages [22, 23] which consisted of decomposition of hard segments and urethane linkages at an early stage, and decomposition of soft segments at the latter stages [24]. At the end of TGA analysis, 61-71% of initial mass was not decomposed (see residue sample). This residue can correspond to the mass of rigid segment within the cured resin [25].

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\text{R-N=C=O + HO-wood} \rightarrow \text{R-N-C=O-wood}
\]

(2)

Table 3. Comparison of TGA data of the mixtures of isocyanate and wood particle at two different heating rates.

| Sample    | Heating rate (°C/mins) | Temperature (°C) Range | Temperature (°C) Peak | Residue sample (%) Actual | Residue sample (%) Calculated |
|-----------|------------------------|------------------------|------------------------|--------------------------|-------------------------------|
| IC+5% WP  | 2.5                    | 23-136                 | 166-308                | 65                       | 57.47                         | 57.48                         |
|           |                        | 308-351                | 362-447                | 326                      |                               |                               |
|           |                        | 28-138                 | 28-138                 | 98                       |                               |                               |
|           | 20                     | 138-172                | 138-172                | 152                      | 56.94                         | 56.96                         |
|           |                        | 175-398                | 175-398                | 321                      |                               |                               |
|           |                        | 158-313                | 158-313                | 273                      |                               |                               |
| IC+7% WP  | 2.5                    | 313-354                | 313-354                | 323                      | 58.04                         | 58.04                         |
|           |                        | 380-462                | 380-462                | 421                      |                               |                               |
|           | 20                     | 36-162                 | 36-162                 | 98                       | 58.28                         | 58.28                         |
|           |                        | 196-394                | 196-394                | 315                      |                               |                               |
|           |                        | 25-128                 | 25-128                 | 66                       |                               |                               |
| IC+10% WP | 2.5                    | 168-306                | 168-306                | 268                      | 55.56                         | 55.60                         |
|           |                        | 306-349                | 306-349                | 321                      |                               |                               |
|           | 20                     | 363-443                | 363-443                | 406                      | 61.77                         | 61.74                         |
|           |                        | 31-138                 | 31-138                 | 101                      |                               |                               |
|           |                        | 140-396                | 140-396                | 319                      |                               |                               |
|           |                        | 32-133                 | 32-133                 | 66                       |                               |                               |
|           |                        | 163-304                | 163-304                | 268                      | 53.93                         | 53.96                         |
|           |                        | 304-352                | 304-352                | 327                      |                               |                               |
| IC+12% WP | 2.5                    | 363-438                | 363-438                | 398                      | 53.93                         | 53.96                         |
|           |                        | 35-167                 | 35-167                 | 106                      |                               |                               |
|           | 20                     | 192-348                | 192-348                | 308                      | 56.49                         | 56.53                         |
|           |                        | 348-393                | 348-393                | 360                      |                               |                               |
|           |                        | 44-130                 | 44-130                 | 66                       |                               |                               |
|           |                        | 166-299                | 166-299                | 260                      | 54.48                         | 54.50                         |
|           |                        | 299-349                | 299-349                | 323                      |                               |                               |
| IC+15% WP | 2.5                    | 351-437                | 351-437                | 391                      | 56.62                         | 56.62                         |
|           |                        | 35-165                 | 35-165                 | 111                      |                               |                               |
|           | 20                     | 206-347                | 206-347                | 307                      | 56.62                         | 56.62                         |
|           |                        | 347-392                | 347-392                | 359                      |                               |                               |

Table 3 compares data of the mixture of isocyanate-wood particle system. Up to four main regions of mass loss were observed (see IC+10%; 12%; and 15% wood particle) at slow heating rate; first region with the peak 66°C was due to the evaporation of absorbed water and the formation of small
volatile compounds such as CO$_2$ release as the explanation of the equation (1). It is believed that isocyanate will react with either free or bound water from wood particle if the water is present in the wood materials; -NCO group within the isocyanate will react with water in preference [11]. The second, third, and fourth main regions were related to degradation or decomposition of hard and soft segment, respectively [24] or decomposition of wood component (hemicelluloses, cellulose and lignin) reacted with isocyanate as proved by infrared spectroscopy [11]. Equation (2) confirms that –NCO group within isocyanate reacted with hydroxyl groups (OH) from wood provided a set of combination and variety of polymer containing ester, ether, urea, alkyl or aryl units that affect thermal stability of the material [24].

At the end of TGA analysis, 54-62% of initial mass was not decomposed (see residue sample). This percentage was lower than the case of isocyanate-water system presumably because the mass of rigid segment within the cured resin consisted of different compounds, such as cellulose, hemicelluloses, or lignin. Moreover, the peak temperature of the respective data in table 3 confirms the condition.

For sum up, the comparison of peak temperature and residue sample between isocyanate-water or wood particle system shows different thermal stability depended mainly on the composition of the mixture. Even though the isocyanate-water system was more resistant to heat than to isocyanate-wood particle system showed from residue sample, the first mixture need less step to degrade compare to the latter showed from the number of the peak temperature. Further, isocyanate preferred to react with water first rather than with wood components showing the existence of lower peak temperature at isocyanate-wood particle system.

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