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### RESEARCH ARTICLE

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## Tuning the microstructure of polyurethane foam using nanocellulose for improved thermal insulation properties through an efficient dispersion methodology

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### Abstract

Nanocellulose is explored as an eco-friendly cell modifier and reinforcer for improving the thermal insulation and mechanical performance of rigid polyurethane foam (RPUF). In this study, we report on a promising method for achieving 'solvent-free' dispersion of cellulose nanocrystals (CNCs) into polyether polyol for the production of RPUF. This was achieved through wet grinding of CNC powder in polyol in an agitator bead mill and the dispersion of CNCs in polyol was superior to classical ultrasonication. While the improvements (reduction) in thermal conductivity, due to the nucleation effect of CNCs, in the RPUF from the milling method is comparable to that from the ultrasonication method, it should be noted that it was achieved despite of a reduction in closed cell content ( $\sim$ 80%) and at a similar average cell size. This effect has been attributed to either superior dispersion quality of the milling method and/or involvement of a zirconium impurity within the CNC-RPUF.

### **Research Highlights**

- Enhanced properties of polyurethane foam using well-dispersed nanocellulose.
- Superior dispersion of nanocellulose in polyol using agitator bead mill.
- Involvement of zirconium for tuning microstructure of polyurethane foam.

### K E Y W O R D S

biomaterials, dispersion, microstructure, nanocomposites, polyurethane

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## **1** | INTRODUCTION

Cellulose, the most plentiful source of biopolymer, is found in both plant and non-plant sources such as algae, tunicate (a family of sea animals) and bacteria. Cotton is the main commercial source of cellulose because it provides a high yield with minimal purification.<sup>1</sup> There is growing interest in nanocellulose as a "building block" and depending on the sources and processing method; nanocellulose can be produced in the form of rod-shaped nanocrystals, longentangled nanofibrils and sphere-like nanocrystals.<sup>2,3</sup>

Rod-shaped cellulose nanocrystals (CNCs) have been the subject of a broad array of research interest as promising reinforcing fillers. The excellent physical properties of the individual CNC, combined with easy surface modification plus lightweight, providing the primary interest. The secondary factor is the abundant availability from sustainable biologically renewable sources. The inter and intra- molecular hydrogen bonding of hydroxyl groups on the CNCs enhances the mechanical properties and chemical stability of CNC reinforced polymers.<sup>4,5</sup>

Rigid polyurethane foam (RPUF) has been used as an insulation material for many years, nevertheless, there remains a commercial interest in improving the thermal insulation and mechanical performance. The presence of CNCs in RPUF, as a reinforcing nanofiller, have shown enhanced performance in mechanical<sup>6,7</sup> and thermal insulation properties<sup>8,9</sup> of RPUF. In the later studies, it

was found that the thermal conductivity decreased up to a loading of 0.4 wt% At this loading level, the compressive mechanical properties were also improved perpendicular to the direction of foam rise.<sup>10,11</sup> However, above that loading the CNCs flocculated (re-agglomerated) and interfered with the foam cell formation adversely affecting the thermal conductivity.

Tuning the microstructure (cell size and closed cell content) of RPUF through the selection of optimum concentration of the filler and the efficient dispersion of the filler into the RPUF composites<sup>12</sup> is one of the most effective means to control the physio-mechanical properties of RPUF. While the most common solvent free methods for dispersing nanoparticles into RPUF precursors (pMDI, polyol or blowing agent) are ultra-sonication<sup>13,14</sup> simple high shear stirring<sup>15,16</sup> and microwave irradiation<sup>17,18</sup> it is worth noting that wet-grinding or milling with balls (low speed mixing, bead size above 10 mm) or beads (high speed agitation, bead size below 5 mm) can also be a promising approach for this purpose.

Agitator bead mill (ABM) is known for efficient nanonization of highly agglomerated particles.<sup>19</sup> As shown in Figure 1 ABM operates via dynamic impact mechanisms (head-on, oblique and multi-ball impact) to effectively fragment the particles.<sup>20</sup> When the mill operates, the centrifugal force is induced in the mill which rotates the balls around the mill wall. The particles collide, are trapped and forced between the moving



(A)Head-on impact

(B) Oblique impact

(C) Multi-ball impact

**FIGURE 1** Schematic representation of the dispersion of cellulose nanocrystals (CNCs) into polyol via agitator bead mill.

balls which results in breaking and fragmentation of agglomerated particles.<sup>20,21</sup> While studies have been done on the use of ABM to reduce the size of microcellu-lose<sup>22,23</sup> and cellulose nanomaterials<sup>24,25</sup> to the best of our knowledge no study has looked at ABM to disperse nanosized cellulose into polyether polyols for the production of RPUF. However, one study from our group has reported the use of ABM to disperse nanocellulose into poly(tetramethylene glycol) for the production of thermoplastic polyurethane.<sup>26</sup>

Herein, the objective of this research was to investigate the use of ABM in comparison to our earlier paper<sup>10</sup> using ultrasonication, to provide more efficient dispersion of CNCs in polyol, to improve the thermal insulating properties of RPUF without compromising the compressive mechanical properties or increasing the RPUF density. The rheology properties of the polyol dispersions and final properties of the RPUF were thoroughly studied to provide a comprehensive understanding about the impact of the milling, and identified interaction between the polyol and zirconium impurities from the zirconium oxide beads used in the ABM process, on the polyurethane matrix microstructure (cell size and closed cell content).

## 2 | EXPERIMENTAL

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## 2.1 | Materials

Voranol 446<sup>®</sup> was tested as supplied at Huntsman Australia Pty Ltd according to ASTM D4274 and the hydroxyl value and water content found to be 456 mgKOH/g and 0.2%, respectively. Polymeric methylene diphenyl diisocyanate (pMDI), DMCHA (dimethylcyclohexylamine), Tegostab 8460<sup>®</sup>, HFC M1, sulfuric acid (98 wt %) and Whatman filter paper no 1 were used as received.

# 2.2 | Preparation of CNC dispersions in polyol via ABM

CNCs were prepared from cotton (Whatman filter paper no. 1) by our protocol based on sulfuric acid hydrolysis.<sup>27</sup> The rod-shaped CNCs were obtained with a yield of up to 75% and an aspect ratio of  $11.3 \pm 3.2$  (average width of  $15.7 \pm 4.9$  nm and length of  $169.3 \pm 48.6$  nm). A Netzsch ABM, Zeta@Type LMZ 10, was employed to incorporate CNCs into the polyol. The polyol with 0.4wt% CNCs was

 TABLE 1
 Process parameter of agitator bead mill and formulation of rigid polyurethane foam (RPUF).

Process parameter of ABM								
Parameter	Loading (g)	Mill speed (rpm)	Pump speed (rpm)	ZrO <sub>2</sub> beads (mm)	Bead loading (L)	<i>T</i> (°C)	<i>t</i> (h)	
Setting	1200	1500	14	0.4	0.4	35	2.5	
Formulation	n of RPUF							
Formulation	ıs	F <sub>0</sub>	$F_{\mathbf{M}}$	FC4 <sub>M</sub>	$F_{U}$	FC4	4 <sub>U</sub>	
Part B: Polyo	l blend (pphp)							
Voranol 446		100	100	100	100	100		
CNC (% wt)		0	0	0.4	0.4	0.4		
Tegostab 84	460	2	2	2	2	2		
Water		1.5	1.5	1.5	1.5	1.5		
HFC M1		30	30	30	30	30		
Catalyst								
DMCHA		1	1	1	1	1		
Part A: pMDI	[							
Nominal ir	ndex	110	110	110	110	110		
Processing		None	ABM	ABM	Ultrasonic	Ulti	rasonic	
Reactivity (±2	2 s)							
Cream time	e	40	36	35	40	37		
Gelling tim	ie	248	239	231	248	226		
Free rise ti	me	362	342	339	358	341		
Tack free t	ime	656	601	593	655	650		
Apparent cor	e density (kg/m3	3) $37.4 \pm 0.8$	$37.5 \pm 0.8$	$37.2 \pm 0.7$	$37.3 \pm 0$	37.6	$5 \pm 0.8$	

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designated as VC4<sub>M</sub>. The process parameters are summarized in Table 1. After milling the polyol dispersion was dried in a thin/wiped film evaporator (VTA, Verfahrenstechnische Anlagen GmbH & Co. KG, Germany) to a water content of less than 100 ppm.

# 2.3 | Preparation of rigid polyurethane foam

The CNC polyol dispersions were mixed with other chemicals (according to the formulations in Table 1) to afford a homogenous Part B. The Part B was then blended with pMDI (Part A) at an index of 110 and was directly transferred into a preheated (50°C) aluminum mold and securely covered with the lid. After 24 h, the foam was removed from the mold and left for a further 1 week for post-cure before further characterization. RPUF was also prepared without CNCs under milling treatment ( $F_{\rm M}$ ) and without milling treatment (control foam  $F_0$ ) to investigate the effect of dispersing method on RPUF properties. The data for the formulation prepared by ultrasonication neat foam ( $F_{\rm U}$ ) and nanocomposite foam containing 0.4 wt% CNCs (FC4<sub>U</sub>) was adapted from our previous publication.<sup>10</sup>

## 2.4 | Analysis of CNC polyol dispersions

The effect of different processing conditions on the quality of the CNC dispersion in polyol was investigated using light microscopy, visual observation of storage stability over 6 months and by measuring the viscosity of the CNC polyol dispersions on a AR-G2 rheometer under isothermal conditions at 25°C and a shear rate sweep from 0.1 to 100 s<sup>-1</sup>.

The effect of different processing methods (ultrasonication and ABM) on the polyol structure was investigated using FTIR, <sup>1</sup>H-NMR and matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF). The <sup>1</sup>H-NMR spectra of polyol was recorded on an AV3400 NMR spectrometer at a concentration of 6 mg of the sample in 600  $\mu$ L of deuterated chloroform (CDCl<sub>3</sub>). The distribution of the molecular weight of polyol before and after processing treatment was analyzed by MALDI-TOF by applying 1 µL of the specimen to the MALDI-TOF target plate, followed by 1 µL of 2,5-dihydroxybenzoic acid (DHB) matrix (saturated solution in 50% acetonitrile/0.1% formic acid). Samples were analyzed in reflection mode across 400-3000 m/z. An external calibration was performed using the ABSciex 6-peptide mix, and a minimum of 1000 shots acquired for each sample on a Bruker Autoflex III MALDI-TOF/TOF mass spectrometer. ATR-FTIR spectroscopy was conducted on a Thermo-Nicolet 5700 (Waltham, USA) at a resolution of  $4 \text{ cm}^{-1}$ and the wavenumber range of  $500-4000 \text{ cm}^{-1}$ .

ICP-OES was used to measure the zirconia content in polyol and foam samples. Samples were digested using nitric acid and analyzed using a Varian Vista Pro ICP-OES instrument.

## 2.5 | Analysis of RPUF properties

ATR-FTIR spectroscopy was also performed on RPUF, similar to the CNC polyol, using a Thermo-Nicolet 5700 (Waltham, USA).

Scanning electron microscopy analysis using a Neoscope JCM-5000 (JEOL 1011, Japan) operating at 10 kV was used to study the surface morphology of the RPUF. Cell size was measured using ImageJ software at a minimum of 25 measurements to calculate the average value and the standard deviation. Closed cell content of the RPUF was measured at Huntsman Australia Pty Ltd using an air pycnometer according to ASTM D2856.

Five rectangular specimens (51 mm in length and width and 40 mm thick) were prepared for analysis of mechanical properties using an Instron 5584 equipped with a 5 kN load cell under compression mode according to ASTM D1621-10.

Dynamic Mechanical Analysis (DMA) was conducted on cylindrical specimens (diameter of 10 mm) in compression mode using simultaneous differential thermal analysis (SDTA) on a Mettler Toledo  $861^{e}$  at a frequency of 1 Hz and a heating rate of  $2^{\circ}$ C/ min between 20 and  $250^{\circ}$ C.

Rectangular specimens with dimensions of 200 mm × 200 mm × 25 mm were prepared for thermal conductivity ( $\lambda$ ) analysis using a heat flow meter (FOX200, Laser-Comp, USA) equipped with a cooling unit (Huber) according to ASTM C518-10. The specimens were placed between the upper plate at 10°C and the bottom plate at 35°C.

Dimensional stability of foam specimens (100 mm  $\times$  100 mm  $\times$  5 mm blocks) was performed at 70  $\pm$  2 and - 73  $\pm$  3°C according to ASTM D 2126-09. The % linear changes were obtained by measuring the dimensions using digital calipers over a period of time up to14 days.

## 3 | RESULTS AND DISCUSSION

# 3.1 | Data analysis of CNC polyol dispersions

# 3.1.1 | Storage stability of CNC polyol dispersion

In the commercial production of RPUF the viscosity of the polyol blend (Part B) component must be low



FIGURE 2 (A) Storage stability of CNC polyol dispersions and (B) microscopic images of CNC polyol dispersions: neat treated ABM polyol ( $V_{\rm M}$ ); CNC-polyol via ABM (VC4<sub>M</sub>); CNC-polyol dispersion via ultrasonication (VC4<sub>U</sub>).

enough to allow efficient mixing with the pMDI using only a high shear mixer and preferably to be stable (no phase separation) over time. As the viscosity of the polyol blend depends on the viscosity of the base polyol, the degree of dispersion<sup>28</sup> of the nano-filler and the nano-filler loading level, there is a balance that needs to be achieved between these three parameters. The physical dispersions of CNCs in polyol were monitored for a period of 6 months (Figure 2A). Neat polyol, subjected to ultrasonication  $(V_{\rm U})$ , was indistinguishable to the control polyol  $(V_0)$ , but the polyol processed by ABM  $(V_{\rm M})$  was cloudy.

The difference was postulated as the result of contamination by the zirconia beads from the milling process forming a zirconia-polyol gel which was stable for the duration of the study. Zirconium was detected at 21 mg/kg in sample  $V_M$ , as measured by ICP-OES. The precedence for formation of zirconia-polyol gel is consistent with the use of block poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) polyether polyols as a

stabilizer for making nano-zirconia.<sup>29</sup> It is also consistent with the following facts.

First, while the dispersion of CNCs in polyol processed by ultrasonication (VC4<sub>II</sub>) gradually phase separated over a timeframe of between 3 and 5 months, the polyol-CNC dispersion obtained through the milling method (VC4<sub>M</sub>) was visually stable. Photo-microscopy (Figure 2B) also confirmed the better dispersion quality of the ABM process compared to the ultrasonication process, showing much smaller CNC agglomerates.

Second, hydroxypropylcellulose is used as a stabilizer to prevent agglomeration of nanozirconia (by forming a covalently bound ligand) prepared by the sol-gel process.<sup>30</sup> Third, zirconium compounds are known as inorganic crosslinkers with reactive groups on polymers.<sup>31</sup> Possible interactions of zirconia with polyol or other polymers containing hydroxyl groups is depicted in Figure 3. Zirconia has a very high affinity for oxyanions and hydroxyl groups, such as the hydroxyl groups on

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**FIGURE 3** Possible interactions of a polymer containing hydroxyl groups with zirconia.

CNCs and polyol, to give strong adsorption.<sup>32</sup> Fourth, the preparation of zirconium impregnated CNCs has been previously reported.<sup>33</sup> Finally, zirconium was detected at 19 mg/kg in sample VC4<sub>M</sub>.

# 3.1.2 | Rheology studies of CNC polyol dispersion

According to Harikrishnan et al.<sup>34</sup> independence of the storage modulus from the frequency sweep during rheology testing is evidence for the presence of a highly cross-linked 3D gel network. Obviously, such an effect will be very evident above the percolation network threshold.<sup>28</sup> In this case, due to the low level of zirconia contamination, the gel structure formed was weak (Figure 4A) as reflected by higher loss modulus (G'') for all the polyol samples compared to that of storage modulus (G') which implies there was only a weak network between individual molecules in polyol samples. However, the plateau of storage modulus curve at low frequency was more apparent and smoother with the milled samples ( $V_{\rm M}$  and VC4<sub>M</sub>) compared to the ultrasonicated polyol samples ( $V_{\rm II}$  and VC4<sub>IJ</sub>) and this was considered to be evidence of viscoelastic behavior<sup>35</sup> due to the presence of a zirconia-polyol  $(V_{\rm M})$  and/or zirconia-CNC  $(\rm VC4_{\rm M})$ 3D gel.

Another way to confirm the quality of a nano-particle dispersion is by investigating the independency of viscosity values towards shear rate. Figure 4B shows the viscosity of the base polyol ( $V_0$ ) and the polyol containing CNCs using the different processing methods. In regards to polyol samples containing CNCs by ultrasonication the viscosity of VC4<sub>U</sub> was only slightly higher than the base polyol at low shear rate but approached that of the base polyol at higher shear rate. This behavior was analogous to a rheology study of CNC in castor oil polyol<sup>36</sup> and supported by phase separation and CNC agglomeration observed in this study in the macroscopic analysis (Figure 2).

In contrast the milled sample  $VC4_M$  was significantly higher in viscosity and was also strongly shear



**FIGURE 4** Comparison of rheological properties of polyol/ cellulose nanocrystal dispersion under agitator bead mill and ultrasonication; (A) storage modulus (G') and loss modulus (G'') (B) viscosity.

thinning. We interpreted this pronounced viscosity increase as evidence for exfoliation of the CNCs in polyol analogous to the work of Harikrishnan et al,<sup>28</sup> who reported such behavior as evidence for exfoliation of nanoclay in polyol.

## 3.1.3 | Chemical and molecular structure changes of polyol upon ABM process

In regards to polyol samples without CNCs,  $V_M$  shows similar viscosity to  $V_0$  at low shear rate but slightly decreased viscosity at higher shear rate. It has been reported that ABM can have deleterious effects on polymers such as polyisoprene, poly (methyl methacrylate), and poly(ethylene-*alt*-polypropylene),<sup>37</sup> that can affect the viscosity of the polymer after treatment. Hence, the effect of ABM on the polyether polyol (Voranol<sup>TM</sup> 446) chemical and molecular structure was further examined by using FTIR, <sup>1</sup>H-NMR and MALDI–TOF as shown in Figure S1.

Based on these analyses, there was no evidence of any significant chemical and molecular distribution change detected after ABM. Further, the facts that hydroxyl values of the polyether polyol, before and after ABM were determined to be 456 and 457 KOH/g, respectively, and the statistically insignificant difference ( $\alpha = 0.05$ ) between the viscosity of polyether polyol before  $(V_0)$  and after ABM treatment  $(V_{\rm M})$  (Figure 4B) also supports the conclusion that no significant change in chemical structure occurred.

#### 3.2 **Properties of RPUF**

#### The chemical interaction of CNCs 3.2.1 with RPUF

Figure 5A shows the infrared spectra of the RPUF samples. All of which shows the typical urethane peaks at 3320 and 1510 cm<sup>-1</sup> (stretching and bending modes of the N-H group), 1704 cm<sup>-1</sup> (stretching vibration of urethane carbonyl OC=O),  $1220 \text{ cm}^{-1}$  (O-CO vibration) and  $1060 \text{ cm}^{-1}$  (C–O vibration). In principle, the chemical



interaction between CNCs and the RPUF matrix can be estimated qualitatively<sup>7</sup> from the reduction in intensity of the OH stretching and NH vibration signal at 3500 cm<sup>-1</sup> normalized to the carbonyl group at 1710  $\text{cm}^{-1}$  (Figure 5B).

Unfortunately, it would appear that the trace zirconia in the milled samples interferes with the IR analysis because the milled sample  $F_{\rm M}$  exhibits a significant reduction of the ratio of the hydroxyl peak to the carbonyl group, compared to the same ratio for the ultrasonicated sample F<sub>U</sub>, presumably due to the high affinity of zirconia for hydroxyl groups.<sup>32</sup> Therefore, although the dispersion of CNCs into polyol by milling  $(VC4_M)$  was clearly better than by ultrasonication (VC4<sub>U</sub>), it is difficult to judge the difference in the level of cross-linking between the FC4<sub>U</sub> and FC4<sub>M</sub> samples by this IR methodology.

Nevertheless, whatever the difference on the level of the cross-linking between samples  $VC4_M$  and  $VC4_U$ , it is assumed that the absolute levels of cross-linking are small which would be consistent with the following facts. First, it has been estimated that the number of accessible OH groups available at the surface is only one-third of the OH groups in the cellulosic chain.<sup>38</sup> Second, these accessible OH groups on the surface of CNCs are further reduced by



FIGURE 5 (A) Fourier transform infrared spectroscopy attenuated total reflectance (FTIR-ATR) of rigid polyurethane foam (RPUF) and (B) FTIR-ATR spectra after normalization to the carbonyl group at 1710 cm $^{-1}$ .



FIGURE 6 Scanning electron microscopy of rigid polyure than foam for (A) parallel to the foam rise  $(\uparrow_{rise})$  and (B) perpendicular to the foam rise  $(\Theta_{rise})$  direction.

conversion to sulfonic acid groups during the acid hydrolysis process.<sup>39,40</sup> Third, the overall number of hydroxyl groups at the CNC surface that can react with isocyanates is restrained by the level of accessible OH groups and estimated at only around 5% in the case with n-octyldecylisocyanate.<sup>41</sup>

## 3.2.2 | Structural morphology of RPUF

The structural morphology of the RPUF, parallel and perpendicular to foam rise, was predominantly a polygon closed cell structure (Figure 6). The average foam cell size of the RPUF, at about 523  $\pm$  140 µm, was measured using ImageJ software and there was no significant difference between the neat RPUF ( $F_0$  and  $F_M$ ) and the nanocomposite RPUF (FC4<sub>M</sub>) containing 0.4 wt% of CNCs for all the samples both parallel and perpendicular to foam rise direction, including no statistically significant ( $\alpha = 0.05$ ) anisotropic behavior.

The insignificant difference in the morphology between the control foam ( $F_0$ ) and milled neat RPUF ( $F_M$ ) was in good agreement with the previous results that there were no chemical changes in the polyol before and after ABM ( $V_0$  and  $V_M$  respectively). In the case of the milled RPUF nanocomposite (FC4<sub>M</sub>), the presence of zirconium-polyol-CNC gel clearly prevented the CNCs from acting as a nucleating agent.

## 3.2.3 | Dynamic mechanical analysis data

DMA is a sensitive method to understand the molecular movement of materials in response to stress, temperature, and other variables in a cyclic manner. Figure 7 shows the storage modulus (*E*) and loss peak (tan  $\delta$ ) of all the RPUF samples at temperature dependencies.

Wu et al.,<sup>42</sup> has reported that for an RPUF, the  $T_g$  reflects the rigidity of the polymer matrix. Thus, the higher the cross-link density, or the higher the aromaticity level of the RPUF, the higher the  $T_g$ . The crosslink density can be increased through either an increase in the functionality of the polyols used or the index of the pMDI. In regard to the milled sample, it is more complex due to the potential for alternative competitive hydrogen bonding. In addition to the competition between polymer-CNC and CNC-CNC hydrogen bonding (agglomeration) there is an option for zirconia-polyol interactions and zirconia-CNC interactions. The zirconia-polyol interaction and the zirconia-CNC interaction has been previously discussed. In the case of  $F_M$  and FC4<sub>M</sub>.



**FIGURE 7** Storage modulus and tan  $\delta$  of rigid polyurethane foam.

TABLE 2 Thermomechanical properties of foams.

Samples	Storage modulus at T <sub>room</sub> (MPa)	Damping peak/T <sub>g</sub> (°C)	Activation energy of hydrogen bond dissociation $E_{\rm a}$ (KJ/mol)
$F_0$	5.49	170.43	55.50
$F_{\rm U}$	5.26	169.96	53.10
$FC4_U$	6.89	172.74	59.45
$F_{\mathbf{M}}$	5.66	166.64	51.39
FC4 <sub>M</sub>	6.01	168.89	56.37

there is a slight reduction in the  $T_g$  compared to the base formulation  $F_0$  (Figure 7 and Table 2) and it was postulated that the zirconia-polyol ( $F_M$ ) and/or zirconia-CNC (FC4<sub>M</sub>) interaction interfered with the normal hydrogen bonding in RPUF.

A schematic description of hydrogen bonding formed in the presence of CNCs in RPUF is illustrated in Figure 8. The hydrogen bonding network in the polymer matrices can be estimated as the activation energy for the dissociation of polymer chains in the 'rubbery regime'. The primary relaxation of polymer segments might occur at the glass transition temperature, whereas the secondary relaxations or dissociation of hydrogen bonding occur above their  $T_g$ . This can be quantified according to kinetic theory, as activation energy for the dissociation at 'rubbery region' the 'storage modulus curve', using the following Equations (1) and (2).<sup>43,44</sup>

$$E' = \operatorname{ARTexp}\left(\frac{E_a}{RT}\right),$$
 (1)

$$\ln\left(\frac{E'}{T}\right) = \ln AR + \frac{E_a}{R} \left(\frac{1}{T}\right),\tag{2}$$

 $E_a$  is apparent activation energy of hydrogen bonding dissociation, A is a constant, and R is gas constant. Thus,  $E_a$  can be obtained from the slope plotting of  $ln(\frac{E'}{T})$  versus  $(\frac{1}{T})$  as described in Table 2.

Although the CNC dispersion under ABM was superior to ultrasonication, *Ea* for FC4<sub>M</sub> was less than for FC4<sub>U</sub>. Similarly, in the case of  $F_{\rm M}$  it was less than  $F_{\rm U}$  (Table 2). The surface chemistry of zirconia is chemically very complex. For example, the presence of hard Lewis acid sites leads to a very high affinity for hard Lewis bases, like the residual sulphate groups on the CNCs, and subsequent strong adsorption.<sup>32</sup> In addition to the glass transition ( $T_{\rm g}$ ), the tan  $\delta$  curve (Figure 7) also shows a temperature transition ( $T_{\alpha}$ ) of around 50°C for milled samples ( $F_{\rm M}$  and FC4<sub>M</sub>). Thus, although the presence of the zirconia-polyol ( $F_{\rm M}$ ) and/or zirconia-CNC



**FIGURE 8** Possible polymer-filler interactions in nanocomposite foam. Hashed lines represent hydrogen bonding between cellulose nanocrystals (CNCs) and rigid polyurethane foam while dashed lines represent inter (green and blue) and intra (red) hydrogen bonding in CNCs.

(FC4<sub>M</sub>) gel was relatively small, the  $T_{\alpha}$  at 50°C was postulated as partially or wholly preserved segments of zirconia-polyol and/or zirconia-CNC gel formed during the RPUF formation. Further work will be required in the future to fully elucidate the underlying mechanisms. The zirconium content in the RPUF formulations  $F_{\rm M}$  and FC4<sub>M</sub> was 64 and 61 mg/kg, respectively, or around about 0.006 wt%.

## 3.2.4 | Mechanical properties of RPUF

The compressive strength and Young's modulus of the RPUF samples are shown in Table 3. The compressive strength between any of the RPUF samples ( $F_0$ ,  $F_M$ , FC4<sub>M</sub> and FC4<sub>U</sub>) both parallel and perpendicular to foam rise showed no statistical difference in comparison to  $F_0$ . Further, there was no statistical difference in Young's modulus parallel to foam rise but a statistically significant (<5%) increase perpendicular to foam rise with both the FC4<sub>M</sub> and the FC4<sub>U</sub> sample (Table 3).

This approximate 15% increase in stiffness of the milled nanocomposite sample (FC4<sub>M</sub>) perpendicular to foam rise was postulated to arise due to CNC alignment within the cell struts. This CNC alignment in the struts is consistent with carbon nanofiber alignment in polystyrene foam parallel to foam rise<sup>45</sup> and was confirmed in our previous study by using aluminum oxide coated CNCs which allowed direct observation of the CNC alignment.<sup>11</sup> Because the cross-sectional area of the reinforcing CNCs in the perpendicular (to rise) direction is greater than that parallel (to rise) direction, the compressive strength in the perpendicular direction was greater than that in the parallel direction due to the more effective stress transfer from matrix to CNCs (filler).

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Samples	Compressive stress (MPa)	% Change (unit mass)	Young's modulus (MPa)	% Change (unit mass)			
Parallel to foam rise							
$F_0$	$0.21 \pm 0.02$	-	$5.11 \pm 0.26$	_			
$F_{\mathbf{M}}$	$0.20 \pm 0.02$	-5.25	$4.87 \pm 0.36$	-5.11			
FC4 <sub>M</sub>	$0.21 \pm 0.03$	-1.23	$4.96 \pm 0.58$	-2.24			
$FC4_U$	$0.21 \pm 0.03$	0.05	$5.45 \pm 0.93$	5.70			
Perpendicular to foam rise							
$F_0$	$0.15 \pm 0.02$	-	$3.47 \pm 0.32$	-			
$F_{\mathbf{M}}$	$0.17 \pm 0.02$	7.26	$3.76 \pm 0.32$	5.26			
FC4 <sub>M</sub>	$0.15 \pm 0.02$	-0.11	$4.01 \pm 0.43$	15.41			
FC4 <sub>U</sub>	$0.17 \pm 0.02$	7.38	$3.97 \pm 0.20$	13.28			

**TABLE 3** Mechanical properties of rigid polyurethane foam (RPUF) in two directions.



**FIGURE 9** Thermal conductivity for (A) fresh and (B) aged cellulose nanocrystal (CNC) dispersed rigid polyurethane foam.

## 3.2.5 | Thermal conductivity of RPUF

The thermal conductivity was monitored over 6 months. The initial thermal conductivity value is depended on several factors, but the most crucial factors are the selection of blowing agent and the cell size.<sup>46,47</sup>

## 3.3 | Initial thermal conductivity of RPUF

Given a constant blowing agent, the cell size and closed cell content are the usual crucial factors affecting the thermal conductivity. Figure 9A shows the thermal conductivity of RPUF samples in relation to the closed cell content. The RPUF nanocomposites containing CNCs from both the ultrasonication (FC4<sub>U</sub>) and milling (FC4<sub>M</sub>) process had similar initial thermal conductivity values which were lower than that of the control sample ( $F_0$ ).

While the lower thermal conductivity of ultrasonicated RPUF nanocomposite (FC4<sub>U</sub>) is due to the smaller cell size and the higher closed cell content<sup>10</sup> the milled nanocomposites foam (FC4<sub>M</sub>) which contained the zirconia-polyol and zirconia-CNCs gels also exhibited lower initial thermal conductivity than the control sample ( $F_0$ ) despite having similar cell sizes and a lower closed cell content. Further, the milled neat sample ( $F_M$ ) also exhibited significantly lower thermal conductivity than the ultrasonicated neat sample ( $F_U$ ) and control sample ( $F_0$ ). The overall thermal conductivity ( $\lambda$ ) of a material is a function of the  $\lambda_{radiative}$ ,  $\lambda_{solid}$ ,  $\lambda_{gas}$ , and  $\lambda_{convection}$ .

## $\lambda_{\text{total}} = \lambda_{\text{radiative}} + \lambda_{\text{solid}} + \lambda_{\text{gas}} + \lambda_{\text{convection}}.$

In the current study both the  $\lambda_{convection}$  and  $\lambda_{radiative}$  can be ignored as the source of this difference due to the similar density and small and consistent cell size in the RPUF samples. Similarly  $\lambda_{gas}$  can be dismissed as the blowing agent composition is constant across all samples. While the significant increase of closed cell content up to 99% of neat milled sample ( $F_{\rm M}$ ) can be attributed to improved thermal insulation (similar to the FC4<sub>U</sub>), it does not explain the lower thermal conductivity of the milled sample containing 0.4 wt% CNCs (FC4<sub>M</sub>) which has a lower closed cell content (Figure 9A).

**TABLE 4** Dimensional stability of rigid polyurethane foam at  $-73 \pm 3^{\circ}$ C and  $+70 \pm 2^{\circ}$ C.

Samples	Duration (days)	% Linear change at $-73 \pm 3^{\circ}C$			% Linear change at +70 $\pm$ 2°C		
$F_M$	1	$-0.01\pm0.01$	$-0.02\pm0.00$	$-0.30 \pm 0.11$	$0.04\pm0.00$	$0.03\pm0.00$	$0.18\pm0.10$
	7	$-0.04 \pm 0.02$	$-0.04 \pm 0.00$	$-0.92\pm0.10$	$0.07\pm0.02$	$0.08\pm0.10$	$0.30\pm0.00$
	14	$-0.05\pm0.00$	$-0.05\pm0.00$	$-1.21\pm0.02$	$0.09\pm0.02$	$0.10\pm0.00$	$0.48 \pm 0.06$
FC4 <sub>M</sub>	1	$-0.02\pm0.01$	$-0.01\pm0.00$	$-0.32 \pm 0.13$	$0.05\pm0.02$	$0.02\pm0.01$	$0.23 \pm 0.05$
	7	$-0.04 \pm 0.02$	$-0.03 \pm 0.00$	$-0.86 \pm 0.14$	$0.06\pm0.02$	$0.10\pm0.01$	$0.39\pm0.12$
	14	$-0.05\pm0.01$	$-0.06 \pm 0.02$	$-0.52 \pm 0.15$	$0.09\pm0.01$	$0.12\pm0.00$	$0.48\pm0.09$

The effective thermal conductivity of a composite is influenced by the interfacial thermal resistance between constituents. As the heat carriers (electron or phonon) flow through an interface between two constituents, they may undergo scattering, leading to a temperature drop between the interfaces.<sup>48</sup> Localized atomic disorder or crystal imperfections may also enhance the phonon scattering.<sup>48</sup> Hence, the addition of small (nano-sized) particles, even those having a higher solid conductivity than the polyurethane, and at an addition level below the percolation threshold can decrease the effective thermal conductivity (increase the thermal resistance) of the composite due to the interfacial thermal resistance effect by the formation of a phonon barrier.<sup>49–51</sup>

It was also postulated that possibly the presence of nanoscale soft domains as supported by the  $T_{\alpha}$  in DMA (Figure 7), enhanced the phonon effect and the interfacial thermal resistance of the RPUF polymer matrix ( $\lambda_{SOLID}$ ). The reduction of thermal conductivity because of increased interfacial thermal resistance between two different constituents (between nanofiller and PU matrix or between nanofillers) was also in agreement with the observations of a previous study on RPUF containing CNCs in mixed polyol systems (PKObP and Voranol<sup>TM</sup> 446).<sup>9</sup>

## 3.4 | Aged thermal conductivity of RPUF

The data for long-term retention of thermal conductivity is summarized in Figure 9B. As expected, the ultrasonicated sample ( $F_U$ ) had negligible difference with respect to the control sample ( $F_0$ ). The ultrasonicated sample (FC4<sub>U</sub>) also had similar rates of aging to the control sample ( $F_0$ ) which is not surprising considering the low loading of CNCs and the fact that the CNCs are more likely to go into the struts rather than the windows. This is similar to a study by Minogue<sup>52</sup> who reported that graphite gathered exclusively in the foam struts.

In contrast, both milled samples ( $F_M$  and FC4<sub>M</sub>) exhibited a lower rate of aging compared to the control

 $(F_0)$ . This was hypothesized to arise due to the presence of a zirconia-polyol  $(F_M)$  and/or zirconia-CNC (FC4<sub>M</sub>) gel. Perhaps, the zirconia-polyol and/or zirconia-CNC gel was partially or wholly preserved during the formation of the RPUF in the cell windows as well as the struts because the gas diffusion occurs through the cell windows rather than the struts. The fact that the rate of aging for milled samples ( $F_M$  and FC4<sub>M</sub>) was similar, negated the idea that the superior dispersion of the CNCs by ABM decreased permeability due to increased tortuosity.

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## 3.4.1 | Dimensional stability of RPUF

All RPUF specimens (Table 4) exhibited acceptable dimensional stability after 14 days exposure at both  $-73 \pm 3^{\circ}$ C and  $+70 \pm 2^{\circ}$ C according to BS4370: Part1: 1988 which requires linear change of less than 3% when tested at 70°C and 1% when tested at  $-15^{\circ}$ C for 24 h.<sup>53</sup> Further, the compressive strength of milled RPUF samples in this study exceeds the recommended minimum value of 100 kPa to achieve excellent dimensional stability.<sup>54</sup>

## 4 | CONCLUSION

CNCs were incorporated into RPUF by dispersion into polyol using the ABM process. The initial thermal conductivity of the milled samples, with and without CNCs, were lower than the control foam. While the significantly improved thermal conductivity can be attributed to the increase of closed cell content up to 99% of the neat milled sample  $(F_{\rm M})$ , the milled nanocomposite foam (FC4<sub>M</sub>) also exhibited a lower initial thermal conductivity than the control sample  $(F_0)$ , despite having a similar cell size and lower closed cell content. It was postulated that the improved thermal conductivity was due to the increased presence of soft zirconium-polyol-CNC domains in the polyurethane matrix, as well as the possible interfacial thermal resistance between the nanofillers (CNC-CNC) and the matrix. Further, in terms of mechanical properties, the compressive strength between

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milled RPUF samples with and without CNCs showed no statistical difference, but the stiffness perpendicular to foam rise of milled samples containing 0.4 wt% CNCs significantly improved.

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## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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## REFERENCES

- 1. Eichhorn S, Dufresne A, Aranguren M, et al. Review: current international research into cellulose nanofibres and nanocomposites. J Mater Sci. 2010;45:1-33. doi:10.1007/s10853-009-3874-0
- 2. Septevani AA, Rifathin A, Sari AA, Sampora Y, Ariani G, Sudiyarmanto DS. Oil palm empty fruit bunch-based nanocellulose as a super-adsorbent for water remediation. Carbohydr Polvm. 2020;229:115433. doi:10.1016/j.carbpol.2019.115433
- 3. Septevani AA, Burhani D, Sampora Y. Nanocellulose in electronics and electrical industry. Nanocellulose materials: fabrication and industrial applications. Elsevier. 2022:217-246. doi:10. 1016/B978-0-12-823963-6.00010-7
- 4. Ouled Ltaief A, Ghorbel N, Benhamou K, Arous M, Kaddami H, Kallel A. Impact of cellulose nanocrystals reinforcement on molecular dynamics and dielectric properties of PCL-based polyurethane. Polym Compos. 2021;42:2737-2750. doi:10.1002/pc.26009
- 5. Ganapathy V, Muthukumaran G, Sudhagar PE, et al. Mechanical properties of cellulose-based multiscale composites: a review. Polym Compos. 2023;44(2):734-756. doi:10.1002/pc.27175
- 6. Li Y, Ragauskas AJ. Ethanol organosolv lignin-based rigid polyurethane foam reinforced with cellulose nanowhiskers. RSC Adv. 2012;2:3347. doi:10.1039/C2RA00646D
- 7. Li Y, Ren H, Ragauskas AJ. Rigid polyurethane foam reinforced with cellulose whiskers: synthesis and characterization. Nano Lett. 2010;2:89-94. doi:10.1007/BF03353624
- 8. Li S, Li C, Li C, et al. Fabrication of nano-crystalline cellulose with phosphoric acid and its full application in a modified

polyurethane foam. Polym Degrad Stab. 1940;2013:98-1944. doi: 10.1016/j.polymdegradstab.2013.06.017

- 9. Septevani AA, Evans DAC, Martin DJ, Annamalai PK. Hybrid polyether-palm oil polyester polyol based rigid polyurethane foam reinforced with cellulose nanocrystal. Ind Crop Prod. 2018;112:112-388. doi:10.1016/j.indcrop.2017.12.032
- 10. Septevani AA, Evans DAC, Annamalai PK, Martin DJ. The use of cellulose nanocrystals to enhance the thermal insulation properties and sustainability of rigid polyurethane foam. Ind Crop Prod. 2017;107:107-121. doi:10.1016/j.indcrop.2017. 05.039
- 11. Septevani A, Evans D, Hosseinmardi A, et al. Atomic laver deposition of metal oxide on nanocellulose for enabling microscopic characterization of polymer nanocomposites. Small. 2018;14:1803439. doi:10.1002/smll.201803439
- 12. Członka S, Kairytė A, Miedzińska K, Strakowska A. Polyurethane composites reinforced with walnut shell filler treated with perlite, montmorillonite and hallovsite. Int J Mol Sci. 2021;22:14. doi:10.3390/ijms22147304
- 13. Saha MC, Kabir ME, Jeelani S. Effect of nanoparticles on mode-I fracture toughness of polyurethane foams. Polym Compos. 2009;30:1058-1064. doi:10.1002/pc.20656
- 14. Saha MC, Kabir ME, Jeelani S, Enhancement in thermal and mechanical properties of polyurethane foam infused with nanoparticles. Mater Sci Eng A. 2008;479:213-222. doi:10.1016/ j.msea.2007.06.060
- 15. Luo F, Wu K, Li D, et al. A novel intumescent flame retardant with nanocellulose as charring agent and its flame retardancy in polyurethane foam. Polym Compos. 2017;38:2762-2770. doi: 10.1002/pc.23874
- 16. Kupka V, Zhou Q, Ansari F, et al. Well-dispersed polyurethane/cellulose nanocrystal nanocomposites synthesized by a solvent-free procedure in bulk. Polym Compos. 2019; 40:E456-E465. doi:10.1002/pc.24748
- 17. Lorenzetti A, Hrelja D, Besco S, Roso M, Modesti M. Improvement of nanoclays dispersion through microwave processing in polyurethane rigid nanocomposite foams. J Appl Polym Sci. 2010;115:3667-3674. doi:10.1002/app.31449
- 18. Semenzato S, Lorenzetti A, Modesti M, et al. A novel phosphorus polvurethane FOAM/montmorillonite nanocomposite: preparation, characterization and thermal behaviour. Appl Clay Sci. 2009;44:35-42. doi:10.1016/j.clay.2009.01.003
- 19. Inkyo M, Tahara T, Iwaki T, Iskandar F, Hogan CJ, Okuyama K. Experimental investigation of nanoparticle dispersion by beads milling with centrifugal bead separation. J Colloid Interface Sci. 2006;304:535-540. doi:10.1016/j.jcis.2006. 09.021
- 20. Zhang DL. Processing of advanced materials using high-energy mechanical milling. Prog Mater Sci. 2004;49:537-560. doi:10. 1016/S0079-6425(03)00034-3
- 21. Kopp AA, Bergmann Carlos P, Amorim BF. Novel Synthesis and Characterization of Nanostructured Materials. Springer Berlin Heidelberg; 2013. doi:10.1007/978-3-642-41275-2
- 22. Ling Z, Wang T, Makarem M, et al. Effects of ball milling on the structure of cotton cellulose. Cellulose. 2019;26:305-328. doi:10.1007/s10570-018-02230-x
- 23. Stanzione M, Oliviero M, Cocca M, et al. Tuning of polyurethane foam mechanical and thermal properties using ballmilled cellulose. Carbohydr Polym. 2020;231:231. doi:10.1016/j. carbpol.2019.115772

- Zhang L, Tsuzuki T, Wang X. Preparation of cellulose nanofiber from softwood pulp by ball milling. *Cellulose*. 2015;22:1729-1741. doi:10.1007/s10570-015-0582-6
- Mohd Amin KN, Annamalai PK, Morrow IC, Martin D. Production of cellulose nanocrystals via a scalable mechanical method. *RSC Adv.* 2015;5:57133-57140. doi:10.1039/C5RA06862B
- Amin KNM, Amiralian N, Annamalai PK, Edwards G, Chaleat C, Martin DJ. Scalable processing of thermoplastic polyurethane nanocomposites toughened with nanocellulose. *Chem Eng J.* 2016;302:406-416. doi:10.1016/J.CEJ.2016.05.067
- Annamalai PK, Dagnon KL, Monemian S, Foster EJ, Rowan SJ, Weder C. Water-responsive mechanically adaptive nanocomposites based on styrene-butadiene rubber and cellulose nanocrystals-processing matters. ACS Appl Mater Interfaces. 2014;6:967-976. doi:10.1021/am404382x
- Harikrishnan G, Lindsay CI, Arunagirinathan MA, Macosko CW. Probing nanodispersions of clays for reactive foaming. ACS Appl Mater Interfaces. 1913;2009:1-1918. doi:10. 1021/am9003123
- Escobar-Chávez JJ, López-Cervantes M, Naïk A, Kalia YN, Quintanar-Guerrero D, Ganem-Quintanar A. Applications of thermo-reversible pluronic F-127 gels in pharmaceutical formulations. *J Pharm Pharm Sci.* 2006;9:339.
- Shukla S, Seal S, Vij R, Bandyopadhyay S. Effect of HPC and water concentration on the evolution of size, aggregation and crystallization of sol-gel nano zirconia. *J Nanopart Res.* 2002;4:553. doi:10.1023/A:1022886518620
- 31. Delong S. Starch crosslinking for cellulose fiber modification and starch nanoparticle formation. Ph.D Thesis, Georgia Institute of Technology 2011.
- Glavanovich MH, Carr PW. Easily regenerable affinity chromatographic zirconia-based support with concanavalin a as a model ligand. *Anal Chem.* 1994;66:2584-2589. doi:10.1021/ac00087a025
- Mulinari DR, Camargo LMD, Cioffi MOH. Study of the Mechanical properties of cellulose cellulose/ZrO<sub>2</sub>.nH<sub>2</sub>O nanocomposites, 19th International Congress of Mechanical Engineering. 2007.
- Harikrishnan G, Singh SN, Kiesel E, Macosko CW. Nanodispersions of carbon nanofiber for polyurethane foaming. *Polymer*. 2010;51:3349-3353. doi:10.1016/j.polymer.2010.05.017
- Solomon MJ, Almusallam AS, Seefeldt KF, Somwangthanaroj A, Varadan P. Rheology of polypropylene/clay hybrid materials. *Macromolecules*. 1864;2001:34-1872. doi:10.1021/ma001122e
- Wik VM, Aranguren MI, Mosiewicki MA. Castor oil-based polyurethanes containing cellulose nanocrystals. *Polym Eng Sci.* 2011;51(7):1389-1396. doi:10.1002/pen.21939
- Smith A, Shay J, Spontak R, et al. High-energy mechanical milling of poly(methyl methacrylate), polyisoprene and poly(ethylene-alt-propylene). *Polymer*. 2000;41:6271-6283. doi: 10.1016/S0032-3861(99)00830-7
- Siqueira G, Bras J, Dufresne A. New process of chemical grafting of cellulose nanoparticles with a long chain isocyanate. *Langmuir*. 2010;26:402-411. doi:10.1021/la9028595
- Dong XM, Revol J-F, Gray DG. Effect of microcrystallite preparation conditions on the formation of colloid crystals of cellulose. *Cellulose*. 1998;5:19. doi:10.1023/A:1009260511939
- Abitbol T, Palermo A, Moran-Mirabal JM, Cranston ED. Fluorescent labeling and characterization of cellulose nanocrystals with varying charge contents. *Biomacromolecules*. 2013;14: 3278-3284. doi:10.1021/bm400879x

 Eyley S, Thielemans W. Surface modification of cellulose nanocrystals. *Nanoscale*. 2014;6:7764-7779. doi:10.1039/C4NR01756K

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8869

- 42. Wu L, Gemert JV, Camargo RE. *Rheology Study in Polyurethane Rigid Foams*. Huntsman Corporation; 2008.
- Pan H, Chen D. Preparation and characterization of waterborne polyurethane/attapulgite nanocomposites. *Eur Polym J*. 2007;43:3766-3772. doi:10.1016/j.eurpolymj.2007.06.031
- Wang Y, Tian H, Zhang L. Role of starch nanocrystals and cellulose whiskers in synergistic reinforcement of waterborne polyurethane. *Carbohydr Polym.* 2010;80:665-671. doi:10.1016/j. carbpol.2009.10.043
- Shen J, Han X, Lee LJ. Nanoscaled reinforcement of polystyrene foams using carbon nanofibers. *J Cell Plast.* 2006;42:105-126. doi:10.1177/0021955X06060947
- Modesti M, Lorenzetti A, Besco S. Influence of nanofillers on thermal insulating properties of polyurethane nanocomposites foams. *Polym Eng Sci.* 2007;47:1351-1358. doi:10.1002/PEN.20819
- 47. Septevani AA, Evans DAC, Chaleat C, Martin DJ, Annamalai PK. A systematic study substituting polyether polyol with palm kernel oil based polyester polyol in rigid polyurethane foam. *Ind Crop Prod.* 2015;66:16-66. doi:10.1016/j.indcrop.2014.11.053
- Pietrak K, Wi'sniewski TSW. A review of models for effective thermal conductivity of composite materials. J Power Tech. 2015;95:14-24.
- Losego MD, Grady ME, Sottos NR, Cahill DG, Braun PV. Effects of chemical bonding on heat transport across interfaces. *Nat Mater*. 2012;11:502-506. doi:10.1038/nmat3303
- Pernot G, Stoffel M, Savic I, et al. Precise control of thermal conductivity at the nanoscale through individual phonon-scattering barriers. *Nat Mater*. 2010;9:491-495. doi:10.1038/nmat2752
- Yu J-K, Mitrovic S, Tham D, Varghese J, Heath JR. Reduction of thermal conductivity in phononic nanomesh structures. *Nat Nanotechnol.* 2010;5:718-721. doi:10.1038/nnano.2010.149
- 52. Minogue E. An in-Situ Study of the Nucleation Process of Polyurethane Rigid Foam Formation. PhD thesis, Dublin City University 2000.
- Badri KH, Ahmad SH, Zakaria S. Production of a highfunctionality RBD palm kernel oil-based polyester polyol. *J Appl Polym Sci.* 2001;81:384-389. doi:10.1002/app.1449
- 54. Federation of European Polyurethane Foam Associations. Thermal Insulation Materials Made of Rigid Polyurethane Foam (PUR/PIR). BING; 2006.

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