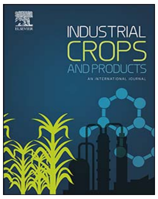
Industrial Crops & Products 107 (2017) 114–121

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop



Research Paper

The use of cellulose nanocrystals to enhance the thermal insulation properties and sustainability of rigid polyurethane foam

Athanasia A. Septevani[a,b], David A.C. Evans[a], Pratheep K. Annamalai[a,*], Darren J. Martin[a,*]

[a] *Australian Institute Bioengineering and Nanotechnology (AIBN), Corner College and Cooper Rd (Bldg 75), The University of Queensland, Brisbane Qld, 4072, Australia*
[b] *Research Center for Chemistry, Indonesian Institute of Sciences, Serpong, Tangerang Selatan, 15314, Indonesia*

ARTICLE INFO

Keyword:
Cellulose nanocrystals
Nanocomposites
Rigid polyurethane foam
Taguchi method
Thermal conductivity

ABSTRACT

The enhancement of thermal insulation performance of rigid polyurethane foam (RPUF) achieved through a cost-effective and sustainable approach still remains an ongoing interest in both industry and academia. This study reports an efficient approach of reducing thermal conductivity and enhancing mechanical properties of RPUF without affecting the density, by incorporating a very low fraction of cellulose nanocrystal (CNC) through an optimised solvent-free ultrasonication method. A 5% reduction in thermal conductivity of RPUF afforded by the addition of 0.4 wt.% of CNC without any further surface chemical modification is almost double the effect of any other unmodified nanoparticulate nucleating agent reported so far. This reduction in thermal conductivity is attributed to the better compatibility of the CNC with the polyol and the foam to allow maximum nucleation and therefore the lowest initial thermal conductivity. Further, the Young's modulus of an optimised nanocomposite foam was also enhanced to the control RPUF perpendicular to foam rise.

1. Introduction

The term "sustainable" is often simplistically associated with a material being of a natural origin and preferably a bio-renewable natural source. However, in regards to building insulation, according to the Building Research Establishment (BRE) (Swabey, 2010), which studied the life cycle analysis of various types of building insulation at the total building level, the actual composition (mineral, petrochemical or renewable) or physical nature (fibrous or cellular) of the insulation had little effect on the life cycle analysis. The most influential factor to improve the sustainability of building insulation was to reduce the thermal conductivity of the product itself. Hence the intense ongoing global efforts to reduce the thermal conductivity of RPUF insulation boards, for example, as it represents one of the most robust strategies to reduce the total building life cycle cost (Evans, 2012).

The thermal insulation performance of RPUF can be improved by reducing the initial thermal conductivity and/or the rate of ageing (as characterised by an increase in thermal conductivity with the time). Given a constant blowing agent and RPUF density, both of these goals can be achieved by either reducing the average cell size (Jarfelt and Ramnäs, 2006) which reduces the radiation heat transfer, or inclusion of a filler which blocks the radiation heat transfer and/or acts as a diffusion barrier. Thus a common strategy is to look at fillers to act as a nucleating agent to give a smaller cell size (Harikrishnan et al., 2010; Kim et al., 2007; Seo et al., 2006), block the transmission of infrared radiation (Lorenzetti et al., 2016) or provide a diffusion barrier (Harikrishnan et al., 2009; Lorenzetti et al., 2016).

The use of fillers, such as carbon black, talc or calcium carbonate as nucleating agents in RPUF (Szycher, 1999) is well known, however the use of such micro-size fillers can cause severe disruptions to the cellular structure (Kuranska and Prociak, 2012; Xue et al., 2014). Thus the use of nanofillers as nucleating agents has been recognised as a promising strategy to decrease the thermal conductivity of RPUF (Harikrishnan et al., 2010; Kim et al., 2007; Seo et al., 2006). Their effectiveness as a nucleating agent, however, is dependent on the host polymer compatibility (Massalha et al., 2015; Modesti et al., 2007), method of incorporation (Kim et al., 2007), quality of dispersion (Harikrishnan et al., 2010), and loading of nanoparticles (Siqueira et al., 2010) in the RPUF precursors. Hence different types of nanoparticles have different optimal loadings which result in an optimal dispersion of the nanofiller and nucleation, but the avoidance of re-agglomeration of the nanofiller and thus the associated disruption of the cellular structure in terms of more open (broken) cell content.

Recently, rod-like cellulose nanocrystals (CNC) have attracted a tremendous level of attention as potential reinforcing and functional fillers due to the unprecedented specific mechanical properties of individual nanocrystals, chemically tuneable surface functionality, ease of chemical surface modification, low density, and biological abun-

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[*] Corresponding authors.
E-mail addresses: p.annamalai@uq.edu.au (P.K. Annamalai), darren.martin@uq.edu.au (D.J. Martin).

http://dx.doi.org/10.1016/j.indcrop.2017.05.039
Received 6 December 2016; Received in revised form 6 May 2017; Accepted 21 May 2017

dance from renewable and sustainable sources (Eichhorn, 2011; Habibi et al., 2010). As such CNC has been shown to provide significant improvement in the performance of non-cellular polyurethane nanocomposites (Benhamou et al., 2015; Cordero et al., 2015; Kong et al., 2016; Lin et al., 2013; Wang et al., 2010). The choice of CNC is also interesting from the point of view that it has the potential for covalent tethering (cross linking) with the polyurethane foam matrix and has also been reported to have effective barrier properties (Aloui et al., 2016; Fortunati et al., 2012; Saxena et al., 2010). Up until now, studies employing CNC as reinforcing nanofillers have demonstrated improvements in RPUF in terms of mechanical properties (Li and Ragauskas, 2012; Li et al., 2011; Ragauskas et al., 2010), but only one study has reported a reduction in thermal conductivity. Li et al. (2013) reported that the use of a complex mixture of CNC, hydrolysed oligosaccharides and ammonium phosphate in RPUF resulted in a significant reduction in the thermal conductivity and compressive strength at high CNC loading. However, the influence of CNC on compressive strength was not differentiated from the effect of density.

The incorporation of nanofillers into RPUF precursors can be accomplished using solvent-assisted dispersion, however, due to increased environmental awareness, solvent-free approaches are clearly preferable. While, the incorporation of nanofillers into RPUF precursor can be aided by using ultrasonication (Kabir et al., 2007; Modesti et al., 2007; Nikkhah et al., 2015; Saha et al., 2008; Shi et al., 2014), high-speed homogenisation (Svagan et al., 2010), or microwave irradiation (Lorenzetti et al., 2010; Semenzato et al., 2009), ultrasonication is usually the method of choice as it is particularly effective at re-dispersing CNC, which agglomerate on freeze-drying, by disrupting Coulomb and van der Waal's forces between the particles leading to more homogeneous dispersions.

Contemporary reports (Kabir et al., 2007; Modesti et al., 2007; Saha et al., 2008; Shi et al., 2014) utilising ultrasonication to disperse various nanomaterials in RPUF precursors, do not address the influence of the various processing conditions (loadings, frequency, amplitude and time) on the mechanical and thermal insulation performance of the nanocomposite foam. Hence in this study, we aimed to systematically enhance the thermal insulation without any significant change in density or compromise in the mechanical properties of RPUF using a sustainable nanomaterial CNC without any further surface chemical modifications but by optimising a solvent-free ultrasonication process of CNC incorporation (using the Taguchi methodology). We also report the influence of CNC on the durability (in terms of thermal insulation and dimension stability) of nanocomposite RPUF.

2. Experimental

2.1. Materials

CNC was obtained as a fluffy dry powder from cotton filter paper, (Advantec) via a typical acid hydrolysis protocol (Annamalai et al., 2014) using sulfuric acid (Merck), which involves pulping in deionised water, digestion in acidic media, centrifugation, dialysis, ultrasonication and freeze-drying (see Section 1 in Appendix). The CNC were produced with a yield of up to 75% and they were rod-shaped with an average width, length and aspect ratio of 16 ± 5 nm, 169 ± 49 nm and 11 ± 3, respectively (Fig. 1).

A sucrose/glycerine initiated polyether polyol (Voranol®446, Dow Chemical Company) obtained from Applied Polymers was tested for hydroxyl value (456 mgKOH/g) and water content (0.2 wt.%) prior to use in the laboratory. Polymeric methylene diphenyl diisocyanate (pMDI) (See Fig A.1 in Appendix) from Applied Polymers Australia, dimethylcyclohexylamine (DMCHA) catalyst from Sigma Aldrich, surfactant (Tegostab®8460) from Evonik Industries, a hydrofluorocarbon based physical blowing agent (HFC M1, a proprietary blend of HFC245 fc and HFC365mfc) from A-Gas, were used, as received.

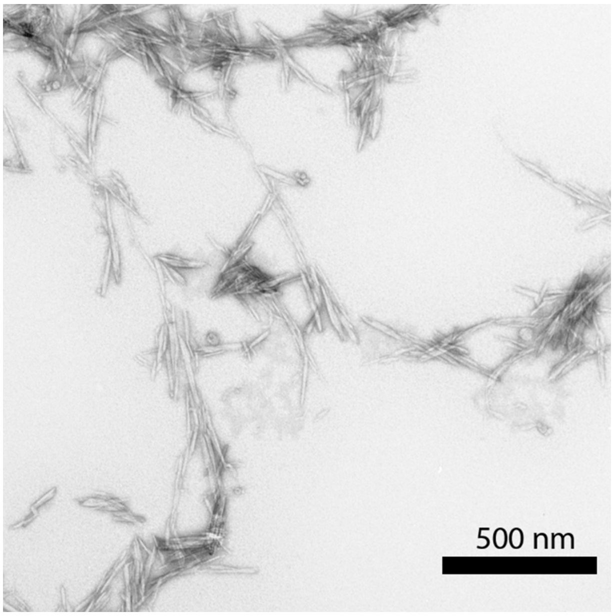

Fig. 1. Transmission electron microscopic image of cellulose nanocrystals obtained from cotton via acid hydrolysis.

2.2. Dispersion of cellulose nanocrystals into polyol

The dry CNC powder was dispersed in Voranol®446 using ultrasonication. The mixture was subjected to a high intensity ultrasonic treatment at 20 kHz with a standard 1/2" diameter probe, (Q500 model, QSonica) with three process parameters; CNC loading, treatment time, and the amplitude of ultrasonication optimised with a Taguchi experimental design using a standard L9 orthogonal array (See Fig. A.2, Table A.1 and Table A.2 in Appendix). The polyol/CNC dispersions with 0.2, 0.4 and 0.8 wt% (in the final composition) processed under the optimised ultrasonication conditions for 40 min at 80% amplitude were labelled as $VC2_U$, $VC4_U$ and $VC8_U$, respectively. In order to understand the influence of ultrasonication, control foams (F_0 and F_U) were also made from the as received Voranol®446 polyol (V_0), and the polyol (V_U) obtained after ultrasonication under same conditions (for 40 min and at 80% amplitude).

2.3. Preparation of rigid polyurethane foam

The preparation of RPUF involves two steps. Firstly the homogeneous polyol blend (Part B) was prepared by mixing neat polyol or the polyol-cellulose suspensions, with catalyst, surfactant, and blowing agent(s) (Table 1) at a speed about 1500 rpm for 20 min using an overhead stirrer (HP2071F hammer drill, Makita). Secondly, the pMDI (Part A) was mixed with Part B at an index of 110, at a speed about 2900 rpm for 20 min using the same overhead stirrer. This mixed formulation was used for following kinetics (cup test) or for moulding. The mixed formulation (Part A and Part B) was immediately poured into a preheated (50 °C) aluminium mould (300 mm x 300 mm x 100 mm), which was then sealed tightly. To reduce the influence of density on the mechanical properties, all the RPUFs were moulded at a density of 41 ± 1 kg/m^3. After 24 h, the foam was de-moulded and allowed to post-cure for one week prior to testing (see Fig. A.3 . in Appendix). Aside from the control RPUF formulation (F_0) without ultrasonication treatment as reported earlier (Septevani et al., 2015), four different formulations (F_U, $FC2_U$, $FC4_U$ and $FC8_U$) were prepared with varying levels of CNC content by using ultrasonication (Table 1).