MALAYSIAN JOURNAL OF ANALYTICAL SCIENCES
Published by The Malaysian Analytical Sciences Society
ISSN
1394 - 2506

CELLULOSE NANOCRYSTALS WITH ENHANCED THERMAL STABILITY REINFORCED THERMOPLASTIC POLYURETHANE

(Nanokristal Selulosa Dengan Ketahanan Haba Yang Tinggi Berasaskan Poliuretina Termoplastik)

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Received: 28 November 2016; Accepted: 5 February 2017

Abstract

Melt compounding processing approach for incorporating cellulose nanocrystals (CNC) into thermoplastic polyurethane (TPU) has not well been explored. This is primarily due to the poor thermal stability and dispersibility of CNCs. As they are typically obtained from sulphuric acid hydrolysis, they give rise to degradation and discolouration of the extruded nanocomposites. The investigation of this research demonstrates sulphuric acid hydrolysis (CNC-S), phosphoric acid hydrolysis (CNC-P) and a novel non-hydrolytic high energy bead milling method (CNC-MC) into a polyether based thermoplastic polyurethane via melt compounding using twin screw extruder. The TPU film incorporated with CNC-S obviously shows the sign of CNC degradation where TPU film was changed to brown colour. The tensile strength of TPU reinforced with CNC-S, CNC-P and CNC-MC shows 18%, 16% and 14% of improvement at CNC loading of 0 to 1 wt.% upon host polymer. CNCs isolated via mild acid hydrolysis and mechanical milling methods, can be easily processed via large scale melt-processing techniques for reinforcing thermoplastic polyurethane without affecting their physical appearance and elastic properties.

Keywords: cellulose nanocrystals, thermoplastic polyurethane, nanocomposites

Abstrak

Kajian mengenai penggunaan nanokristal selulosa (CNC) di dalam termoplastik poliuritena (TPU) amat jarang diterokai. Ini adalah kerana CNC mempunyai ketahanan haba yang rendah. CNC yang dihasilkan melalui proses hidrolisis asid sulfurik mudah terdegradasi apabila digabungkan dengan polimer yang melalui proses meramu pencairan umumnya menggunakan suhu pemprosesan yang tinggi. Kajian ini menggunakan CNC yang dihasilkan daripada hidrolisis asid sulfurik (CNC-S), asid fosforik (CNC-P) dan kaedah novel pengisaran manik (CNC-MC) ke dalam poliuretana termoplastik berasaskan berasas polieter melalui proses meramu pencairan. Filem TPU yang digabungkan dengan CNC-S jelas menunjukkan tanda degradasi CNC apabila filem TPU bertukar warna kepada coklat. Kekuatan tegangan TPU diperkukuhkan dengan CNC-S, CNC-P dan CNC-MC menunjukkan 18%, 16% dan 14% peningkatan pada muatan CNC 0-1 wt.% di dalam komposit. CNC yang dihasilkan melalui hidrolisis asid berkekuatan sederhana dan melalui kaedah mekanikal boleh diproses melalui teknik meramu pencairan yang berskala besar dan mampu meningkatkan kekuatan poliuretana termoplastik tanpa menjejaskan penampilan fizikal mereka dan sifat elastiknya.

Kata kunci: nanokristal selulosa, poliuritena termoplastik, nanokomposit

Introduction

Thermoplastic polyurethane (TPU) is a versatile material which has both thermoplastic and elastomeric properties with unique attributes, for instance, melt-process ability, recyclability and easy to mould [1]. One of the methods to improve the properties of TPU is by using reinforcing filler. Recently nanoscale fillers such as clay, carbon nanotubes, metal and metal oxides have been demonstrated to remarkably enhance the thermal, physical and mechanical properties of TPU within very low loading [2-4]. Recently cellulose nanocrystal (CNC) has gained high attention as reinforcing filler due to its key attributes such as very high specific mechanical properties of individual nanocrystals and renewability. Moreover, CNC reinforced polymer nanocomposites can retain the transparency of the polymer matrix [5]. With polyurethanes and different types of nanocellulose particles, remarkable reinforcements have been demonstrated. Specifically at a low volume fraction of CNC, TPU nanocomposites has demonstrated an extraordinary increase in tensile strength without compromising the tensile strain and stiffness of the material [6]. However, their processing involves solvent based methods. Conventional method like solvent casting poses a challenge in terms of production speed and environmental issue due to the high solvent usage [7]. Thus, for TPU industrial scale production, classical melt-processing methods such as compounding, reactive extrusion and moulding are preferred. Melt compounding method which has been explored with other thermoplastics whose fusion temperatures are below 170°C such as poly lactic acid [8] and polyethylene [9], is however limited due to the poor thermal stability, dispersibility of CNCs and degradation in optical transparency of the host for most of the thermoplastics whose processing temperatures are above 170 °C.

Hence, this work focuses on the processing TPU nanocomposites reinforced with three types of CNCs which were obtained via sulphuric acid hydrolysis (CNC-S), and phosphoric acid hydrolysis (CNC-P) and acid-free high energy bead milling (CNC-MC), via a classical melt compounding method using an intermediate scale twin screw extruder. Their processing and properties enhancement are compared with the nanocomposites processed by solvent casting method.

Materials and Methods

Materials

Cellulose source used was Whatman filter paper (Advantec) and commercial microcrystalline cellulose (Avicel PH-101). Sulphuric acid (H_2SO_4, 98%) and ortho-phosphoric acid (H_3PO_4, 85%) from Merck Australia was used in for acid the hydrolysis process. The TPU grade selected, Texin 990, was purchased from Bayer Materials Science. This grade was specifically selected because it represents one of the highest selling aromatic polyether grades and is employed in a multitude of applications. Dimethylformamide (DMF) was purchased from Merck and used for solvent casting.

Isolation of cellulose nanocrystals: Acid hydrolysis method

The isolation process using sulphuric acid was adapted from Capadona et al. [10] with some modifications. The solid to liquid ratio for this isolation process was 1:75. Filter paper was blended with deionised water. The sulphuric acid was added slowly under vigorous mechanical stirring to the cooled filter paper until the final solution reached an acid concentration of 32%. Since the acid hydrolysis process is exothermic, while adding acid, ice bath is used to keep the temperature below 20 °C. After the acid addition is complete the reaction is set at 50 °C or higher for a stipulated time. The mixture was then heated to 50 °C for 3.5 hours. The cellulose suspension was cooled to room temperature and was subsequently centrifuged four to five times at 4750 rpm until it became turbid. The cellulose suspension was then dialyses against deionised water until the suspension reached the neutral state. Then the cellulose suspension was ultrasonicated using high intensity ultrasonication (QSonica ultrasonicator) for 30 minutes. Finally, the cellulose suspension was lyophilised using liquid nitrogen and was vacuum freeze dried. The CNC obtained was denoted as CNC-S. Meanwhile, acid hydrolysis of cellulose using H_3PO_4 was adapted from Camarero et al. [11], with slight modification, and generally the procedure is very similar to H_2SO_4 hydrolysis. This CNC is denoted as CNC-P.

High energy bead milling method

Isolation of CNC via high energy bead milling (HEBM) was carried out based on the work of Amin et al. [12]. The cellulose source used in this process was microcrystalline cellulose (MCC). Various concentrations of MCC were dispersed in deionised water overnight. Then the dispersion was milled using a laboratory agitator bead mill

(Labstar, Netzsch, Germany). Using various milling times, 0.4 mm of zirconium beads were used to mill the cellulose dispersion at 1000 rpm in a batch process mode. Finally, the resulting suspensions obtained were freeze dried.

Processing of nanocomposites

In these nanocomposites, CNC loading levels were 0.5, 1, and 5 wt.% respectively. In melt compounding method, initially CNC and PU resin were mixed physically. TPU nanocomposites reinforced with three types of CNCs were processed by melt-compounding using a ThermoHaake PolyLab twin-screw extruder. The extrudates were pelletised and compression moulded.

In solvent casting process, TPU resin and CNC were individually dissolved in DMF. 0.5 wt.% of CNC in TPU was prepared by mixing the desired amounts of CNC and TPU solution in DMF. The mixture was stirred vigorously for 1 hour at room temperature. The mixture was then sonicated for 2 minutes at 20 kHz. Subsequently, further stirring was undertaken after the sonication process and immediately cast onto a Teflon petri dish. The films were dried under nitrogen purged for 24 hours and subsequently annealed in a vacuum condition at 80 °C for 12 hours. TPU nanocomposites prepared by solvent casting were denoted as SC-TPU/CNC *X* where *X* represents the volume fraction of CNC. TPU nanocomposites processed via the melt compounding process were denoted as MC-TPU/CNC *X*.

Characterisation and mechanical testing

The morphology and thermal stability of CNCs were characterised by transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). TGA measurements were carried out on a Mettler Toledo DSC/TGA Star^e system using aluminum crucible standard 40 µL. The samples were heated in a nitrogen atmosphere. The samples were first heated from room temperature to 110 °C, at a heating rate of 10 °C/min, isothermally held for 10 minutes and further heated to 500 °C at a heating rate 5 °C/min.

The mechanical properties of the composites were measured at room temperature on an Instron model 5543 universal testing machine equipped with a 500 N load cell. The tensile and hysteresis tests were cut into dumbbell shapes according to ASTM d-638-M-3. The tests were performed with a gauge length of 14 mm and crosshead speed of 50 mm/min and pneumatic grips were employed to prevent slippage.

Results and Discussion

Cellulose Nanocrystals (CNC)

Figure 1 shows the transmission electron micrographs (a-b) and thermograms (d) of the CNCs obtained via hydrolysis using sulphuric acid (CNC-S), phosphoric acid (CNC-P) and mechanical method (CNC-MC). The dimensions of CNCs were measured from at least 10 particles using ImageJ analytical software. From Figure 1a-c, the ‘rod-like’ shape CNC can be seen clearly with an average aspect ratio of 13, 10 and 25, for CNC-S, CNC-P and CNC-MC respectively. The HEBM process is more environmentally friendly than the acid hydrolysis methods as it was produced without using any acids, as well as being a more economically viable and scalable approach to produce CNC.

The thermal stability of CNC was determined using TGA and the associated thermograms are shown in Figure 1 (d). It can be clearly seen that CNC-S have the lowest onset degradation temperature (T_{onset}) noted at 200 °C as presented in Table 1. In contrast, CNC-P and CNC-MC recorded T_{onset} values of 255 °C and 258 °C, respectively. Despite the well-known advantages of CNC isolated via sulphuric acid hydrolysis in terms of stable aqueous colloidal stability, which is due to the negative sulphate group introduced into the surface of CNC, this method leads to poor thermal stability. The sulphate groups formed are known to promote dehydration reactions and act as flame retardants, but this characteristic also gives rise to a low nanocellulose thermal stability [13,14].

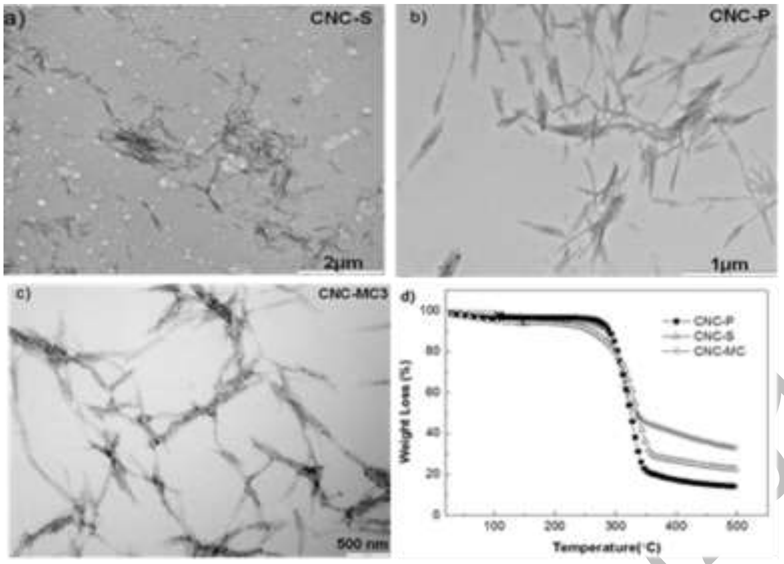

Figure 1. TEM images of CNCs produced from acid hydrolysis; a) CNC-S, b) CNC-P, c) HEBM method (CNC-MC) and d) their corresponding TGA thermograms

On the other hand, CNC-P and CNC-MC isolated from phosphoric acid hydrolysis and HEBM methods both clearly demonstrated a better thermal stability than CNC-S. Possibly phosphate group ($(PO_4)^{3-}$) attached on the surface of CNC-P is also able to assist with aqueous colloidal stability, but in this case without affecting the thermal behaviour of CNC [15]. The CNC-MC nanocellulose sample was successfully produced in a green and clean process (without the use of any acids or oxidising agents), and this approach also appears to have contributed to better thermal stability. Importantly, both of these strategies have shifted the onset degradation temperatures well above the typical melt compounding or reactive extrusion temperature window commonly employed for TPU processing with temperature of 180 – 230 °C, depending on the TPU grade and formulation.

Table 1. Dimensions and production yield of CNC isolated from the acid hydrolysis and HEBM methods

Sample	**Length (nm)**	**Diameter (nm)**	**Aspect Ratio**	**Yield (%)**	**Onset Degradation Temperature (T_{onset})(°C)**
CNC-S	213 ± 50	16 ± 3	13	81	200
CNC-P	270 ± 135	26 ± 13	10	62	255
CNC-MC	424 ± 90	17 ± 4	25	76	258

Physical appearance of TPU nanocomposites

The influence of different thermal stabilities and surface chemistry of CNC on processing can be clearly observed in Figure 2 from the physical appearance of compression moulded nanocomposite films produced via melt compounding and solvent casting. The TPU/CNC nanocomposite films produced via solvent casting retained the transparency of the host TPU at low 0.5-1 wt.% loading levels for all types of CNCs, and at the higher 5 wt.% loading the nanocomposites with CNC-S and CNC-MC showed just some feint discolouration. The solvent cast nanocomposites with CNC-P were able to retain the transparency of the host TPU even at 5 wt.%. However, very obvious and commercially-unacceptable colour changes to darkening for nanocomposites obtained via melt-compounding can be seen from Figure 2, and the order of extent of discolouration is as follows: TPU control (MC-TPU Control) < Nanocomposites using phosphoric acid hydrolysed CNCs (MC-TPU/CNC-P) << Nanocomposites using micronised CNCs (TPU/CNC-MC) < Nanocomposites using conventional sulphuric acid hydrolysed CNCs MC-TPU/CNC-S.

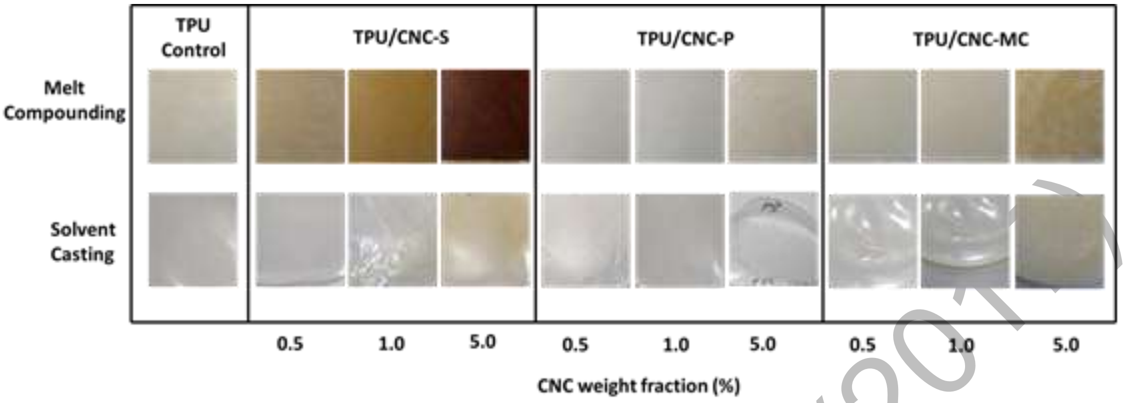

Figure 2. Photographs of TPU control and TPU/CNC nanocomposites processed via solvent casting (bottom) and melt compounding (top)

Even at 0.5 wt.% of CNC-S loading, the light brown colour of nanocomposite films was noticeable. As the processing temperature employed in the extruder was about 225 °C, the CNC isolated from sulphuric acid hydrolysis showed degradation behaviour and darkened. As reported previously, sulphate $(SO_4)^{2-}$ groups, which are present on the surface of CNC might promote the dehydration reactions [14,16,17]. The onset degradation temperature of CNC-P and CNC-MC are 255 and 258 °C, respectively. However, the dispersibility of CNC-P where phosphate groups assist in achieving superior colloidal suspension stability is better than CNC-MC, which also gives rise to the discolouration of nanocomposites incorporating CNC-MC. This strongly suggests that this discolouration in melt compounded TPU nanocomposites is due to relative CNC thermal stability and degradation, which in-turn leads to the aggregation of the less thermally stable nanocellulose.

Mechanical properties

The reinforcement effect of the CNCs was investigated by measuring the tensile properties of the TPU control and its nanocomposites, at room temperature. Figure 3 shows the stress-strain curves of TPU control and nanocomposites produced via both processes and the values determined are summarized in Table 2. Obviously, no significant changes in tensile strength upon 0 to 300% of tensile strain were observed for melt compounded material, whereas solvent cast nanocomposites show the increase difference immediately after 50% of strain. The solvent cast TPU control obtained higher tensile strength than melt compounded materials. The reduction mostly contributed by transurethanisation reaction occurred due to the harsh environment in the extrusion process.

The tensile strength of TPU reinforced with CNC-S, CNC-P and CNC-MC shows 18%, 16% and 14% of improvement respectively upon host polymer via melt compounding method. The increase was recorded at CNC loading of 0 to 1 wt.%, as it reached 5 wt.% mechanical properties of the composites was declined. Regarding percolation model related to volume fraction of filler, the percolation threshold for CNC previously has been determined at 1- 2 volume % [18,19] for CNC to form network with polymer matrix which most probably linked by the hydrogen bonding. Thus, in this work, CNC loading at 5 wt. % have been assumed ineffective as reinforcing element to the TPU matrix.

Moreover, elongation and stiffness at the optimum value of tensile strength were also unaffected indicating the soft-segment domain of TPU was not disrupted by the cellulose addition. Furthermore, the reinforcement of CNC was also can be seen from the improvement in toughness and tear strength of TPU nanocomposites. These results indicate that CNCs able to work as an efficient stress transfer medium without disrupting the original function of the TPU microstructure (hard segment and soft segment). Indeed preventing the undesired stiffening with soft domain was able to maintain the elongation of the TPU composites. The strength of the material fabricated via melt compounding is competent by comparing it with solvent casting process. This also proved that cellulose (CNC-P and CNC-MC) able to be processed with high processing temperature method.

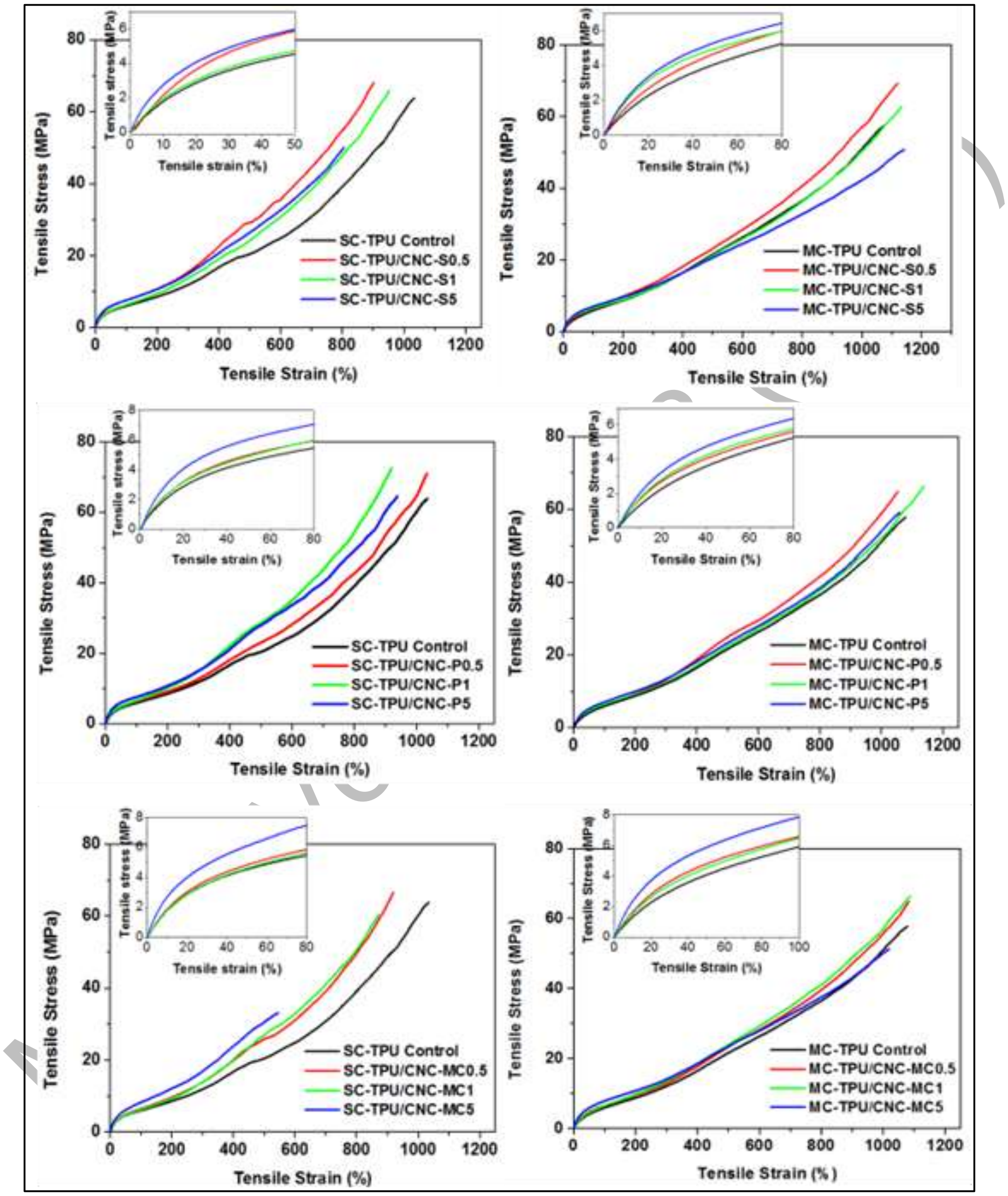

Figure 3. Stress-strain curves TPU nanocomposites fabricated via solvent casting (left column) and melt compounding (right column)

Table 2. Summary of tensile properties of TPU nanocomposites processed via solvent cast (SC) and melt compounding (MC) method.

Sample		**Tensile Stress (MPa)**	**Tensile Strain at Break (%)**	**Modulus (MPa)**	**Toughness (MPa)**	**Tear Strength (N/mm)**
TPU Control	SC	64.7 ± 1	954.6 ± 33	13.6 ± 1	258.9 ± 7	69.4 ± 15
	MC	57.7 ± 3	1041.3 ± 39	11.3± 1	261.5 ± 18	119.9 ± 4
TPU/CNC-S0.5	SC	67.1 ± 8	925.7 ± 27	17.4 ± 3	255.1 ± 35	88.6 ± 8
	MC	67.9 ± 3	1115.7 ± 29	14.3 ± 1	319.3 ± 21	118.7± 4
TPU/CNC-S1.0	SC	65.8 ± 3	964.6 ± 35	16.5 ± 3	261.9 ± 14	96.8 ± 5
	MC	62.1 ± 2	1115.4 ± 26	15.0 ± 1	295.8 ± 12	123.2± 1
TPU/CNC-S5.0	SC	49.4 ± 4	809.2 ± 49	21.6 ± 4	183.9 ± 17	73.7 ± 11
	MC	51.3 ± 1	1137.5 ± 19	17.2 ± 1	281.6 ± 9	129.1 ± 4
TPU/CNC-P0.5	SC	66.0 ± 7	994.8 ± 55	11.3 ± 4	256.2 ± 39	70.5 ± 27
	MC	65.9 ± 2	1062.4 ± 24	13.5 ± 1	296.9 ± 13	121.7± 5
TPU/CNC-P1.0	SC	66.2 ± 6	924.1 ± 21	14.0 ± 1	243.4 ± 20	88.6 ± 3
	MC	66.8 ± 1	1108.8 ± 29	14.0 ± 1	295.8 ± 12	120.9± 2
TPU/CNC-P5.0	SC	64.5 ± 7	950.8 ± 62	20.7 ± 2	271.2 ± 40	78.9 ± 16
	MC	59.9 ± 2	1063.6 ± 25	16.2 ± 1	280.8 ± 8	123.5 ± 7
TPU/CNC-MC0.5	SC	66.9 ± 8	956.0 ± 46	14.9 ± 2	256.3 ± 33	85.7 ± 16
	MC	64.0 ± 2	1062.6 ± 30	12.6 ± 1	290.2 ± 15	113.1± 6
TPU/CNC-MC1.0	SC	60.4 ± 4	822.4 ± 70	14.6 ± 2	210.3 ± 24	81.6 ± 21
	MC	65.6 ± 2	1084.7 ± 5	12.4 ± 1	305.9 ± 7	125.2± 7
TPU/CNC-MC5.0	SC	33.2 ± 3	583.7 ± 75	22.4 ± 4	103.3 ± 19	83.1 ± 12
	MC	51.2 ± 1	1005.6 ± 20	21.1 ± 1	247.2 ± 10	126.6 ± 4

Conclusion

Three types of CNCs isolated via sulphuric acid hydrolysis (CNC-S), phosphoric acid hydrolysis (CNC-P) and mechanical milling method (CNC-MC) were successfully incorporated into TPU via melt compounding method. These nanocomposites were compared with that processed via conventional solvent casting method. The thermally stable CNCs (CNC-P and CNC-MC) have demonstrated the melt process ability with polyether based thermoplastic polyurethane (TPU) without affecting the optical transparency, whereas, CNC-S has shown the degradation behavior. Remarkable reinforcement effect has been observed for nanocomposites with all the three CNCs, in terms of improvement in tensile strength and toughness without affecting elongation. It can be summarized that CNC isolated via mild acid hydrolysis and an optimized mechanical milling methods, can be easily processed via large scale melt-processing techniques for reinforcing thermoplastic polyurethanes at 0.5-1 wt. % without affecting their physical appearance and elastic properties.

Acknowledgement

The authors gratefully acknowledge the facilities as well as the scientific and technical assistance of the Centre for Microscopy and Microanalysis, University of Queensland. Khairatun Najwa also thanks to the Ministry of Education Malaysia and Universiti Malaysia Pahang for the financial support.

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