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Sustainable composites of surface-modified cellulose with low-melting point polyamide

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ABSTRACT

The present study proposed a series of sustainable polyamide/cellulose composites with up to 60% biobased content to address environmental issues arising from using fossil-based polymers. Furthermore, it addressed one of the most challenging cellulose/polymer composites' issues, filler/matrix compatibility. Accordingly, the microcrystalline cellulose (MCC) surface was treated through the grafting of n-octadecyl isocyanate (ODI) molecules. The elemental analysis confirmed the substitution of approximately 9 ODI molecules per 100 anhydroglucose units, resulting in superhydrophobic MCC formation with a water contact angle of 130°. The surface-modified MCC was melt blended with a bio-based low-melting point polyamide, developed through copolymerization of 11-aminoundecanoic acid and 12-aminolauric acid. Scanning electron microscopy images confirmed no evidence of surface-modified MCC agglomeration, even at a high loading of 30 wt%, suggesting a uniform dispersion of the filler particles and excellent compatibility between two phases. Consequently, the storage modulus, tensile modulus, and yield stress were enhanced by 40%, 100%, and 50%, respectively, in the composite sample with 30 wt% of MCC, proving excellent stress transformation from the matrix to particles arose from good adhesion between cellulose particles and polyamide chains. Furthermore, all samples revealed suitable melt flowability and viscoelastic performances, suggesting their excellent processability, a critical property for engineered thermoplastics. On top of that, the presence of the surface-modified particles considerably decreased water uptake capacity and water vapor transmission of the polymer matrix, making it interesting for specific applications like packaging films.

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1. Introduction

In recent decades, the substitution of petroleum-based polymers with bio-based plastics, plastics derived from biomass, has attracted significant attention because of global environmental concerns and finite petroleum feedstocks. Accordingly, several sustainable polymers from renewable sources with comparable mechanical and thermal properties with those obtained from fossil feedstocks have been developed successfully [1–3]. Polyamides (PAs) with outstanding properties, such as superior mechanical strength even at high temperature, good chemical resistance toward a wide range of solvents, high stiffness/toughness, and acceptable thermal stability, are gaining a broad range of applications in different industrial fields, including electronics, buildings, engineering parts, sporting goods, automotive parts, housing, and

[4–7]. PAs are successfully synthesized from biomass, mainly from vegetable oils, over the last decades. For instance, some partially and fully bio-based PAs such as PA4, PA11, PA610, PA1010, and PA1212 have been developed from bioresources, and some of them, like PA11, have been even commercialized [8,9]. PA11, a fully biobased polymer obtained from castor oil, is an attractive PA used as an engineering plastic in different industrial fields, from automotive parts to the offshore oilfield [10]. Because of the low amide:methylene density in the backbone, PA11 has a relatively lower moisture sorption capacity and melting point than other PAs [11–13]. The latter property made PA11 an interesting candidate for blending with bio-based fillers and developing sustainable composites [14-16]. However, the processing temperature of PA11, which is approximately 40 °C higher than its melting point, is on the edge of the degradation temperature of bio-based materials. Therefore, it would be a challenging task to reinforce PA11 using bio-based fillers. Increasing the length of the aliphatic chain,

packaging, and becoming a ubiquitous polymer in our daily life

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causing it to have a more polyethylene-like structure and less methylene:amide density, is one of the well-known methods to reduce the melting point of the PA for specific applications. Accordingly, different research groups have developed several long-chain aliphatic PAs with relatively low melting temperatures [5,17,18]. However, one of the less developed methods to synthesis low—melting point PAs is changing the polymer chain regularity through copolymerization, as previously reported by Telen et al. [19].

On the other side, as one of the most abundant renewable carbohydrate polymers on earth, cellulose has attracted significant attention for developing sustainable composites because of its availability, high chain stiffness, low density, well-defined size and morphology, controllable surface chemistry, environmental sustainability, and low cost [20–24]. Nevertheless, the hydrophilicity of cellulose and compatibility with polar environments have limited its application in hydrophobic polymer matrices such as PAs and have affected the mechanical properties of cellulose-reinforced polymer composites because of the low interface bonding strength. In other words, cellulose-based fillers are not compatible well with non-polar polymers, such as PAs, and do not tend to disperse uniformly into the polymer matrix, and usually, their agglomeration takes place even at low concentrations and, consequently, causes a dramatic reduction in the mechanical performances of the final composite [25–27]. Luckily, the abundant surface hydroxyl groups on cellulose structure can provide an opportunity for surface modification and, consequently, good adhesion and strong interactions with polymers [21,28]. As such, most of the scientific efforts on cellulose-based composites are accompanied by surface modification of the particles. In one recent work, Balasubramaniam et al. [29] investigated the modification of cellulose nanofibril (CNF) films with saturated fatty acids, including lauric, palmitic, and stearic acids, to increase surface hydrophobicity while maintaining the mechanical property of the cellulose. Rueda et al. [30] successfully modified the surface of cellulose nanocrystals (CNCs) using hexamethylene diisocyanate (HDI) by varying the CNC/HDI molar ratio and used it to prepare polyurethane nanocomposites with enhanced mechanical properties. Pourmoazzen et al. [31] furthermore reported CNC surface modification through grafting of bulky cholesterol moieties. Bond formation between the CNC surfaces and cholesterol was confirmed by Fourier transform infrared spectroscopy (FTIR), solid-state nuclear magnetic resonance (NMR), and strong hydrophobic characteristics. Cellulose surface modification through grafting mono- and di-isocyanates, such as phenyl isocyanate, n-octadecyl isocyanate (ODI), toluene diisocyanate, diphenylmethane diisocyanate, and hexamethylene diisocyanate, has also been reported in the literature [32].

In the present study, a relatively low—melting point bio-based copolymer of PA11 and PA12 was synthesized through a polycondensation reaction between 11-aminoundecanoic acid and 12aminolauric acid. It was then reinforced using octadecyl isocyanate—grafted microcrystalline cellulose (MCC). Our findings supported the benefit of surface modification in improving the properties of the developed biocomposites. These newly developed biocomposites with a relatively high bio-based content (up to 60%) might be interesting for substitution with the common petroleumbased polymers for different engineering applications.

2. Materials and methods

2.1. Materials

11-aminoundecanoic acid (97%), MCC (Avicel® PH-101, particle size of approximately 50 μ m), dibutyltin dilaurate (DBTL, 95%), sodium hypophosphite monohydrate (>99%), ODI (technical

grade), chloroform-d (99.8 atom % D), and trifluoroacetic anhydride (reagentPlus®, \geq 99%) were purchased from Sigma-Aldrich. Chloroform (for analysis, EMPARTA® ACS) was delivered from Merck. 12-aminolauric acid (purity >98.0%) was provided from Tokyo Chemical Industry. Toluene (\geq 99.5%) was obtained from VWR and dried using molecular sieve 4A for two weeks before using.

2.2. MCC surface modification

MCC was treated using the method described by Siqueira et al. [33]. Three g of MCC was dried thoroughly in a vacuum oven at 60 °C for 48 h. It was then poured in a three-neck round-bottomed reactor equipped with a reflux condenser. Hundred ml of pre-dried toluene and a tiny amount of DBTL were added to the system, and the temperature was raised to 90 °C while the mixture was stirred. Then, an identical amount of ODI was added drop by drop to the mixture. The reaction was kept under a constant temperature for 24 h. The surface-modified MCC (SMMCC) was filtered using Whatman No. 3, washed with ethanol, and centrifuged several times to remove the formed amine during the reaction and the unreacted ODI. The final SMMCC was dried at 50 °C in a vacuum oven for 24 h before composite preparation.

2.3. Copolymer synthesis and biocomposite preparation

The co-PA was synthesized through a polycondensation reaction between 11-aminoundecanoic acid and 12-aminolauric acid in a high-torque reactor equipped with an overhead mixer, heating jacket, and nitrogen flow. An identical mole of 11aminoundecanoic acid and 12-aminolauric acid and a prescribed amount of sodium hypophosphite monohydrate as a catalyst (0.1 wt% of monomer weight) were mixed physically and then poured into the reactor vessel. The temperature was raised to 200 °C while the system was under nitrogen purge. After 1 h, the melted monomers were stirred under a mild stirring (15 rpm), whereas the produced water was removed efficiently by nitrogen flow. After 4 h, the reactor was cooled down, and the synthesized co-PA was removed. The product was then milled using the Retsch SM 300 Cutting Mill at 1000 RPM with a blade size of 1 mm. Pure PA11 and PA12 were also synthesized with the same procedure for comparison with the co-PA.

Different weight ratios of the synthesized co-PA and SMMCC were gently mixed, dried thoroughly at 50 °C in a vacuum oven, and then fed to an extruder (Brabender DSK, the Netherlands) for melt blending. The temperature and screw speed were fixed at 200 °C and 20 rpm, respectively. The extruded filament was cut using a pelletizer, thoroughly dried at 50 °C in a vacuum oven for 24 h, and then hot-pressed (Fontijne Lab Press - TP 400, the Netherlands) at 200 °C under 150 kPa pressure to prepare film-shape samples for further characterizations. The weight ratios of the polymer and filler were selected as 95:5, 90:10, 80:20, 70:30, and 60:40, and the samples were coded as PA-SMMCC5, PA-SMMCC10, PA-SMMCC20, SMMCC30, and PA-SMMCC40, respectively.

2.4. Characterizations

2.4.1. Fourier transform infrared spectroscopy

The chemical structure of the MCC, SMMCC, synthesized PA11, PA12, copolymer, and composites was investigated using a PerkinElmer FTIR Labsence model with an ATR instrument, USA. The background and sample measurements were carried out in a wavenumber ranging from 4,000 to 500 cm⁻¹, with a scan rate and resolution of 32 and 4 cm⁻¹, respectively. The FTIR spectra of the composite samples are presented in Fig. S1.

2.4.2. Proton nuclear magnetic resonance (¹H NMR)

The structure of the synthesized PA11, PA12, and the copolymer of PA11 and PA12 was determined using the Bruker NMR spectrometer model Avance III 400 (USA) with a hydrogen scan number of 8. The sample was first dissolved in a solvent composed of deuterated chloroform and trifluoroacetic anhydride (90/10, V/V) and then exposed to ¹H NMR spectroscopy.

2.4.3. Gel permeation chromatography (GPC)

GPC (Waters Wyatt Malls model 717 plus Autosampler, USA) was used to measure the different molecular weights of the synthesized PA11, PA12, and the copolymer, including weight average molecular weight (Mw), number average molecular weight (Mn), and the polydispersity index (PDI) of each sample. A 10 wt% solution was prepared by dissolving the sample into chloroform and trifluoroacetic anhydride solvent (90/10, V/V) and used for GPC analysis.

2.4.4. X-ray diffraction (XRD)

The crystallinity of the MCC, SMMCC, synthesized PA11 and PA12, and copolymer was studied by XRD analysis using the PANalytical X'Pert model MPD Alpha 1, the Netherlands. The signals were recorded in an angle region of $5-40^{\circ}$ (2 θ) under voltage and current of 45 kV and 40 mA, respectively, and X-ray radiation with a wavelength of 1.54 Å.

2.4.5. Scanning electron microscopy (SEM)

The morphology of the virgin MCC and SMMCC was studied using SEM images taken from the surface of the Au-coated sample under a high vacuum condition and voltage of 3 kV using a Zeiss Instrument model Sigma VP, Germany. Furthermore, the SEM images were used to investigate the degree of dispersion of the SMMCC particles into the copolymer matrix through imaging from the cryofracture surface area of the composites with different SMMCC contents.

2.4.6. Elemental analysis

The amount of grafted ODI was calculated by measuring the carbon, oxygen, hydrogen, and nitrogen of the unmodified and modified MCC through a Thermo FlashSmart CHNSO Elemental Analyzer, USA. The degree of substitution (DS, number of grafted hydroxyl functions per anhydroglucose unit) can be determined from the weight fraction of carbon or oxygen; nevertheless, because carbon was the element with the highest quantity in the grafting molecules (ODI), it was supposed to give more accurate results [33]. Accordingly, carbon was selected to calculate the DS value via the following equation.

$$DS = \frac{72.07 - C \times 162.14}{295.5 \times C - 228.20} \tag{1}$$

where C is presenting the sample carbon content, 72.07 is the mass of carbon in the anhydroglucose unit, 162.14 is the molecular weight of the anhydroglucose unit, and 295.5 and 228.20 are the molecular weight of ODI and the mass of carbon in ODI, respectively. The precision of measurement was corrected, assuming the unmodified sample was pure cellulose [33,34].

2.4.7. Contact angle measurement

The contact angle of a water droplet (5 μ L) was monitored against time on the surface of virgin MCC, SMMCC, copolymer, and composite samples using a Theta Flex optical tensiometer (Biolin Scientific, UK) at 23 °C. Furthermore, a digital photograph of the water droplet was taken 60 s after droplet deposition. The

measurement accuracy was $\pm 0.1^{\circ}$, and the imaging was started within a few tens of milliseconds after deposition of the drop.

2.4.8. Water vapor transmission (WVT) and water absorption (WA) capacity

The WVT of the film sample was measured based on the method reported in the literature [35] by monitoring the weight changes of the thoroughly dried film. A polyethylene cup was filled with calcium chloride as a desiccating agent; its lid was sealed with the dried film and weighted (m_0). The cup was put in a desiccator with relative humidity and temperature of 60% and 25 °C, respectively, and weighed daily (m_i) for two weeks. The curve of gained weight ($m_i - m_0$, g) versus time (day) was plotted, and a linear curve was interpolated over the data. The slope of the curve was extracted (g/day), divided by surface area exposed to water vapor (0.0141 m²), and multiplied by sample thickness (m) to obtain the film WVT (g/day/m).

The WA capacity was calculated based on the weight gain of the dried sample (m_0) 24 h after immersion in the water (m_f) using Equation (2).

$$WA(\%) = \frac{m_f - m_0}{m_0} \times 100$$
 (2)

2.4.9. Mechanical properties

A standard tensile test based on ASTM D882 was conducted to calculate the mechanical performances of the copolymer and composite samples. The test was performed using Universal Tester Instron 5944 (USA) under a load cell of 2 kN and tensile speed of 5 mm/ min. The typical stress-strain curves were depicted, and different mechanical properties, including tensile modulus (the slope of the curve at linear region), yield stress (the amount of stress at a zero slope), tensile strength (the ultimate stress before breaking), elongation at break (the final strain value), and the toughness (the force-displacement curve area, kJ/m), were extracted.

2.4.10. Differential scanning calorimetry (DSC)

The melting point (T_m) and melting enthalpy (ΔH_m) of virgin PA11, PA12, and copolymer were extracted from the heatingcooling thermograms obtained from DSC measurements (TA Instruments MT-DSC Q2000, USA). The heating and cooling were performed between -20 and 250 °C with a fixed rate of 10 °C/min. The first heating-cooling cycles were used to eliminate the thermal history of the sample, whereas the second heating-cooling cycles were used to extract the abovementioned properties. The crystallinity of the sample (χ_c) was calculated using Equation (3), in which ΔH_{co}^0 is the melting enthalpy of 100% crystallized copolymer. $\Delta H_{m,co}^0$ was calculated considering the melting enthalpies of 100% crystallized PA11 (226.4 J/g) [13] and PA12 (209.3 J/g) [36] and the mass fraction of each component (PA11 and PA12) [19]. Because an identical amount of monomers were used to synthesis the copolymer, the mass fractions of PA11 and PA12 in the copolymer were 0.481 and 0.519, respectively.

$$X_c = \frac{\Delta H_m}{\Delta H_{m,co}^0} \times 100 \tag{3}$$

2.4.11. Thermogravimetric analysis (TGA)

The thermal degradation behavior of virgin MCC and SMMCC was monitored between 30 and 800 °C through TGA using TA Instruments TGA Q500 (USA) with a heating rate of 10 °C/min under the nitrogen atmosphere. The TGA and derivative thermogravimetry (DTG) thermograms were used to investigate the grafting of ODI on the surface of MCC. Furthermore, the thermal degradation trend of synthesized PA11, PA12, copolymer, and composites was

studied between 30 and 700 °C using the same instrument and test condition. The TGA/DTG thermograms of the composites are presented in Fig. S2.

2.4.12. Dynamic mechanical analysis (DMA)

The dynamic characteristics of the copolymer and composites, including storage modulus (E'), loss modulus (E"), and loss tangent (tan δ), were studied using TA Instruments DMA Q800 (USA) at a multiple strain/frequency mode between 25 and 170 °C with a heating rate of 5 °C/min. The frequency value, strain rate, and preload force were fixed at 1 Hz, 1%, and 1 N, respectively. The trend of E' and E" versus temperature was used to investigate the effect of SMMCC addition on the improvement of dynamic moduli of the samples, whereas the tan δ curve was used to extract the glass transition temperature (Tg) of the samples.

2.4.13. Melt flow index (MFI)

The MFI of the samples was determined as per the ISO1133 standard using a Ceast MFI 6542 machine at 200 °C under the weight of 2.16 kg. Several specimens containing no air bubbles were cut at certain time intervals, weighed, and used to calculate the MFI (g/10 min) of the sample using Equation (4).

$$MFI = \frac{600 \times m}{t} \tag{4}$$

where m is the average weight of the cut samples (g), and t is the time interval (s).

2.4.14. Rheology

The viscoelastic properties of the pure copolymer and composites were investigated at 200 °C under the nitrogen atmosphere using an Anton Paar Physica rheometer model MCR 301 (Austria) rotational rheometer with a parallel geometry (PP25). A strain sweep test was performed from 0.01 to 100% with an oscillatory logarithmic interval at a fixed frequency of 1 Hz. The trend of storage modulus (G') and loss modulus (G'') versus strain rate was then plotted in a logarithmic scale to find the linear viscoelastic region. In the following, a frequency sweep test was conducted at the linear viscoelastic region (strain rate of 10%), from 0.01 to 100 Hz, with an oscillatory logarithmic interval. Afterward, complex viscosity, G', and G'' were schemed in a logarithmic scale as a function of frequency to investigate the effect of SMMCC on the improvement of viscoelastic performances of the copolymer.

3. Results and discussion

First, the results of different analytical techniques, including FTIR, TGA, contact angle, elemental analysis, and SEM images, were presented, discussed, and compared with the similar scientific literature to confirm the surface modification of MCC via grafting ODI molecules. Afterward, the successful synthesis of the copolymer was investigated through FTIR, ¹H NMR, XRD, DSC, and TGA analyses. Finally, the effect of SMMCC addition on different matrix characteristics, including mechanical properties, dynamic mechanical performances, viscoelastic behavior, and WVT, was thoroughly discussed and compared with those reported in the literature.

3.1. MCC surface modification

Fig. 1a illustrates the FTIR spectra of virgin MCC and SMMCC. The characteristic peaks of MCC were as follows: a peak at 662 cm⁻¹ assigned to C–OH out-of-plane bending, a peak at 896 cm⁻¹ ascribed to ring CH₂ rocking, a peak at 1,028 cm⁻¹ attributed to

C–O–C stretching absorptions, two peaks at 1,104 \mbox{cm}^{-1} and 1,160 cm⁻¹ arose from C–O–C pyranose ring skeletal vibration, a peak at 1,314 cm⁻¹ due to CH₂ wagging vibration in cellulose, a peak at 1,427 cm⁻¹ originated from CH₂ bending vibration, a peak at 1,628 cm⁻¹ corresponded to O–H bending vibration of adsorbed water, a peak at 2,893 cm⁻¹ proportioned to C–H asymmetrically stretching vibration of in a pyranoid ring, and a peak at 3,331 cm⁻¹ related to –OH stretching vibration [37]. These characteristic peaks were repeated in the SMMCC sample; moreover, some new peaks appeared, confirming ODI was grafted on the MCC surface. These peaks were as follows: two strong peaks at 2,852 cm^{-1} and 2,918 cm⁻¹ due to asymmetric and symmetric –CH₂ stretches of the grafted alkyl chain and two peaks at 1,615 cm⁻¹ and 1,570 cm⁻¹ originated from amide I and amide II vibration, respectively. It is worth noticing that no characteristic peak was detected in the region of 2,260 cm^{-1} corresponding to the isocyanate groups, suggesting the successful removing of ODI after several times washing [33].

Fig. 1b demonstrates the TGA/DTG thermograms of virgin MCC and SMMCC. The virgin MCC revealed a preliminary slight mass loss at 100 °C due to water evaporation followed by a major mass loss region between 300 and 400 °C with a maximum at 331 °C (DTG curve) attributed to the decomposition of cellulose structure (anhydroglucose unit) [38,39]. These two mass loss regions could be detected in the SMMCC thermogram; furthermore, a new degradation area appeared within the range of 220–300 °C, which could be caused by pyrolysis of the modifier molecule alkyl chain (ODI). Accordingly, one new peak at 240 °C was added to the DTG thermogram of SMMCC. Both maximum degradation temperature and char yield were increased in SMMCC, suggesting a slight enhancement in thermal stability of surface-modified sample compared with the virgin one.

The effect of surface modification on the crystallinity of MCC was investigated through XRD analysis. Fig. 1c represents the XRD patterns of virgin MCC and SMMCC. The MCC pattern displayed three diffraction peaks at 14.92°, 22.46°, and 34.41°, corresponding to the (1 0 1), (0 0 2), and (0 4 0) crystallographic planes, respectively. Furthermore, one peak could be detected at 18.52°, attributed to the amorphous cellulose region [40]. In other words, both crystal and amorphous domains were included in the MCC structure. The abovementioned peaks were repeated in the surface-modified sample, indicating that the crystalline structure of the MCC was kept intact after grafting the ODI [33].

The water contact angle was measured to investigate the hydrophobicity of the surface-modified sample. The water was absorbed immediately once dripped on the surface of MCC, making it impossible to determine its contact angle value, indicating a highly hydrophilic surface [41]. The water contact angle was 130° for SMMCC (Fig. 1d), revealing that water was retained in the outer region without entering the sample. It also suggested a decrease in the surface energy of the surface-treated sample and the formation of a more hydrophobic surface via the tiny grafting amount of ODI molecules [42]. The contact angle did not change significantly over time in SMMCC (Fig. 1d), confirming the absence of any considerable WA. On the one hand, the measured water contact angle in the present study had good agreement with that reported for oleic acid-grafted MCC [43] and toluene-2,4-diisocyanate-grafted MCC [41], whereas it was pretty higher than that reported for polyvinyl carbazole–grafted CNFs [42]. On the other hand, by comparing the water contact angle of the SMMCC sample with that reported in the literature for hydrophobic surfaces, it can be concluded that the prepared surface-modified samples behave as super-hydrophobic materials [44,45].

The morphology of the MCC before and after surface modification was studied via SEM images. Fig. 1e and f show the SEM images



Fig. 1. (a) FTIR spectra, (b) TGA/DTG thermograms, and (c) XRD patterns of MCC and surface-modified MCC (SMMCC). (d) The trend of contact angle versus time and the digital photos of the droplet 60 s after deposition on SMMCC surface. (e) and (f) SEM images of MCC before and after surface treatment (magnification 200×).

of MCC and SMMCC, respectively. MCC microparticles revealed a smooth surface and lamellar and rod-shaped morphology with an average diameter and length of $150 \pm 50 \ \mu m$ and $15 \pm 5 \ \mu m$, respectively, in good agreement with the literature [46]. The morphology of MCC did not change significantly after surface treatment, indicating that the surface modification was mild and did not cause any damage to the particles [43]. Nevertheless, the MCC surface became eroded and split, revealing an alteration in surface morphology caused by the physical swelling and untwisting of pristine cellulose fibers during the grafting of ODI molecules that covered the surface of the cellulose fibers [47].

The amount of grafted ODI on the surface of the MCC was calculated using elemental analysis (Table 1). First, the theoretical amounts of carbon, oxygen, and hydrogen in the anhydroglucose unit of virgin MCC (assumed as pure cellulose) were used to plot the calibration curve for the measured data (Fig. S3). This curve was used to modify the measured elemental values of the SMMCC. On the one hand, there was a good agreement between the theoretical and measured elemental values; on the other hand, significant

changes could be observed in the values of the elements after surface modification. Because the surface-modified sample was thoroughly washed after the treatment, it could be concluded that the measured nitrogen value could be due to the successful grafting of ODI molecules on the surface of the MCC. The measured nitrogen value was in good agreement with the literature that used the same modification method for surface treatment of nanocellulose [33,34]. The elemental analysis results were further used to calculate the DS via Equation (1). It was 0.093, indicating that approximately 9 ODI chains were grafted per 100 anhydroglucose units. By considering the DS value and molecular weight of the anhydroglucose unit and ODI (162.14 g/mol and 295.5 g/mol), the mass ratio of the grafted ODI molecules was approximately 16%. This low amount of grafted ODI molecules converted hydrophilic MCC surface to super-hydrophobic one, as previously observed in contact angle measurement. The relatively high hydrophobicity will be advantageous for cellulose-based fillers if used for polymer composite preparation, as they can easily disperse into the hydrophobic matrix and improve its different properties.

Table 1 Theoretical, measured, and corrected elemental values of the virgin and surface-modified samples.

Sample	Theoretical values				Measured values				Corrected values ^a			
	C,%	H,%	N,%	0,%	С,%	H,%	N,%	0,%	C,%	H,%	N,%	0,%
MCC SMMCC	44.44 —	6.22 —	0 —	49.34 —	42.8 46.15	6.2 6.7	_ 0.78	45.7 44.9	_ 49.22	- 6.80	_ 0.79	- 47.88

^a Calculated from the calibration curve (Fig. S3).

3.2. Synthesized copolymer characterization

Different analytical techniques, including FTIR, ¹H NMR, XRD, DSC, and TGA, were used to characterize the synthesized copolymer structure. Because it was a copolymer of PA11 and PA12, the results were compared with those obtained for virgin PA11 and PA12, synthesized with similar polymerization conditions.

The chemical structures of the synthesized samples were investigated through the FTIR spectroscopy technique. Fig. 2a represents the FTIR spectra of the synthesized PA11, PA12, and the copolymer of PA11 and PA12. On the one hand, all the polymers revealed similar FTIR spectra, suggesting they had the same chemical structure. On the other hand, they presented characteristic peaks similar to those reported in the literature for PAs [6,48]. They were as follows: a peak at 3,300 cm⁻¹ assigned to hydrogen-bonded N–H stretching mode, a peak at 3,084 cm⁻¹ attributed to N–H stretching mode with amide II overtone mode, two strong peaks at 2,921 cm⁻¹ and 2,854 cm⁻¹ related to asymmetric and symmetric -CH₂ stretches of the alkyl chain, respectively, a peak at 1,640 cm⁻¹ originated from C=0stretching mode, a peak at 1,548 cm⁻¹ due to N–H stretching mode of amide II, a peak at 1,371 cm⁻¹ corresponded to NH–CO stretching mode of amide III, and a peak at 941 cm^{-1} arose from C–CO stretching mode of amide IV.

The molecular structure of the synthesized PA11, PA12, and the copolymer was identified through ¹H NMR spectroscopy, Fig. 2b. All samples revealed six groups of peaks as follows: the peaks at 7.3 ppm and 10.4 ppm were attributed to chloroformd trifluoroacetic anhydride solvents, respectively, the peaks at around 1.3 ppm and 1.6 ppm, coded as b and d, were attributed to the proton signals of methylene units in the aliphatic chain, the peaks at around 2.7 ppm, coded as a, were corresponded to the proton signals of methylene units adjusted to the carbonyl group, and the peaks around 3.7 ppm, coded as c, were related to the proton signals of methylene units adjusted to the amino group [17,18]. The appearance of these peaks confirmed the successful synthesis of PAs and copolymer through the used polycondensation polymerization; furthermore, they approved that the synthesized copolymer had good coherence with the ¹H NMR spectra of pure PA11 and PA12 [49].

The different molecular weights of the synthesized polymers, including the Mn and Mw, as well as the PDI, measured via the GPC technique, are provided in Table 2. Both PA11 and PA12 and the copolymer presented relatively high Mw comparable with that reported for the commercial PAs and long-chain aliphatic PAs. For instance, Mw of commercial PA610 and experimentally synthesized PA614 has been reported as 83,000 g/mol and 93,000 g/mol, respectively, [17,18], which were in good agreement with the Mw of the synthesized copolymer (83,000 g/mol). It is worth noticing that such a high molecular weight was obtained in a relatively low polymerization time (4 h), making it attractive industrially. On the other hand, this high molecular weight proposed excellent polymerization conditions, including effective water removal and mechanical agitation during the polycondensation reaction, encouraged chain growth, and reduced the likelihood of chain scission (degradation) or reaction termination [18]. All the samples

revealed a low PDI, a narrow molecular weight distribution, confirming the absence of side reactions during polymerization. Furthermore, no secondary peak was observed in the GPC curve of the copolymer (Fig. S4), indicating both monomers (11aminoundecanoic acid and 12-aminolauric acid) grew up in the same polymer chains, not separately. In other words, no secondary reactions occurred during copolymer synthesis.

The crystallinity of the synthesized polymers and copolymer was studied via XRD and DSC analyses. The XRD patterns and DSC thermograms of the samples are provided in Fig. 2c and d, respectively. PAs usually display two crystalline forms: α - and γ phases. The diffraction peaks of the former appear at approximately $2\theta = 20^{\circ}$ and $2\theta = 24^{\circ}$, corresponding to α_1 - (for hydrogen-bonded chains) and α_2 -form (for chains bonded by Van der Waals forces, hydrogen-bonded sheets), respectively, whereas the latter displays a diffraction peak at approximately $2\theta = 22^{\circ}$. The γ -form is formed by the hydrogen bonding almost perpendicular to the carbon plane and between parallel pleated chains and is thermodynamically less stable. The α -form consists of hydrogen bonds between antiparallel molecules in a full-extended zigzag chain conformation, in which the planes of the methylene and amide groups are parallel. This crystalline form is more thermodynamically stable [5,50-53]. In the present study, PA11 and PA12 presented one sharp diffraction peak at approximately $2\theta = 20.7^{\circ}$, whereas the copolymer revealed two diffraction peaks at $2\theta = 20.16^{\circ}$ and $2\theta = 21.89^{\circ}$. The presence of one strong diffraction peak, which was accompanied by a single melting point (Fig. 2d), suggested the formation of α_1 -crystalline form in the synthesized PA11 and PA12. However, double peaks were observed in the copolymer XRD pattern, indicating the formation of α_1 -and γ -crystalline forms, which was in good agreement with the DSC results, where the copolymer revealed two endothermic peaks, a major peak at 160 °C and a minor one at 154 °C, corresponding to the melting of different crystalline forms. On the whole, it can be concluded that in the copolymer sample, the intensity of the hydrogen bonds was altered, and consequently, the formation of γ -crystalline forms was promoted [54].

The degree of crystallinity of the synthesized PA11, PA12, and copolymer was calculated using Equation (3). The results are summarized in Table 2. The crystallinity of the synthesized PA11 and PA12 was relatively lower than that reported in the literature, 22.8% [13] and 27.9% [36], respectively, because of the different polymerization conditions that have been selected. Nevertheless, the crystallinity did not change significantly in the copolymer. The crystallinity of the synthesized copolymer in the present study had an acceptable agreement with that reported by Telen et al. [19] for the random copolymer of PA11 and PA12, synthesized through transamidation reactions during high-temperature reactive extrusion ($\chi_c = 19\%$).

A low melting point could be advantageous for PAs when they are supposed to blend with thermally unstable fillers like cellulose. In the present study, the melting point of the synthesized PA11 and PA12 was 191 °C and 178 °C, respectively. The lower melting point of PA12 was due to the lower amount of hydrogen bonds per unit of mass in its structure. Surprisingly, the melting temperature of the synthesized copolymer was 160 °C, which was not only lower than



Fig. 2. (a) FTIR spectra, (b) ¹H NMR spectra, (c) XRD patterns, (d) DSC curves, and (e) TGA (solid lines) and DTG (dash lines) thermograms of the synthesized polymers and copolymer.

the melting point of PA11 and PA12 homopolymers but also lower than that reported for most of the long-chain aliphatic PAs in the literature. For instance, the melting point of PA1212, PA1216, and PA1218 has been reported as $184 \degree C$ [55], $171 \degree C$ [56], and $171 \degree C$ [5], respectively, which are relatively higher than that obtained in the present study. It is worth notifying that Telen et al. [19] succeeded in reaching a low melting point of 140 °C in a copolymer composed

 Table 2

 Melting point, melting enthalpy, crystallinity, and different molecular weights of the synthesized polymers.

Sample	Mn (g/mol)	Mw (g/mol)	PDI	T_m (°C)	ΔH_m (J/g)	χc (%)
PA11	55,200	109,000	1.97	191	36.18	16.17
PA12	58,500	110,500	1.89	178	38.16	18.23
Copolymer	42,200	83,000	1.97	154, 160	34.88	16.03

of PA11 and PA12 with a 50/50 mass ratio; nevertheless, they used pretty harsh processing conditions (30 min extruding at 350 $^{\circ}$ C under the nitrogen atmosphere) which may not be industrially interesting.

TGA was used to further investigate the absence of any side reactions or the formation of significant oligomers during copolymerization. Fig. 2e depicted the obtained thermograms for pure PA11, PA12, and the copolymer. On one side, all samples presented a similar one-step mechanism in the degradation process, indicating that no significant oligomers were prepared during polymerization and no side reaction took place during the copolymerization of PA11 and PA12. On the other side, all thermograms were in good agreement with those reported for thermal degradation of PAs, a stable mass up to 400 °C, followed by entirely thermal decomposition between 420°C and 500°C with a maximum thermal degradation at 460 °C [11,57].

3.3. Composites' characterization

3.3.1. Microstructure study

The degree of dispersion of microparticles and nanoparticles onto the polymer matrix is one of the crucial factors affecting the properties of the final composites. It mainly depends on the compatibility between two phases, the filler and polymer matrix, as well as on the composite production methods. Fig. 3 depicts SEM images taken from the cross-section area of the cryofracture surfaces of samples with different SMMCC contents. Moreover, the SEM images from the surface of the neat copolymer and the composite sample which contained 30 wt% virgin MCC are presented in Figure S5 for comparison. The surface of the neat copolymer was smooth without the presence of any particles; furthermore, no evidence of brittle fracture was observed. Nevertheless, the SMMCC was partially covered and dispersed within the matrix in all composite samples with no particle aggregation evidence, even at high filler contents. Notably, fibrillation of the MCC fibers happened at the lower filler content, indicating that the applied shear stress during the melt blending in the extruder overcame the strong intermolecular hydrogen bonds between crystalline cellulose domains [58,59]. It is worth noting that agglomeration of particles and phase separation could be observed in the composite sample containing untreated MCC (Figure S5b). Large agglomerates of the fillers are observed with the increase of the MCC loading because of the strong hydrogen bonding interactions between the hydroxyl groups of MCC particles [59]. In the present study, the absence of particle agglomerations at a high filler content could be due to the successful surface modification of the MCC surface, which made it more hydrophobic and improved its dispersion into the matrix. Furthermore, surface modification enhanced the MCC compatibility with the polymer phase and caused the interfacial interactions between the matrix and particles; therefore, no cracks were observed in the fracture surface area of the composite samples.

3.3.2. Mechanical properties

A uniaxial tensile test was conducted to evaluate the mechanical properties of the prepared samples. Fig. 4a illustrates the stress-

strain curves of the different samples at 25 °C and 50% relative humidity (RH). Furthermore, the values of yield stress, Young's modulus, and toughness of the samples are provided in Fig. 4b and Table S1. All samples first revealed a linear elastic deformation at low strain values, followed by a yield point and a plastic deformation region at higher strain values. The neat copolymer had the lowest tensile (Young's) modulus and vield stress, whereas it had the highest elongation at break and tensile strength. Although both tensile modulus and yield stress increased systematically on increasing SMMCC simultaneously, elongation at break and tensile strength were reduced. In other words, the addition of the filler improved the mechanical performances at the elastic deformation region, whereas it depressed the properties in the plastic deformation area. For instance, the tensile modulus and yield stress increased by approximately 100% and 50%, respectively, in the sample containing 30 wt% SMMCC, suggesting the formation of stiffer structure on the filler addition. On the other side, the tensile strength and elongation at break decreased by approximately 40% and 140%, respectively. Accordingly, it may be concluded that SMMCC did not act as a reinforcing material. To better judge the reinforcing effect of the SMMCC, the stress-strain curves of the samples were more investigated. The pure copolymer presented strain hardening at large strain deformation, in which the polymer chains and lamellar crystals oriented along with the applied force and consequently caused the sample to reveal higher tensile strength at a breaking point and toughness. This behavior can explain why it presented ductile rather than brittle failure, as previously observed in the SEM images. By introducing the SMMCC into the matrix, the polymer chains could not orient easily along with the applied force because of the formation of rigid and robust networks. As a result, they revealed lower tensile strength and elongation break values. Expressly, these lower values could not be the criteria for judging the negative impact of the addition of SMMCC on the mechanical properties of the matric because in most engineering applications, the structures are not supposed to stretch too much, and they are used in their linear elastic region. On the other hand, because both tensile modulus and yield stress values were improved significantly over the addition of SMMCC, it can be concluded that the SMMCC acted as a reinforcing material. To



Fig. 3. SEM images of the cryofracture surfaces of (a) PA-SMMCC5, (b) PA-SMMCC10, (c) PA-SMMCC20, and (d) PA-SMMCC30 (magnification 400×).



Fig. 4. (a) Stress-strain curves, (b) comparison between Young's modulus, yield stress, and toughness, (c) storage modulus and loss modulus versus temperature, and (d) tan δ versus temperature. Solid and blank symbols indicate E' and E", respectively.

further substantiate this claim, the mechanical properties of the composite sample with 30 wt% virgin MCC (untreated) are provided in Fig. 4a and Table S1. The mechanical properties dropped considerably, confirming the poor adhesion between MCC and the matrix as well as ununiform dispersion of the particles into the matrix, as previously observed in the SEM image, which arose from the super-hydrophilic nature of MCC. This result strongly supported the need for cellulose surface modification when it was supposed to be used as a reinforcing filler.

It is interesting to note that the improvement in the mechanical properties of the PA-cellulose composites reported in the literature was observed at a significantly lower filler content (less than 10 wt %) [2,16,21] because of embrittlement of the matrix at higher loading of the cellulose; nevertheless, in the present study, the improvement was discovered at a relatively higher amount of the filler (30 wt%), and the sample was not still brittle. Although the toughness of the sample with 30 wt% SMMCC was 40% of the value calculated for the pure copolymer, it was reported as less than 5% of the pure PA matrix in similar kinds of literature [16,21]. Of note, in the present study, the composite sample with 40 wt% SMMCC was also prepared. However, because its mechanical properties (Fig. S6) and rheology (Fig. S7) were poor, it was not further examined.

The dynamic mechanical properties of the samples were also investigated using DMA. Fig. 4c presents the trend of storage modulus (E') and loss modulus (E'') versus temperature and SMMCC loading. E' and E'' increased on increasing the SMMCC content throughout the entire temperature range, indicating that the fillers dispersed uniformly and reinforced the polymer matrix. The results were in good agreement with similar research reports on cellulose-reinforced PA matrices [2,13,16,60]. The improvement was more dominant at the higher loading of the filler. For instance, at 30 °C, E' was 907, 972, 1,172, 1,173, and 1,407 MPa for pure matrix and composite samples with 5, 10, 20, and 30 wt% of SMMCC,

respectively. In other words, 40% improvement was obtained by the addition of 30 wt% SMMCC. On the other side, the storage modulus of all samples revealed a severe drop in temperatures between 50 and 60 °C, suggesting that the polymer chains experienced a transition from a rigid state to a more flexible rubbery state. The temperature at which this transition occurs, known as the glass transition temperature (Tg), can be extracted from the maximum of the tan δ -temperature curve. Fig. 4d displays the tan δ curves of all samples as a function of SMMCC content. T_g of the samples varied between 52 °C and 60 °C, corresponding to α relaxation in the amorphous phase of the copolymer. It was elevated slightly when increasing the filler content, revealing that SMMCC promoted a positive enhancement in modifying the Tg because of the improved compatibility at the filler-matrix interface, similar to that reported in the literature on polymer cellulose composites [26,61]. This improvement could also be attributed to the restriction of mobility of PA chains, arising from strong hydrogen bonding between cellulose particles and polymer chains [62].

3.3.3. MFI, viscosity, and viscoelastic properties

Melt flow properties of the pure copolymer and composite samples were evaluated through MFI and rheology measurements to further investigate the compatibility between the two phases and the state of dispersion of fillers into the polymer matrix [63]. The MFI represents the ability of the molted thermoplastic polymer to flow under pressure, being inversely proportional to viscosity; the higher the MFI, the lower the melt viscosity [64,65]. Fig. 5a shows the MFI of the PA11, PA12, copolymer, and composite samples. The MFI of the synthesized PA11 and PA12 in the present study had good agreement with those reported in the literature [66]. The MFI of the copolymer was significantly higher than that of PA11 and PA12, indicating its better flowability at the test conditions that could be attributed to its relatively lower melting point and molecular weight than the synthesized PA11 and PA12 [67]. It has been reported that the higher MFI of the polymer leads to better interaction between the wood fillers and the matrix and better adhesion and overlapping between them [64]. Accordingly, the synthesized copolymer could be a better candidate for blending with cellulose-based fillers than the PA11 and PA12.

A systematic decrease was observed in the MFI of composite samples with different loading of SMMCC particles, suggesting an increase in the viscosity of the samples attributing to the stiffening effect of the filler particles and the formation of the robust networks into the copolymer matrix. Fig. 5b represents the complex viscosity of the melt samples as a function of the shear rate. All samples displayed frequency independence or Newtonian behavior at lower frequency values, whereas the viscosity dropped at higher shear rates, indicating a non-Newtonian trend known as shearthinning behavior. The Newtonian behavior transition to the non-Newtonian one happened at lower frequencies on increasing the filler concentration. At lower frequency values, the polymer chains have enough time to orient along with the applied shear force, whereas at higher frequencies, because of the lack of time for PA chains to orient during the applied shear force, the samples revealed a shear-thinning viscosity. Disturbing the formation of PA chain entanglements in the composites caused by the orientation of rigid MCC molecules, as well as the temporary destruction of the MCC network-like structure at higher frequencies, has also been reported as a reason for the shear-thinning behavior of PA/cellulose composites [63,68]. A more considerable shear-thinning behavior in the composite samples suggested that the stress transfer from the matrix to the filler particles, enhanced by the presence of interfacial bonds, resulted in more orientation of cellulose

molecules [21]. On the other side, the viscosity of the composite samples was significantly higher than that of the pure matrix, particularly at lower frequencies. For instance, at an angular frequency of 0.103 rad/s, the complex viscosity was approximately 740 Pa s for the copolymer, whereas it was approximately 1,160 Pa s, 1,370 Pa s, 1,320 Pa s, and 2,100 Pa s for composite samples with 5 wt%, 10 wt%, 20 wt%, and 30 wt% of SMMCC, respectively. This improvement, ascribing to the hindering of the mobility of the PA chains by the MCC particles, suggested the strong interfacial adhesion between PA chains and cellulose molecules obtained through successful surface modification of MCC with long-chain aliphatic isocyanate molecules [68,69].

A strain sweep test at a fixed frequency of 1 Hz was conducted to find the linear viscoelastic region of the samples. As Fig. 5c depicts, both storage and loss moduli revealed linear behavior throughout the strain rate. Accordingly, 10% was selected as a strain value to guarantee the frequency sweep test was in the linear viscoelastic region. The variation of storage modulus and loss modulus versus frequency is provided in Fig. 5d. Both G' and G" increased with increasing frequency, especially at higher frequencies, and were considerably higher in composites than those in the copolymer, indicating that the SMMCC particles had a substantial effect on the chain relaxation of the copolymer. It has been reported that most of the deformation energy is lost to the friction between the mutual relative motion polymer chains; therefore, at lower frequencies where the polymer chains had sufficient time to start disentangling, G' was low. Nevertheless, the polymer chains revealed more rigidity and inflexibility at higher frequencies, resulting in higher storage modulus values [63]. On the other side, the higher storage modulus values in composite samples, particularly at lower



Fig. 5. (a) MFI, (b) complex viscosity versus angular frequency, (c) strain sweep at a fixed frequency of 1 Hz, and (d) frequency sweep at a fixed strain rate of 10% at 200 °C. Solid and blank symbols indicate G' and G'', respectively.



Fig. 6. (a) Water vapor transmission of the pure matrix and composites at 25 °C and 50% RH and water absorption capacity after 24 h, (b) water contact angle of the pure matrix and composites at 25 °C versus time, and (c) to (g) digital photographs of the water droplet on the surface of different samples after 60 s.

frequencies, indicating the excellent stress transfer from the matrix to the filler particles, could be explained by the fact that cellulose particles restricted the deformation of the polymer chains by the formation of robust networks into the polymer matrix. It could also be attributed to the stiffness imparted by the MCC particles [68]. Further investigation of Fig. 5d identified that G' was more sensitive to the filler concentration than G", and throughout the frequency range, G["] was always higher than G'. The latter suggested a terminal of a liquid-like behavior in which the polymer chains were fully relaxed at the test conditions, and both moduli were dependent on the frequency [5]. The reduction of the modulus dependency on frequency in the composite samples indicated the desire of the polymer chain to present a solid-like behavior, which could be due to the interconnected or network-like structure formation through filler-filler and strong polymer-filler (interfacial) interactions, restricted the viscous motion of polymer chains, and enhanced the system's elasticity [21]. In the composite sample with a 40 wt% filler, Fig. S7a, G' was always higher than G", suggesting that the polymer chains were not fully relaxed at the test conditions and a semi-solid structure formed at such a high filler content. Accordingly, this sample exhibited extremely higher complex viscosity (357,000 Pa/s at an angular frequency of 0.103 rad/s) than the pure matrix and the other composites, Fig. S7b. Of note, its processing was also poor during melt blending in extrusion. All in all, it seems 30 wt% was the highest possible filler content to have suitable viscoelastic performances for melt blending.

3.3.4. WVT, WA capacity, and contact angle

WVT, indicating the amount of vapor transmitting per unit area, is an important polymer film property in certain applications like the packaging. It can also be used to evaluate the adhesion between the particles and the polymer matrix in the interface region. The WVT will be low if an excellent adhesion takes place between the fillers and matrix because, in this case, there will be few places for water to penetrate [70]. As Fig. 6a depicts, the WVT of the pure matrix was relatively low (8.64×10^{-05} g/m/day), which further decreased in composite samples. For instance, the WVT of the PA-

SMMCC30 sample was 3.83×10^{-05} g/m//day, 44% lower than that of the pure matrix. This reduction proposed the uniform dispersion of the hydrophobic components into the PA matrix, even at very high filler content and excellent adhesion between two phases, which blocked the moisture pathway between the polymer chains and made impermeable regions in the matrix [71]. This reduction, known as the tortuosity effect induced by well-dispersed cellulose, was previously reported for polylactic acid nanocellulose composites [72].

The result of the WA measurement is provided in Fig. 6a. It was approximately 1% for pure co-PA, which was relatively lower than that reported for short-chain PAs, whereas it was close to reported values for long-chain aliphatic PAs [5,18]. This relatively low WA capacity could be due to the low amide:methylene density in the polymer backbone. On the other hand, although our results confirmed that the surface modification successfully converted the MCC surface to a hydrophobic one, its addition to the matrix slightly increased water uptake capacity, which could be explained by intrinsically higher hydrophilicity of SMMCC than pure co-PA.

The hydrophobicity of the film surface was further investigated through water contact angle measurements, Fig. 6b–g. The measured water contact angle was in the range of 70° – 85° , which might be defined as being hydrophobic [43]. The contact angle increased slightly on increasing the SMMCC content, in good agreement with the WVT results, suggesting an improvement in water hydrophobicity of the film surface after presenting the filler. The contact angle did not show considerable change against time; furthermore, the droplet volume preserved significantly after 60 s, suggesting that no considerable WA happened on the surface of the samples [73].

4. Conclusion

A new type of low—melting point PA with a melting degree of 160 °C was synthesized through a polycondensation reaction between 11-aminoundecanoic acid and 12-aminolauric acid. The MCC surface was also treated by substituting ODI molecules with hydroxyl groups of MCC. Approximately 16 wt% ODI molecules were grafted on the surface of MCC, and a super-hydrophobic surface with a water contact angle of 130° was prepared. The SMMCC was dispersed uniformly into the PA matrix even at a high filler content of 30 wt%. Furthermore, excellent adhesion between the fillers and the matrix led to significant improvement in visco-elastic performances, mechanical properties, and WVT of the pure matrix. Altogether, the current findings proposed the sustainable low—melting point composites with a bio-based content of up to 60% for substitution with petroleum-based polymers for specific engineering applications.

Author statement

Hossein Baniasadi: Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, and Visualization; Jon Trifol: Formal analysis, Investigation; Sami Lipponen: Formal analysis, Investigation; Jukka Seppälä: Supervision, Funding acquisition, Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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