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Using Hansen Solubility Parameters to Predict Dispersion of Nano-Particles in Polymeric Films

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S. Gårdebjer,[a,b*] M. Andersson,[c] J. Engström,[d] P. Restorp,[d] M. Persson, [b,d] and A. Larsson [a,b]

We suggest a rough and straightforward method to predict the dispersability of modified cellulose nanocrystals (CNC) in nanocomposites using Hansen solubility parameters (HSP). The surface of CNC was modified using a novel approach where Y-shaped substituents with two different carbon chain lengths were attached. Approximate HSP values were calculated for the modified CNC and the dispersion of unmodified and modified CNC in solvents with varying HSP's was studied. The best dispersability was observed in dichloromethane, when the CNC surface was modified with longer carbon chains. Dichloromethane has HSP similar to low-density polyethylene (LDPE). Therefore, nanocomposites with both unmodified and modified CNC were produced. The materials with modified CNC showed increased adhesion between the filler and the matrix, followed by a decreased water permeability compared to unmodified CNC; suggesting a better dispersability of modified CNC in LDPE and confirming the usefulness of this approach.

Introduction

Incorporation of nano-rods to enhance mechanical and barrier properties of a thermoplastic polymer has been widely studied[1-4]. One type of nano-rods that can be used is cellulose nanocrystals (CNC) which is derived from natural cellulose sources. CNC has a high strength and stiffness and is usually produced via acid hydrolysis[5, 6]. A major problem with the production of these nanocomposites, where a hydrophobic matrix material is combined with the more hydrophilic cellulose, is that the CNC tend to form aggregates which results in inhomogeneous nanocomposite films[5, 7, 8]. By attaching hydrophobic chains to the surface of cellulose, the CNC becomes more similar to the matrix material hence, an increased compatibility between the matrix and the filler can be achieved[1, 9, 10]. The cellulose surface modification can be done by polymerize hydrophobic chains directly on the surface, for example using a ring opening polymerization[10-13]. It is often difficult to know the length of the final chains attached to the surface and several complementary analysis techniques needs to be used. Another way to modify the surface of cellulose is to simply attach a known reactant to the surface, in this way the chemical structure of the substituent will be directly known[1, 14]. In a recent study, CNC were chemically modified with substituents of either 6, 12 or 18 carbon atoms in a straight chain and nanocomposites of LDPE were produced[1]. An increased homogeneity and dispersion was observed when longer chains were attached to the surface. In this study, we use a similar approach with varying chain lengths but we use a Y-shaped substituent and attach it to the surface of CNC as shown in Figure 1.

Even though there is a large amount of published work on different types of surface modifications, it can be difficult to predict the behavior and dispersability of newly modified CNC in a matrix. Hansen and Hildebrand solubility parameters can be used to predict the solubility of polymers in different solvents[15]. Similar methods for predicting the disperability of CNC as fillers in nanocomposites are available and the theoretical derivations of these methods give limited support that one could use them to predict the dispersion of CNC in solvents or polymer matrix materials. Recently, the dispersability of single-walled carbon nanotubes have been measured in a large amounts of solvents with varying Hildebrand and Hansen solubility parameters to propose appropriate solubility parameters for the nanotubes and graphene[16]. In another study, the Hildebrand solubility parameter for boron nitride nanotubes was extracted from light scattering experiments[17]. To achieve good properties of nanocomposites it is essential that the filler materials are well dispersed in the matrix. For old filler materials the industry have experience of how to disperse the fillers and get good nanocomposites, but for new modified fillers we urgently need calculations methods to rationalize and predict if successful nanocomposites can be manufactured or not. In this study we suggest a rough method by using standard calculation tool for Hansen solubility parameters for polymers and apply it to surface modified CNC when knowing the chemical structure of the substituents and approximatively degree of surface coverage.

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[a] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Göteborg, Sweden
[b] SuMo Biomaterials, VINN Excellence Centre, Chalmers University of Technology, 412 96 Göteborg, Sweden
[c] SP Technical Research Institute of Sweden, Box 5607, 114 86, Sweden
[d] Akzo Nobel Pulp and Performance Chemicals AB, 445 80 Bohus, Sweden
*Corresponding author

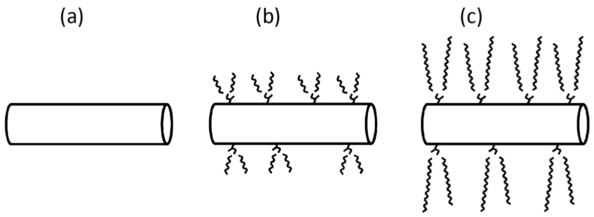

Figure 1: *Schematic image of the surface modification of CNC (a), where two types of chlorohydrin were used as reagents, one with chains consisting of 6 carbons as shown in (b) and one with chains equal to an average of 17 carbons as shown in (c).*

The aim of this study was two-fold: first to introduce a new way of modifying CNC by attaching Y-shaped hydrophobic chains to the surface of CNC by the reaction of a chlorohydrin. Second, we suggest a new efficient way predicting the compatibility between modified CNC and a matrix material of low density polyethylene (LDPE). Our hypothesis was that the dispersion behavior of CNC in solvents with different Hildebrand and Hansen solubility parameters will mirror the dispersability of the nanocomposites in matrix polymers. Furthermore, we assume that the Hansen solubility parameters could be predicted for surface modified CNC by using a computer method developed for compatibility studies of polymers in different solvents. Additionally, we also incorporate the unmodified and modified CNC in a matrix of LDPE, and show that our hypothesis seems to be valid. To support our work an extensive characterization of the nanocomposites was made.

Theoretical background

This section aims to describe the thermodynamics of a system of solvent and/or polymer in combination with nano-rods. In order to mix two materials thermodynamics require that Gibbs free energy, ΔG_{mix}, is zero or smaller at a certain temperature given by:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0 \qquad (1)$$

where ΔH_{mix} is the enthalpy of mixing and ΔS_{mix} is the entropy of mixing. It should be noted that a negative sign on ΔG_{mix} could also be a result of phase-separation resulting in a stable structure and hence not mixing and/or dissolution. However, for dissolution of polymers, the term ΔS_{mix} is positive due to the increased disorder. Flory have shown that ΔS_{mix} for a rigid rod, like cellulose nanocrystals, can be described by assuming formation of an isotropic solution at low concentration, and a nematic phase at higher concentrations according to Equation 2[18, 19]:

$$\Delta S_{mix} = -\frac{k}{v_0}\left[(1-\phi)ln(1-\phi) + \frac{\phi}{\frac{v_{NT}}{v_0}}\left(\ln\left(\frac{\phi}{x}\right) + (x-1)\right)\right] \qquad (2)$$

where ΔS_{mix} is the entropy of mixing per volume of mixture, ϕ is the solute volume fraction, v_0 and v_{NT} is the solvent and rod molecular volume respectively and x is the aspect ratio of the rods. Since rigid rods are much larger than a polymer, nano-rods have relatively small ΔS_{mix} compared to polymers[18].

For mixing of small molecules in a solvent ΔH_{mix} can be expressed as Flory-Huggins expression[20] :

$$\Delta H_{mix} = \chi\phi_1\phi_2 kT/v_0 \qquad (3)$$

or the Hildebrand-Scratchard expression:

$$\Delta H_{mix} = (\delta_{T,A} - \delta_{T,B})^2\phi_1\phi_2 \qquad (4)$$

where χ is the Flory-Huggins interaction parameter, and $\delta_{T,A}$ and $\delta_{T,B}$ are the Hildebrand solubility parameters of the solute and the solvent. The Hildebrand solubility parameter was first described by Hildebrand and Scott and is defined as the square root of the cohesive energy density[21] according to Equation 5:

$$\delta_T = \sqrt{\frac{E_{coh}}{V}} \qquad (5)$$

where V is the molar volume of the solvent and E_{coh} is the energy of vaporization. Combining Equation 3 and 4 gives Equation 6:

$$\chi = \frac{v_0}{kT}(\delta_{T,A} - \delta_{T,B})^2 \qquad (6)$$

where it can be seen that the Flory-Huggins parameter χ always is positive. Thereby, if mixing should occur, the solubility parameters for species A and B should be as close as possible in order to decrease χ and also ΔH_{mix} and ΔG_{mix}. It can be noted from Equation 4 that the concept using solubility parameters can never give negative ΔH_{mix} , which could happen for systems with specific interactions (e.g. hydrogen bonds). This is thus a limitation in the use of Hildebrand solubility parameters, there it is questionable to use this concept for such systems. In this study there e.g. carbon chain surface modified CNC and LDPE is used, no specific interactions are likely to occur.Even though, the Hildebrand solubility parameters are well documented for many solvents [22], it is also well known that it cannot describe a system alone. Hildebrand parameter is based on geometric mean approximation which only can be used for molecules or compounds that interact through London or dispersion interactions. However, molecular interactions also depends on dispersive, polar and hydrogen bonding interactions, which are described by the Hansen solubility parameter. Using Hansen solubility parameters, the solubility is divided into three parts:

$$\delta_{TOT}^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \qquad (7)$$

where δ_D, δ_P and δ_H represents the dispersion, polar and hydrogen-bonding interactions respectively.

Each component is evaluated indirectly and materials having similar Hansen solubility parameters have high affinity for each other[23]. Hansen solubility parameters for an unknown solvent or solute can be calculated by using software like Hansen Solubility Parameters in Practice (HSPiP)[24]. The HSPiP software consists of a database of Hansen parameters for a large number of solvents, but also allows estimation of Hansen parameters using molecular structure (entered in SMILES or InChI format) as input. The obtained Hansen parameters are calculated by an adapted neural network methodology where the full Hansen database dataset has been fitted to a model which takes inter-group interactions into account.Skaarup and Hansen further developed an equation to calculate the solubility parameter distance, R, between two materials[23]:

$$R = \sqrt{4(\delta_{D,1} - \delta_{D,2})^2 + (\delta_{P,1} - \delta_{P,2})^2 + (\delta_{H,1} - \delta_{H,2})^2} \quad (8)$$

The equations have so far been applied to low molecular weight molecules or polymers. In our case we have nano-rods - which are aggregates of polymer chains and not single chains dispersed in a solvent as was the principle concepts behind the models by Hansen and Skaarup. However, in comparison with the study for dispersion of carbon nanotubes in solvents, we suggest that the Hansen parameters for the CNC should match the Hansen parameters for the solvents, where longer carbon chains on the surface gives better dispersion of the nano-rods in the solvents. In order to make a first attempt following this suggestions, the unmodified and modified CNC will be dispersed in different solvents and the best dispersion in the solvent with similar Hansen solubility parameters as the matrix is suggested to give the best nanocomposite. This is not obvious, but goes back to the Hildebrand discussion around cohesive energies around the solute and solvent and assuming that the solvent only interacts with the surface of the nano-rod and that the majority of the materials in the nano-rods is not influencing the dispersion in either solvents or matrix materials. We also suggest that a software for prediction of dispersability in solvents for polymers could be used to calculate the Hansen parameter for a cellulose unit with either one or two substituents attached to the surface.

More in detail it has been discussed for nano-rods if surface energy may be a more appropriate way to predict the dispersability, instead of the cohesive energy. Bergin and coworkers suggested an equation[18]:

$$\chi_s = \frac{2v_0}{rkT}(\delta_{T,NT} - \delta_{T,sol})^2 \quad (9)$$

where *r* is the radius of a nano-rod and $\delta=\sqrt{E_{sur}}$ and E_{sur} is the surface energy of the nano-tubes and solvent respectively. An interesting observation is that in Equation 9 the radius - and not the aspect ratio - is included. In an attempt to calculate $\delta_{T,NT}$, Bergin and co-workers used Equation 5 and incorporated expressions for the volume of the nano-rods and the surface energy required to unattached the rods from each other in dry state. By doing so they could correlate to the surface energy rather than the cohesive energy according to:

$$\delta_T = 2\sqrt{\frac{E_{S,T}}{d}} \quad (10)$$

where E_{ST} is the surface energy and *d* is the diameter of the nano-rod. Equation 9 suggests that the dispersion of nano-rods in a solvent (or polymer) is maximized when the surface energies are as equal as possible. The surface energy can also be affected by the attachment of carbon chains. Both the length of the chains and the surface coverage will have an impact on the surface energy. In Equation 10, δ_T correlate directly to the surface energies and one can assume that the same reasoning can be made for dispersion of nano-rods in polymer matrices in composite materials.

Experimental

Production and surface modification of CNC

CNC was produced as earlier described by Bondesson et al[25]. In short, 40 g microcrystalline cellulose was hydrolyzed in 64% of sulfuric acid for 130 minutes in 45°C, followed by centrifugation at 4700 rpm (Sigma 4K15, Sigma Zentrifuges, Germany). The sediment was washed with several liters of deionized water and dialyzed in deionized water for 10 days, followed by ultrasonic treatment for 30 minutes on ice-bath. The CNC suspension was neutralized by the addition of 0.02 M NaOH and had a final concentration of approximately 0.5 wt% and the reaction yield was 40%.

Figure 1 shows a schematic image of the unmodified and modified CNC where the Y-shaped chlorohydrin has been attached to the surface. The R-groups represent carbon chains of either 6 or an average of 17 carbons. The reaction was carried out in a 90:10 volume mixture of DMSO:toluene. Exchange of water was performed by adding DMSO to the water suspension of CNC, followed by evaporation of water in a rotary evaporator. An additional amount of toluene was added and remaining water was evaporated by azeotrope formation with toluene.

The chemical modification of CNC was performed in a sealed round-bottomed reaction flask which contained 50 mL of CNC-DMSO:toluene suspension and either C6 or C17 chlorohydrin; four equivalents was used to be sure to cover all the available sulfate ester groups on the CNC surface. The content of hydroxyl groups/sulfate ester groups available to react in the surface of CNC is approximately equal to $1.14\cdot10^{-3}$ mmol OH[26], meaning that 0.7 g and 1.2 g of chlorohydrin C6 and C17 was added, respectively. The reaction was carried out for 17 hours at 90°C in an oil bath under constant mechanical stirring. The excess of chlorohydrin was removed by adding the reaction mixture drop wise to a beaker with approximately 400 ml ethanol under constant stirring. The suspension was centrifuged at 5100 rpm for 10 minutes and the centrifugation was repeated twice. The washed modified CNC was kept in ethanol until further use. The modified CNC with the different chlorohydrins will be denoted as CNC6, and CNC17, respectively.

Characterization of modified CNC

Fourier Transform Infrared (FT-IR) analysis was performed on modified CNC, unmodified CNC and the pure chlorohydrins. The samples were pulverized and mixed with KBr at a ratio of 10:1 (KBr/sample). KBr-tablets with an area of 132 mm^2 were prepared by pressing the mixture at 1 ton for 1 min and then at 10 tonfor 1 min. Spectra were scanned from 400–4000 cm^{-1} in a 2000 FT-IR spectrometer (Perkin Elmer, England) with a resolution of 4.0 cm^{-1} and 20 scans per sample. A pure KBr-tablet was used for background subtraction.

Elemental analysis (Vario Micro Cube, Frankfurt) was used to determine the amount of carbon, nitrogen and oxygen in unmodified CNC as well as modified CNC. The sample was wrapped in small tin capsules and tin canisters and introduced into a firing tube where it was burned at 1150°C. The product gases N_2, CO_2, H_2O and SO_2 were measured by a hot wire detector.

Approximate Hansen solubility parameters for the addition of either one or two substituents to one glucose unit (Figure 2) were calculated using the software Hansen Solubility in Practice (HSPiP) developed by Abbott and Yamamoto[24]. The reason both one and two substituents were calculated is that it is not possible to know exactly how many substituents are attached per glucose, but using HSP values for both one and two substituents will give enough information to test the suggested hypothesis.

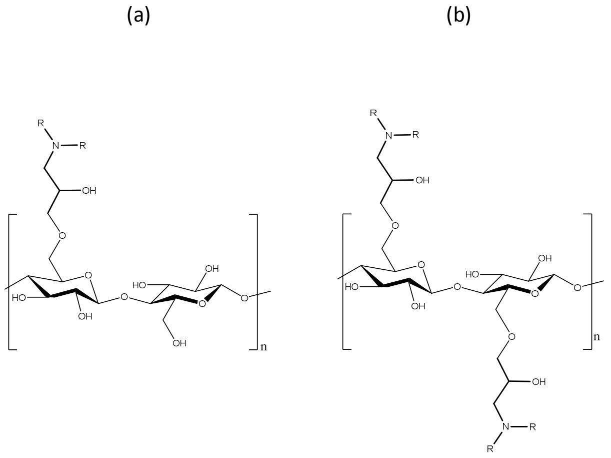

Figure 2: *Schematic image of the molecules used for calculation of Hansen solubility parameters, in (a) one substituent and (b) two substituents. R represents carbon chains of either 6 or an average of 17 carbons.*

Table 1. *Hildebrand (δ) and Hansen (δ_{TOT}) solubility parameters for solvents used in the study[22] (where δ_D is the dispersive, δ_P is the polar and δ_H is the hydrogen bonding interactions of HSP).*

Solvent	**δ (MPa$^{1/2}$)**	**δ_{TOT} (MPa$^{1/2}$)**	**δ_D (MPa$^{1/2}$)**	**δ_P (MPa$^{1/2}$)**	**δ_H (MPa$^{1/2}$)**
Water	23.5	47.8	15.6	16.0	42.3
Methanol	14.3	29.6	15.1	12.3	22.3
Ethanol	12.9	26.5	15.8	8.8	19.4
Butanol	11.3	23.2	16.0	5.7	15.8
Dichloromethane	9.8	20.2	18.2	6.3	6.1
Toluene	8.9	18.2	18.0	1.4	2.0
Heptane	7.4	15.3	15.3	0	0
LDPE[‡]	7.9	17.8	16.5.	5.9	4.1

[‡] 27, 28

Dispersion test of cellulose nanocrystals in solvents with varying solubility parameters

Solvents with varying Hildebrand and Hansen solubility parameters were chosen according to Table 1. 0.5 wt% of the unmodified and modified CNC were added to the different solvents. Due to the large differences in solubility parameters, it is not possible to change directly from water to dichloromethane and the solvents with lower solubility parameters. Therefore, the solvent had to be exchanged by centrifugation, using either methanol or acetone as an intermediate solvent. In these cases the CNC was washed for at least three times to remove all access water and thereafter the desired solvent was added. The dispersability of CNC in the different solvents was visually studied immediately after exchange.

The parameters for LDPE are shown at the bottom of the table, where Hildebrand parameter for LDPE is equal to 7.9 and Hansen parameter is equal to 17.8 for LDPE[27,28]. Toluene and Heptane have Hildebrand values closest to LDPE, while dichloromethane have similar Hansen solubility parameters. These solvents are therefore the preferred solvents to study for indication of dispersability of modified CNC in LDPE.

Production and characterization of nanocomposite materials

Nanocomposites were prepared by combining LDPE (Sigma Aldrich, USA) with either unmodified or modified CNC. The film preparation was done via solvent casting followed by hot-melt pressing. The filler content were chosen to 1, 3, and 5 wt% to a total amount of 400 mg. The solvent of CNC or modified CNC was exchanged by centrifugation to *p*-xylene through several centrifugation steps using ethanol and dichloromethane as intermediate solvents. The dispersion of the different CNC:s and *p*-xylene was transferred to a glass vial and LDPE was added. The vial was placed in an oil bath with a temperature of 110°C and left for LDPE to dissolve while stirred. The hot dispersion was immediately poured onto a pre-heated Petri dish (100°C) and a lid was placed on top. The dishes were left in a fume hood to evaporate for 24 hours and the dry films were kept in a vacuum oven at 40°C for three days. Nanocomposite films were hot-melt pressed at 120°C and 3 bars for 4 minutes and final films were kept in a desiccator with silica orange until use.

Film transparency was determined by measuring the percent transmittance between 1000 and 200 nm using a spectrophotometer (Algient Technologies Cary60 UV-Vis, USA). Creep and strain recovery of the films were tested in a dynamic mechanical analyzer at 25°C (DMA Q-800, TA Instruments, USA). Film samples of 5.7 mm wide were mounted using a conventional film clamp. The average thickness of the films was 50 µm and the preload force was set to 0.01 N. The films were displaced at a pressure of 1 MPa for 10 minutes and recovered for 10 minutes.

Permeability measurements were performed in diffusion cells[8, 29]. A film sample, with recorded average thickness, was placed in between a donor and an acceptor chamber. 15 ml of MilliQ-water was added to each chamber and 10 µl of ^{3}[H]-labeled water was added to the donor chamber. The solution was stirred by placing the diffusion chambers on a rotating table at 50 rpm (Edmund Bühler 7400, Germany). Due to the large difference in radioactivity between the donor and acceptor chambers, the donor chamber concentration was considered as constant during the whole experiment. Following the permeation measurement, samples of 500 µl were taken from the acceptor chamber and immediately replaced with an equal amount of pure MilliQ-water. Samples were assayed with a scintillation liquid, Ultima Gold, and run in a liquid scintillation analyzer (Tri-Carb B2810TR, Perkin-Elmer, USA). The mass transfer rate was calculated according to Equation 11, using Fick's first law for steady state mass transfer rate through a film:

$$J = DKA\frac{c_d - c_a}{h} = PA\frac{c_d - c_a}{h} \qquad (11)$$

where *J* is the flux, c_d and c_a correspond to the donor and acceptor chamber concentrations respectively, *A* is the membrane area, *h* is the film thickness, *D* is the diffusion coefficient, *K* is the partition coefficient and P is the permeability. The flux J, was calculated from the linear slope in a plot of accumulated water against time.

Results and discussion

This section will first describe the new synthesis and characterization of the modified CNC. Thereafter, we use the modified CNC to suggest how one can predict the dispersion in nanocomposite materials in polymer matrixes by (i) disperse the different CNC in solvents, and (ii) disperse CNC and modified CNC in the model polymer matrix (in this case LDPE). An extensive characterization of the films will be presented in the end to support the findings.

Characterization of surface modification

Figure 3 shows the FT-IR spectra for the unmodified CNC (black line), modified CNC17 (dashed line) and the pure chlorohydrin (dotted line). The spectrum of the modified CNC is similar to the spectrum with unmodified CNC; however the peaks appearing around 2922 cm^{-1}, corresponding to methylene groups, are different for the unmodified and modified CNC. For the chlorohydrin, a second peak appears at 2852 cm^{-1} and a third at 1446 cm^{-1} which correspond to the methyl groups present only in the chlorohydrin. These peaks are also present for the modified CNC, which indicates a successful modification. Additionally, CNC is produced via acid hydrolysis using sulfuric acid, and therefore it is believed that the surface of CNC is covered with C-O-SO_3 groups[30]. The peak at 807 cm^{-1} corresponds to the vibration of C-O-S and is present for both CNC and CNC17 which confirms presence of sulfate ester groups.

Elemental analysis was run on unmodified CNC and modified CNC and the amount of nitrogen was compared for the samples, since the chlorohydrins have nitrogen in the molecular structure. The unmodified CNC showed a nitrogen amount less than 0.2 %, while the CNC6 showed a value around 0.7 %. The CNC17 showed the highest value of nitrogen (1.4%), indicating that the surface modification with the longest chains was most successful.

An average distance between substituents on the surface of the nanocellulose was estimated to around 5 Å for CNC17. This was done by using the nitrogen content and assuming that the size of the nano-rods are equal before and after substitution, a density of the cellulose nano-rods equal 1.5 g/ml and a diameter of 10 nm. This estimation shows that the coverage of substituents on the cellulose nanocrystals are high.

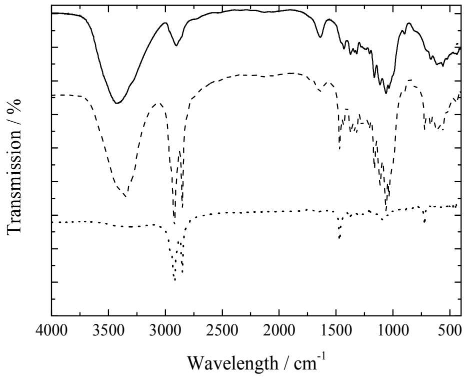

Figure 3: *FT-IR spectra for unmodified CNC (black line), surface modified CNC17 (dashed line) and the pure chlorohydrin (dotted line) used in the reaction for surface modification.*

Dispersion of cellulose nanocrystals in solvents with varying solubility parameters

Hansen solubility parameters were calculated for the molecules presented in Figure 2 as well as a cellulose unit without any substituents. Using Equation 8, the distance between the solvents and the unmodified and modified CNC could be calculated. Figure 4a-c shows the calculated distances in the different solvents and photographs of the dispersions of unmodified and modified CNC going from higher to lower solubility parameters from left to right. According to the calculations, unmodified cellulose (Figure 4a) has the shortest distance to methanol and hence should show the best dispersability in this solvent, which also can be seen to be the case. However, water also shows an almost transparent appearance while the distance to water is equal to 22. It should be noted that the CNC has charged sulfate ester groups attached on the surface, and is thereby stabilized by electrostatic interactions, which explains the good dispersion in water. Using solvents with lower solubility parameters resulted in aggregation of the unmodified cellulose, which can be seen as white assemblies in the bottom of the flask.

Figure 4b shows the calculated distance for CNC modified with one or two attached substituents with short chains. In the graphs one can see that the calculated R values for one and two substituents varies as expected with the solubility parameters and has a minimum. This minimum appears differently for one and two substituents; indicating as expected that the disperability of modified CNC in solvents depends on the number attached substituents. For one substituent, MeOH, EtOH and BuOH shows the shortest distances according to the graph. When instead two substituents were attached to the cellulose unit, BuOH and DCM are the preferred solvents. Studying the dispersions in the flasks, solvent 2-5 were also observed to be the favored ones for the modified CNC6, while aggregation and sedimentation is seen for water, toluene and heptane, i.e. solvent 1, 6 and 7. Interestingly, the calculated R values for one and two substituents crosses each other when the solubility parameters for the solvents are decreased. For the largest solubility parameters (water) the R values is lowest for CNC with two attached substituents per monomer unit compared to one unit and the opposite is observed for the solvent with lowest solubility parameter. This appears at a first glance strange and can be explained by the differences in interaction parameters as presented in Figure 5.

For the CNC17 with one chain attached to the cellulose unit, BuOH and DCM are the preferred solvents according to the graph (Figure 4c). Two longer chains of C17 have the shortest distance to DCM according to Equation 8, which also correlate well with the observations in Figure 4c. For the modified CNC17, solvent 1-3 show an opaque appearance, meaning that aggregation has occurred. Further, the dispersion looks more transparent in butanol, DCM and toluene which then indicates a better dispersion. However, solvent 8 i.e. heptane shows an opaque appearance and hence agglomeration has occurred.

Going into more details, the different interaction parameters (δ_D, δ_P and δ_H) for the Hansen solubility parameters both for solvents and calculated ones are shown in Figure 5. Cellulose shows values closest to methanol while the addition of two substituents are closer to butanol and dichloromethane. It should also be noted that the longer chains show interactions parameters closer to dichloromethane compared to the shorter chains.

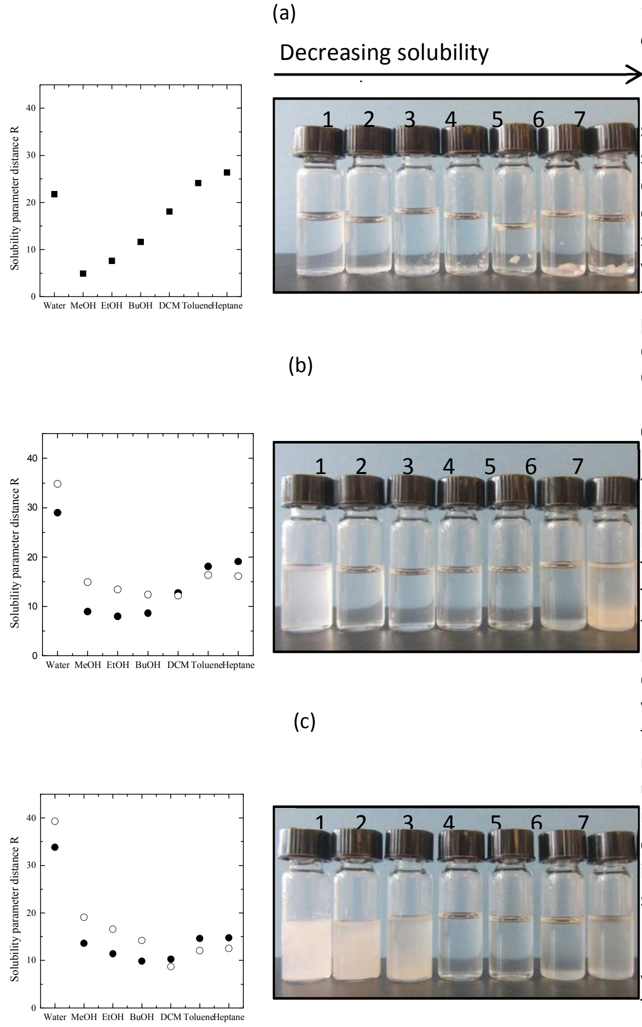

Figure 4: *Graphs showing calculated solubility parameter distances between the indicated solvents and unmodified cellulose (■), cellulose with either one (○) or two (●) substituents attached. Photographs show the dispersion in the different solvents immediately after mixing in a) unmodified CNC; b) CNC6 and c) CNC17.*

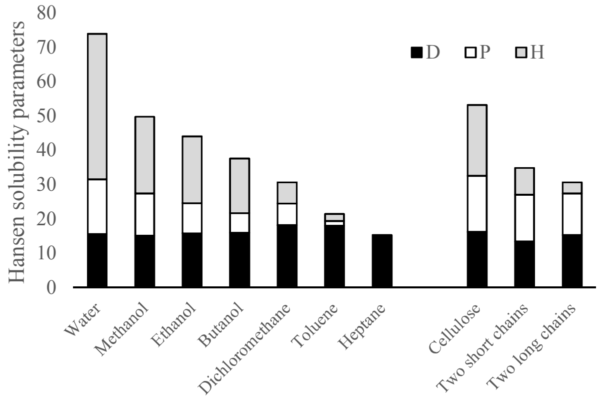

Figure 5: *Interaction parameters for Hansen solubility parameters. Tabulated values for solvents are used and the calculated values for cellulose and surface modified CNC.*

From these findings, it can be suggested that unmodified CNC has Hansen solubility parameters similar to methanol (δ_{TOT}=29.6). The surface modification of CNC decreased the calculated Hansen solubility parameters for both CNC6 and CNC17 at the same time as clearer dispersions was observed for solvents correlating to values of δ_{TOT} =23.2-29.6 for CNC6 and δ_{TOT}=20.1-23.2 for CNC17. This suggests that the modified CNC should disperse better in LDPE which has a Hansen solubility parameter equal to 17.8, compared to the unmodified CNC. Since LDPE has the Hansen solubility parameters closest to DCM, this method suggests that the dispersion of CNC17 should be the most homogenous, followed by CNC6 and unmodified CNC.

Characterization of nanocomposite material

The transmittance, creep properties, and water permeability for the produced nanocomposites were studied. The films were produced by solvent casting from *p*-xylene, followed by hot-melt pressing. The appearance of the films after solvent casting was a bit opaque. This can be due to solvent residues or the formation of pores in the films during the casting as earlier discussed[8]. After hot-melt pressing, the films were more or less transparent and no major differences could be seen by visual inspection. The transmittance was measured using UV-Vis at 660 nm. Pure LDPE shows the highest transmittance of 95%. The addition of both unmodified and modified CNC resulted in a decreased transmittance, for unmodified CNC 66±3% and for CNC6 65±6%. The films with modified CNC17 showed the smallest decrease and a transmittance of 73±4% were observed for these films. The smaller decrease indicate that the nano-rods with the longer chains attached to the surface are better dispersed in the matrix.

Figure 6a-b shows the creep and strain recovery for pure LDPE as well as the films consisting of 5 wt% unmodified and modified CNC. The film of pure LDPE as well as the films containing unmodified CNC or CNC6 crept to approximately 130%, while the film with CNC17 only crept to 97%. Since the creep was not affected after addition of unmodified CNC or CNC6, this indicates that the adhesion is poor between LDPE and unmodified CNC, and between LDPE and CNC6. For the films with an addition of 5 wt% CNC17, an increased adhesion between the matrix and filler modified CNC can explain the improved resistance to creep. The film with CNC17 does also recover the fastest to an extent of 93 %. The nanocomposite with CNC6 do also recover to 93% but takes a bit longer time. Pure LDPE film and the film with unmodified CNC recover to 90% and 89% respectively.

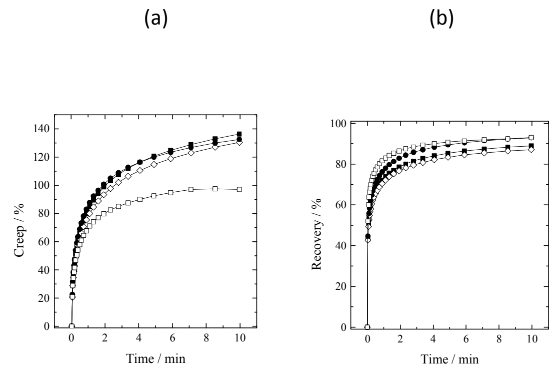

Figure 6: *(a) Creep and (b) strain recovery for the composite films consisting of 5 wt% CNC, showing LDPE (■), CNC (◊), CNC6 (●), and CNC17 (□). (n=2)*

Water permeability was measured in diffusion cells and the results are shown in Figure 7. Pure LDPE film showed a water permeability of $6.6{\cdot}10^{-13}$ m^2/s while the addition of unmodified CNC resulted in an increased water permeability compared to pure LDPE. However, the high standard deviations for the unmodified CNC make it difficult to interpret the data and are probably a result of the poor dispersion and aggregation formation in the hydrophobic matrix. The addition of modified CNC6 resulted in a small decrease of the water permeability compared with the pure LDPE film. The addition of CNC17 resulted in a larger decrease of water permeability compared to pure LDPE. According to Nielsen theory, the addition of an impermeable filler is believed to decrease the permeability due to an increased tortuosity path for the permeant [31]. Another factor known to decrease the permeability is increased crystallinity of the matrix, which can be induced upon addition of a filler. In these cases, the filler function as a nucleating site from where crystals can grow in the matrix material. This has been shown to be advantageous when the filler is well dispersed[13]. In our case, the addition of CNC17 is believed to result in improved dispersion compared to unmodified CNC and CNC6, which is strengthen by the results from the creep test. Another important issue is that even if the filler is considered impermeable, there could be available sites where water molecules could be trapped, hence resulting in a decreased water permeability when the water in that case follow the dual-sorption kinetics. Improved dispersability is advantageous also in this case. If so, the permeability should be lowest for the nanocomposites where CNC17 have been added, which is confirmed in Figure 7.

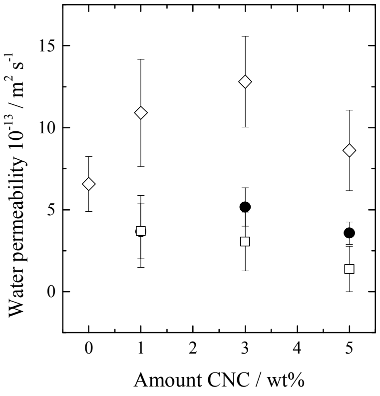

Figure 7: *Water permeability of LDPE and the composite films showing the addition of CNC (◊), CNC6 (●), and CNC17 (□). (n=3-5)*

In summary, we have presented a new way to synthesize the surface of cellulose nanocrystals and we have made a first trial to suggest a rough and straightforward method where we can predict good dispersability in a hydrophobic polymer by the use of solvents with varying Hansen solubility parameters. The modified CNC with the longest chains attached to the surface dispersed well in LDPE, in agreement with the results from the dispersability test in different solvents. The properties such as creep resistance and strain recovery of the composite materials were improved compared to the pure LDPE films or the films with unmodified CNC. Water permeability decreased for the nanocomposites with modified CNC, which indicates an improved adhesion and compatibility between the filler and the matrix material. It should however be pointed out that it was only the dispersability of three different nano-fillers that were tested in one polymer in this study. Other effects such as conformation entropy and steric constraints due to the surface modification could have impact on the dispersability and to further validate the suggested method several nano-fillers and polymers has to be evaluated. One way to do so is to disperse CNC in several solvents, and correlate the Hansen solubility parameters directly with different polymers.

Conclusions

This study proposes a simple and straightforward approach to predict the dispersion of unmodified and modified cellulose nanocrystals in a hydrophobic polymer. At the same time, we present a new synthesis for surface modification of cellulose with a Y-shaped substituent. Two different chain lengths of the substituent were used and approximate Hansen solubility parameters were calculated for modified and unmodified CNC. Longer chains on the substituent suggested improved dispersion in a hydrophobic polymer, which was shown when producing nanocomposite materials of LDPE. The creep and recovery properties as well as the water permeability of the produced composite materials were studied and the results showed that surface modification with longer chains improved the adhesion between the matrix and the filler. The water permeability also decreased to a higher extent for the materials with longer carbon chains on CNC, which can indicate that a better adhesion between the filler and the matrix materials. However, in order to fully validate this suggested method, dispersion of the CNC should be tested in additional solvents. These solvents should then be chosen to correlate their Hansen solubility values with different polymers.

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New surface modification and calculation of Hansen solubility parameters to predict the dispersability of cellulose nanocrystals in LDPE.