



(51) International Patent Classification:

C08B 15/00 (2006.01) *C08J 9/28* (2006.01)
B01J 20/285 (2006.01) *C08L 1/02* (2006.01)
C08J 5/24 (2006.01) *C08L 61/00* (2006.01)

(21) International Application Number:

PCT/CA2014/000289

(22) International Filing Date:

25 March 2014 (25.03.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/804,999 25 March 2013 (25.03.2013) US

(71) Applicant: **THE UNIVERSITY OF BRITISH COLUMBIA** [CA/CA]; University - Industry Liaison Office, #103 - 6190 Agronomy Road, Vancouver, British Columbia V6T 1Z3 (CA).

(72) Inventors: **MACLACHLAN, Mark**; #310 - 1696 West 10th Avenue, Vancouver, British Columbia V6J 2A1 (CA). **KHAN, Mohammad**; 117-8675 French Street, Vancouver, British Columbia V6P 4W5 (CA). **GIESE, Michael**; 3651 West 14th Avenue, Vancouver, British Columbia V6R 2W6 (CA).

(74) Agent: **SMART & BIGGAR**; Suite 2200, 1055 West Georgia Street, Box 11115, Vancouver, British Columbia V6E 3P3 (CA).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: POLYMER MATERIALS AND COMPOSITE MATERIALS WITH CHIRAL NEMATIC STRUCTURES AND PREPARATION METHODS THEREOF

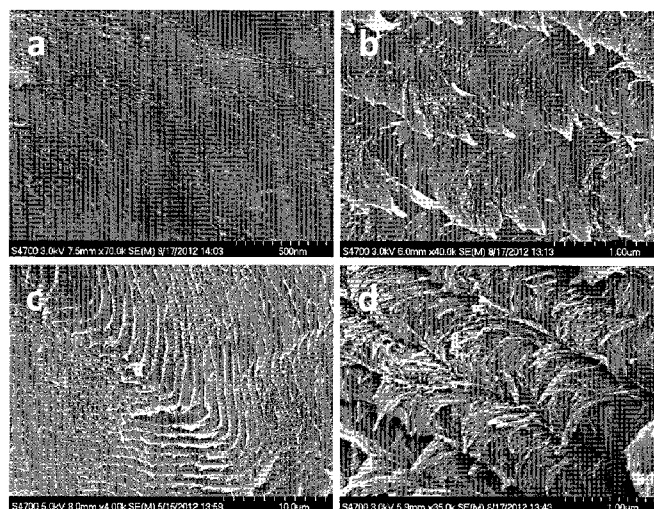


FIG. 10

(57) Abstract: A composite material comprising a thermosetting polymer and a nanocrystalline cellulose (NCC) is provided. The thermosetting polymer forms a polymeric matrix and nanocrystals of the nanocrystalline cellulose are embedded in the polymeric matrix. A process of producing such composite material is also provided. The process comprises the steps of combining a pre-polymer of a thermosetting polymer and an aqueous suspension of a NCC to form an aqueous mixture of the pre-polymer and the NCC, and subsequently removing water from the aqueous mixture to produce the composite material.

POLYMER MATERIALS AND COMPOSITE MATERIALS WITH CHIRAL NEMATIC STRUCTURES AND PREPARATION METHODS THEREOF

5 Cross Reference to Related Applications

This application claims the priority benefit of United States patent application no. 61/804,999, the contents of which are incorporated herein by reference.

Field of Invention

10 The invention is related to composite materials and porous polymer materials having a chiral structure, and processes of producing the composite materials and the porous polymer materials. In particular, the invention is related to composite materials having chiral nematic order, wherein the composite materials comprise a thermosetting polymer and a nanocrystalline cellulose (NCC). The invention is also
15 related to mesoporous polymer and cellulose materials having chiral nematic order, wherein the mesoporous polymer materials comprise a thermosetting polymer.

Description of Related Art

20 Cellulose is an abundant renewable material found in nature and is a main structural component of plants. As cellulose is derived from D-glucose molecules that are linked by covalent bonds, cellulose is inherently chiral. Long cellulose chains exist as microfibrils comprising crystalline and amorphous domains. Controlled hydrolysis of the amorphous domains of microfibrils yields spindle-shaped nanocrystalline cellulose (also referred to as "cellulose nanocrystals", (CNCs)) that behaves as a lyotropic liquid crystal. The dimensions of NCC depend
25 on its biological source and typically range from 3 – 20 nm in diameter and 100 – 1000 nm in length.¹ The Young's modulus of NCC has been reported to be in the range of 138 to 167 GPa² which is comparable to that of steel. Because of these superb mechanical and physical properties along with their excellent
30 biocompatibility and biodegradability, NCC is an interesting candidate for polymeric composite materials with various potential applications. NCC has been used as a nanofiller in polymer matrices including poly(lactic acid), polycaprolactone,

poly(vinyl alcohol), poly(vinyl chloride), polyethylene, polypropylene, and waterborne polyurethane.^{1,3-4} In most of these nanocomposite materials, NCC is used primarily to enhance the mechanical properties of the composite materials owing to its better dispersibility compared to higher-aspect-ratio cellulose microfibrils and lower susceptibility to bulk moisture absorption due to its high crystallinity. There has been no report of exploiting NCC's ability to imprint chiral nematic ordering into a thermosetting polymer matrix leading to photonic polymeric materials.

Periodically organized three dimensional structures (known as photonic crystals) with periodicities on the same length scale as the wavelength of visible light have garnered tremendous interest for their various potential applications.⁵⁻⁶ Many methods have so far been developed to synthesize photonic crystals of both organic and inorganic compositions.⁷⁻¹⁰ In particular, polymeric photonic crystals with three dimensional periodicity have been synthesized with various top-down as well as bottom-up methods, and these have interesting properties and applications.¹¹⁻¹⁵ Helical structures that have periodicities on the order of the wavelength of visible light can also have photonic properties. Chiral nematic liquid crystals (LCs), sometimes called cholesteric LCs, have helical arrangements of mesogens – when the pitch of the LC is similar to the wavelength of incident light, then the light is selectively diffracted from the chiral nematic LC. In this case, the light is circularly polarized with a polarization that depends on the organization of the LC. Incorporation of helix-induced chirality into photonic structures constitutes an interesting subclass of chiral photonic crystals. This has been achieved in the case of polymeric photonic crystals with direct laser writing,¹⁶ using chiral dopants along with orientation inducers¹⁷ and by using a chiral monomer end-capped with a cholesteryl group.¹⁸ While chiral photonic polymeric structures of biological origin are abundant in nature,¹⁹⁻²⁰ direct utilization of them in emerging photonic applications is limited by the lack of their thermal, photo- and structural stability and their limited availability. Consequently, research efforts have been invested to mimic biological photonic structures in inorganic materials²¹ by employing similar templating approaches that have been used with synthetic LCs. The synthesis of

chiral nematic mesoporous silica²² and organosilica²³ templated by a lyotropic liquid crystal of biological origin, namely nanocrystalline cellulose (NCC), has been reported.

5 SUMMARY OF THE INVENTION

10 The invention is based in part on the fortuitous discovery that composite materials having chiral nematic order may be obtained by using the chiral nematic ordering of a nanocrystalline cellulose as a template. In this invention one or more organic monomers may be thermally polymerized in the presence of a nanocrystalline cellulose and reinforced by thermally curing to create a composite material with cellulose nanocrystals organized in the polymer matrix. For certain polymers, porous polymer materials may be obtained after selective removal of a fraction of the cellulose template from the corresponding composite materials. Chiral polymer materials, for example, phenol-formaldehyde (PF), urea-formaldehyde (UF),
15 melamine formaldehyde (MF), and melamine-urea-formaldehyde (MUF) resins, having chirality stemming from the chiral nematic ordering of the nanocrystalline cellulose template may be obtained. Alternatively, in certain cases it is possible to remove the resin to obtain a chiral nematic cellulose material that is partially or entirely desulfated.

20 In accordance with one embodiment, there is provided a composite material comprising: a thermosetting polymer and a nanocrystalline cellulose (NCC), wherein the thermosetting polymer forms a polymeric matrix and nanocrystals of the nanocrystalline cellulose are embedded in the polymeric matrix. In accordance with a
25 further embodiment, the composite material has a chiral structure. In accordance with another embodiment, the composite material has chiral nematic order.

In accordance with another embodiment, there is provided a process of producing a composite material, the process comprising: combining a pre-polymer of a
30 thermosetting polymer and an aqueous suspension of a nanocrystalline cellulose (NCC) to form an aqueous mixture of the pre-polymer and the nanocrystalline cellulose; and removing water from the aqueous mixture to produce the composite

material. In accordance with a further embodiment, the composite material has a chiral structure. In accordance with another embodiment, the composite material has chiral nematic order.

5 In accordance with still another embodiment, the process further comprises casting the aqueous mixture of the pre-polymer and the nanocrystalline cellulose before removing water from the aqueous mixture to form a cast mixture, and removing water from the cast mixture to produce the composite material. In accordance with a further embodiment, the process further comprises curing the composite material.

10

In accordance with another embodiment, there is provided a composite material produced by the process of producing the composite material as described anywhere herein.

15 In accordance with still another embodiment, there is provided a mesoporous polymer material comprising a thermosetting polymer, wherein the mesoporous polymer material has a chiral structure. In accordance with a further embodiment, the mesoporous polymer material has chiral nematic order.

20 In accordance with another embodiment, there is provided a process of producing a mesoporous polymer material, the process comprising: combining a pre-polymer of a thermosetting polymer and an aqueous suspension of a nanocrystalline cellulose (NCC) to form an aqueous mixture of the pre-polymer and the nanocrystalline cellulose; removing water from the aqueous mixture to produce a composite material;
25 and removing at least a portion of the nanocrystalline cellulose from the composite material. In accordance with another embodiment, the mesoporous polymer material has a chiral structure. In accordance with still another embodiment, the mesoporous polymer material has chiral nematic order.

30 In accordance with a further embodiment, the process further comprises casting the aqueous mixture of the pre-polymer and the nanocrystalline cellulose before removing water from the aqueous mixture to form a cast mixture, and removing water from the

cast mixture to produce the composite material. In accordance with still another embodiment, the process further comprises curing the composite material.

5 In accordance with another embodiment, there is provided a method for removing the polymer component to obtain a porous cellulose material with chiral nematic order and porosity.

10 In accordance with another embodiment, there is provided a mesoporous polymer material produced by the process of producing the mesoporous polymer material as described anywhere herein.

15 In accordance with a further embodiment, there is provided an article comprising a substrate and the mesoporous polymer material as described anywhere herein, wherein the mesoporous polymer material forms a coating on the substrate.

20 In accordance with another embodiment, there is provided a desulfated nanocrystalline cellulose (NCC) having chiral nematic order. The NCC may be partially desulfated. The NCC may be substantially or completely desulfated. The NCC may be mesoporous.

25 52. In accordance with another embodiment, there is provided a method of making a nanocrystalline cellulose having chiral nematic order, the method comprising combining a pre-polymer of a thermosetting polymer and an aqueous suspension of a nanocrystalline cellulose (NCC) to form an aqueous mixture of the pre-polymer and the NCC; removing water from the aqueous mixture to produce a composite material; and removing at least a portion of the thermosetting polymer from the composite material. Removing at least a portion of the thermosetting polymer from the composite material may comprise hydrolyzing the thermosetting polymer under basic conditions. Hydrolyzing the thermosetting polymer under
30 basic conditions may include treatment with a hydroxide base. After removing at least a portion of the thermosetting polymer from the composite material, the

method may further include critical point drying of the wet films using supercritical carbon dioxide.

5 In accordance with another embodiment, there is provided a nanocrystalline cellulose having chiral nematic order, wherein the nanocrystalline cellulose is produced according to a method as defined above.

10 In accordance with another embodiment, there is provided a chromatographic matrix comprising a composite as defined above.

In accordance with another embodiment, there is provided a chromatographic matrix comprising a desulfated nanocrystalline cellulose having chiral nematic order as defined above.

15 In accordance with another embodiment, there is provided a chromatographic column comprising a chromatographic matrix as defined above.

20 In accordance with another embodiment, there is provided a use of a composite as defined above for the separation of enantiomers from an enantiomeric mixture.

In accordance with another embodiment, there is provided a use of a desulfated chiral nematic nanocrystalline cellulose having chiral nematic order for the separation of enantiomers from an enantiomeric mixture.

25 Applications for the composite materials may include, for example, chemical sensors, pressure sensors, decoration, logos, security features, tags, reflectors, and chromatographic matrices.

30 Porous polymeric and cellulose-based materials with chiral structures are attractive candidates for many applications such as tunable reflective filters, separation membranes, lightweight reinforcement materials, low k dielectric materials, decoration, supports for catalysts, and adsorbents of chemicals and gases. Their

inherent chirality either on their surface (from residual NCC or components thereof, or imprinted chirality on the surface), over the length scale of the chiral nematic order, or both, may enable separation of substances by chromatography or electrophoresis, especially for resolving racemic mixtures into their enantiomers.

5

BRIEF DESCRIPTION OF THE DRAWINGS

In drawings which illustrate embodiments of the invention,

10

Figure 1 is photographs of composite films prepared with 35% resin: (a) photographed in front of a black background, and (b) in front of a white background. The diameter of the circular film is ~100 mm.

15

Figure 2 is polarized optical micrographs of (a) resin-NCC composite film, and (b) chiral nematic resin film after NCC removal (scale bar 200 μm). Insets in both panels (a) and (b) show the fingerprint texture of the respective films observed at higher magnification (scale bar 20 μm).

20

Figure 3 is UV-Vis spectra of the films prepared with 1 mM NaCl and three different compositions with respect NCC and resin precursor: (solid line) 25% resin, (dashed line) 35% resin, and (dotted line) 45% resin.

25

Figure 4 is UV-Vis spectra of composite films containing 35% resin and different NaCl concentrations.

Figure 5 is solid-state ^{13}C CP/MAS NMR spectra of resin-NCC composite film and resin film after NCC removal. (400 MHz, 4 mm rotor with 6000 rpm spin rate).

30

Figure 6 is wide-angle powder X-ray diffraction (PXRD) traces of composite film (dotted line) and resin film after NCC removal (solid line).

Figure 7 is UV-vis spectra of 45% resin films with different NaCl concentrations.

Figure 8 is CD spectra of 45% resin films with different NaCl concentrations.

Figure 9 is SEM images of cross sections of (a) 25% resin composite film before curing, (b) 25% composite film after curing, (c) 70% resin composite film before curing, and (d) 70% resin composite film after curing.

Figure 10 is SEM images of (a) top surface of resin film, (b) cross section of 25% composite film after curing, (c) 25% resin film is showing defects in fingerprint texture, and (d) 25% resin film after NCC removal and scCO_2 drying.

Figure 11 is (a) N_2 adsorption isotherm of chiral nematic resin film, and (b) the BJH pore-size distribution calculated from the adsorption branch of the isotherm.

Figure 12 is TGA thermograms of resin-NCC composite and resin films after NCC removal: (a) under nitrogen, and (b) under air at a heating rate of $10^\circ\text{C}/\text{min}$.

Figure 13 is photographs of the chiral nematic resin films showing flexibility.

Figure 14 is UV-Vis transmittance spectra (top) and CD spectra (below) of dry composite film (dotted line), swollen composite film (dashed-dot line), dry resin film (solid line), and swollen resin film (dashed line).

Figure 15 is UV-Vis transmittance spectra of chiral nematic resin films swollen in composite solvents containing different proportions of water and ethanol. Inset shows the variation in reflected peak wavelengths as a function of water percentage in the binary solvent mixtures.

Figure 16 is a schematic representation of the condensation of amino components with formaldehyde forming urea-formaldehyde and melamine-formaldehyde resins.

Figure 17 is UV-Vis (a) and CD spectra (b) for UF-NCC composites with different compositions (4A – C).

Figure 18 is SEM images of the cross section of UF-NCC composite sample 4A as representative example.

Figure 19 is an IR spectrum for UF-NCC composite sample 4B as representative example.

Figure 20 is thermogravimetric analysis for UF-NCC composite sample 4B and NCC films under air.

Figure 21 is photographs of the UF-NCC composite films with different NaCl concentrations of the precursor solutions (4B, 5A – D).

Figure 22 is UV-Vis (a) and CD spectra (b) for UF-NCC composite samples 4B, 5A-D with different NaCl concentrations during preparation.

Figure 23 is graphs and images showing the swelling behavior of **UF-NCC** composite and dynamically tunable iridescence, including **a)** the UV-vis spectra, **b)** CD spectra, and **c)**, photographs of the **UF-NCC** composite in its dried state and soaked in water are shown. The initially blue film (reflection at ~520 nm), which is shown in the left panel, turns red (~630 nm) after soaking in water and returns to even more blue-shifted film after drying (~490 nm).

Figure 24 is UV-Vis (a) and CD spectra (b) of MF-NCC composite samples 6A-C.

Figure 25 is SEM images of the cross section of the MF-NCC composite sample 6B at different magnifications showing the left-handed organization of the composite materials.

Figure 26 is IR spectra of the MF-NCC composite sample 6B as representative example.

Figure 27 is solid-state ^{13}C CP/MAS NMR (100 MHz, 18496 scans, spinning rate: 6 kHz, contact time: 2 msec, recycle delay: 5 sec) spectrum for MF-NCC composite sample 6B as representative example.

Figure 28 is thermogravimetric analysis for MF-NCC composite sample 6B and NCC films under air.

Figure 29 is photographs of MUF-NCC composite samples (7A – D) with rising concentration of NaCl during preparation.

Figure 30 is UV-Vis (a) and CD spectra (b) for MUF-NCC composite samples 7A – D.

Figure 31 is IR spectrum for MUF-NCC composite sample 7B as a representative example.

Figure 32 is thermogravimetric analysis for MUF-NCC composite sample 7B and NCC film under air.

Figure 33 is UV-Vis spectra as well as photographs for MUF-NCC composite sample 7A before and after applying pressure.

Figure 34 is CD spectra for MUF-NCC composite sample 7A before and after applying pressure.

Figure 35 is SEM images of the cross section of the MUF-NCC composite sample 7B at different magnifications showing the left-handed organisation of the composite materials.

Figure 36 is photographs of sample 8 (a) before imprinting and (b,c) after imprinting. In (b), the sample is on top of black velvet and in (c) it is on a sheet of paper with text to show transparency.

Figure 37 is ^{13}C CP-MAS NMR spectra of (a) UF-NCC composite and (b) CNMC composite after removing the UF resin. Spectra were obtained using a

-11-

Bruker AV400 MHz spectrophotometer with a 4 mm rotor at a spin rate of 6000 rpm with 2 ms contact time and 15000-20000 scans.

Figure 38 is SEM images of (a) CNMC dried from water and (b) CNMC dried using supercritical CO from ethanol.

5 Figure 39 are graphs of thermogravimetric analysis (TGA) films of **a)** three chiral nematic NCCs produced by from the treatment of UF-NCC with base, including A4 ("CNC-UF-A4"), and **b)** sodium salt of NCC, A4 dried from water, A4 dried from supercritical CO₂, and UF-A4.

10 Figure 40 is a graph showing the mechanical properties of CNMC. Micro-tensile testing was carried out on a dry A4 film with the average ultimate tensile stress = 42 ± 5 MPa at a strain of 0.008 ± 0.002 , or 0.8 % (average of three samples).

15 Figure 41 is a graph showing **a)** the optical properties of the composite from which A4 is made ("**CNC-UF-A4**"), A4 dried from water, and A4 dried from dried from ethanol with supercritical CO₂ , and **b)** CD spectra of the same samples as in **a)**, with A4 dried from water, and dried from ethanol with supercritical CO₂, corresponding to left and right peaks, respectively.

20 Figure 42 is graphs showing the sensing performance of the CNMC films, including **a)** UV-vis (solid lines) and CD spectra (dashed lines), **b)** the dependence of the wavelengths on time when a dry sample is immersed in water, **c)** the pressure response of **CNMC** at 0, 0.4, 0.8, 1.6, 2.7, 5.9 and 7.8×10^6 N m⁻² (first and final value given in graphic) showing a clear blue-shift of the peak reflectance wavelengths, and **d)** peak reflection wavelengths vs. pressure plotted, where the data were fitted with an exponential curve.

25 DETAILED DESCRIPTION

Any terms not directly defined herein shall be understood to have the meanings commonly associated with them as understood within the art of the invention. Certain terms are discussed below, or elsewhere in the specification, to provide additional guidance to the practitioner in describing the devices, methods and the

like of embodiments of the invention, and how to make or use them. It will be appreciated that the same thing may be said in more than one way. Consequently, alternative language and synonyms may be used for any one or more of the terms discussed herein. No significance is to be placed upon whether or not a term is
5 elaborated or discussed herein. Some synonyms or substitutable methods, materials and the like are provided. Recital of one or a few synonyms or equivalents does not exclude use of other synonyms or equivalents, unless it may be explicitly stated. Use of examples in the specification, including examples of terms, may be for illustrative purposes only and does not limit the scope and
10 meaning of the embodiments of the invention herein. The invention is further described for convenience with particular reference to the embodiments where the polymer is phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, or melamine-urea-formaldehyde but it should be understood that the invention has application to other polymers derived from mixtures of these components and from
15 related monomers.

This invention provides composite materials with chiral nematic organization and processes to prepare them. "Chiral nematic organization" or "chiral nematic order", as used herein, refers to a structural order that is derived from chiral nematic phases common to liquid crystals. In this order, the orientation of the nanocrystals
20 or pores rotates through the material with a characteristic helical pitch. As with chiral nematic liquid crystals, the chiral nematic order in these materials, which may be in the solid state, is responsible for the reflection of circularly polarized light.

In this invention pre-polymers of thermoset polymers are polymerized in the presence of nanocrystalline cellulose to create composite materials with cellulose
25 nanocrystals organized within the organic matrix. Composite films attain chiral nematic organization originating from the nanocrystalline cellulose template during thermal curing to give stable, iridescent films that may be free-standing. The long-range chiral nematic ordering leads to photonic properties, and the color of the films
30 can be varied by changing the components of the composite materials and the reaction conditions. The films thus prepared may be flexible. In some cases it is

possible to remove most or all of the cellulose template from the composite material to produce mesoporous resins that retain the chiral nematic ordering of the composite.

5 According to an embodiment, there is provided a composite material comprising: a thermosetting polymer; and a nanocrystalline cellulose (NCC), wherein the thermosetting polymer forms a polymeric matrix and nanocrystals of the nanocrystalline cellulose are embedded in the polymeric matrix. In another
10 embodiment, there is provided a composite material comprising: a thermosetting polymer; and a nanocrystalline cellulose (NCC), wherein the thermosetting polymer forms a polymeric matrix and nanocrystals of the nanocrystalline cellulose are embedded in the polymeric matrix, and wherein the composite material has a chiral structure. In a further embodiment, the composite material may have chiral nematic order. In a further embodiment, the nanocrystalline cellulose of the composite
15 material may have a chiral structure. In still another embodiment, the nanocrystalline cellulose of the composite material may have chiral nematic order. In still another embodiment, the thermosetting polymer of the composite material may have a chiral structure. In a further embodiment, the thermosetting polymer of the composite material may have chiral nematic order.

20 In a further embodiment, the composite material may have a left-handed helical structure. In some embodiments, the composite material may have a left-handed helical structure with a helical pitch ranging from about 200 nanometers to about 1800 nanometers. In some embodiments, the composite material may have a left-
25 handed helical structure with a helical pitch ranging from about 300 nanometers to about 1500 nanometers. In some embodiments, the helical pitch may be varied by varying the ratio of the amount of the thermosetting polymer to the amount of the nanocrystalline cellulose (thermosetting polymer:NCC) in the composite material and/or by varying the ionic strength of the aqueous mixture of the pre-polymer and
30 the nanocrystalline cellulose of the process to produce the composite material. In another embodiment, the helical pitch may be varied by varying the ratio of the amount of the thermosetting polymer to the amount of the nanocrystalline cellulose

(thermosetting polymer:NCC) in the composite material. In another embodiment, the ratio of the amount of the thermosetting polymer to the amount of the nanocrystalline cellulose (thermosetting polymer:NCC) in the composite material may be from 0.1 to 3.5 (by weight). In another embodiment, the ratio of the amount of the thermosetting polymer to the amount of the nanocrystalline cellulose (thermosetting polymer:NCC) in the composite material may be from 0.2 to 2.5 (by weight). In a further embodiment, the helical pitch may be varied by varying the ionic strength of the aqueous mixture of the pre-polymer and the nanocrystalline cellulose of the process to produce the composite material. In another embodiment, the helical pitch may be varied by applying a mechanical stress to the composite material. In a further embodiment, applying a mechanical stress may comprise applying pressure to the composite material. In another embodiment, applying a mechanical stress may comprise stretching the composite material.

In another embodiment, the composite material may reflect left-handed circularly polarized light. In a further embodiment, the composite material may reflect left-handed circularly polarized light with a reflection peak at a wavelength in a region of the electromagnetic spectrum that includes one or more of the visible region, the ultra violet region, and the near-infrared region. In a further embodiment, the composite material may reflect left-handed circularly polarized light with a reflection peak at a wavelength in the region of the electromagnetic spectrum that spans from the blue region to the near-infrared region. In a further embodiment, the wavelength of the reflection peak may be tuned by varying the ratio of the amount of the thermosetting polymer to the amount of the nanocrystalline cellulose (thermosetting polymer:NCC) in the composite material and/or by varying the ionic strength of the aqueous mixture of the pre-polymer and the nanocrystalline cellulose of the process to produce the composite material. In some embodiments, the wavelength of the reflection peak may be tuned by varying the ratio of the amount of the thermosetting polymer to the amount of the nanocrystalline cellulose (thermosetting polymer:NCC) in the composite material. In another embodiment, the ratio of the amount of the thermosetting polymer to the amount of the nanocrystalline cellulose (thermosetting polymer:NCC) in the composite material may be from about 0.2 to

2.5 (by weight). In a further embodiment, the wavelength of the reflection peak may be tuned by varying the ionic strength of the aqueous mixture of the pre-polymer and the nanocrystalline cellulose of the process to produce the composite material.

5 In another embodiment, the composite material may have a color that may be varied from the blue region to the near infrared region of the electromagnetic spectrum by varying the ratio of the amount of the thermosetting polymer to the amount of the nanocrystalline cellulose (thermosetting polymer:NCC) in the composite material and/or by varying the ionic strength of the aqueous mixture of
10 the pre-polymer and the nanocrystalline cellulose of the process to produce the composite material. In another embodiment, the composite material may have a color that may be varied by applying a mechanical stress to the composite material. In a further embodiment, applying a mechanical stress may comprise applying pressure to the composite material. In another embodiment, applying a mechanical
15 stress may comprise stretching the composite material.

In some embodiments, the composite material may have iridescence. In another embodiment, the composite material may have birefringence. In some
20 embodiments, the composite material may have birefringence as observed by polarizing optical microscopy.

As used herein, the phrase 'thermosetting polymer' may be used as it is normally understood to a person skilled in the art and often refers to a polymer that can change irreversibly from a pre-polymer form to an infusible, insoluble polymer
25 network by curing. In an embodiment, the thermosetting polymer of the composite material may be an aldehyde-based polymer. In a further embodiment, the thermosetting polymer may be an amine aldehyde polymer. In another embodiment, the thermosetting polymer may be a phenol aldehyde polymer. In a further embodiment, the thermosetting polymer may be a phenol-formaldehyde (PF)
30 polymer, a urea-formaldehyde (UF) polymer, a melamine-formaldehyde (MF) polymer, a melamine-urea-formaldehyde (MUF) polymer, a resorcinol-formaldehyde polymer, a phenol-acetaldehyde polymer, a resorcinol-acetaldehyde

-16-

polymer, a urea-acetaldehyde polymer, or a melamine-acetaldehyde polymer or any combination thereof. The polymer may be, for example, a phenol-formaldehyde polymer, a urea-formaldehyde polymer, a melamine-formaldehyde polymer, or a urea-melamine-formaldehyde polymer, or any combination thereof. In another
5 embodiment, the thermosetting polymer may be a phenol-formaldehyde (PF) polymer. In a further embodiment, the thermosetting polymer may be a urea-formaldehyde (UF) polymer. In still another embodiment, the thermosetting polymer may be a melamine-formaldehyde (MF) polymer. In a further embodiment, the thermosetting polymer may be a melamine-urea-formaldehyde (MUF) polymer. In
10 another embodiment, the thermosetting polymer may be a resorcinol-formaldehyde polymer. In a further embodiment, the thermosetting polymer may be a phenol-acetaldehyde polymer. In another embodiment, the thermosetting polymer may be a resorcinol-acetaldehyde polymer. In a further embodiment, the thermosetting polymer may be a urea-acetaldehyde polymer. In another embodiment, the
15 thermosetting polymer may be a melamine-acetaldehyde polymer. The skilled person will appreciate that other polymers formed by reaction of phenol, amino and aldehyde compounds, or derivatives thereof, will also work in this procedure. Non limiting examples include polymers comprising: resorcinol-formaldehyde, phenol-acetaldehyde, resorcinol-acetaldehyde, urea-acetaldehyde, melamine-acetaldehyde and any combinations of these. Other related polymers known to
20 those skilled in the art may also be used.

In some embodiments, the composite material may further comprise an additive. Suitable additives would be understood to and can be determined by those of
25 ordinary skill in the art. For example, the additive may comprise a plasticizer. In another embodiment, the additive may comprise glycerol or phthalate or any combination thereof. In a further embodiment, the additive may comprise glycerol. In still another embodiment, the additive may comprise phthalate.

In a further embodiment, the composite material may further comprise an electrolyte. In accordance with some embodiments, the electrolyte may comprise a salt, a base or an acid, or any combination thereof. In another embodiment, the
30

electrolyte may comprise a salt. In a further embodiment, the electrolyte may comprise a base. In another embodiment, the electrolyte may comprise an acid. In a further embodiment, the electrolyte may comprise NaCl, KCl, HCl, or a combination thereof. In some embodiments, the electrolyte may comprise NaCl.

5

In some embodiments, the composite material may be self-supporting. In another embodiment, the composite material may be free-standing. In some embodiments, the composite material may be in the form of a film.

10

In some embodiments, the composite material may have thermal stability in air or nitrogen of up to about 200 °C.

15

In some embodiments, the composite material may reversibly absorb a solvent. In a further embodiment, the solvent may comprise a polar solvent. In another embodiment, the solvent may comprise a nonpolar solvent. In a further embodiment, the solvent may comprise water or an alcohol or any combination thereof. In an embodiment, the solvent may comprise water. In another embodiment, the solvent may comprise an alcohol. In a further embodiment, the solvent may comprise ethanol.

20

In accordance with another embodiment, there is provided an article comprising the composite material as described anywhere herein. In some embodiments, the article may be a chemical sensor, a pressure sensor, a decoration, a logo, a security feature, a tag, or a reflector.

25

In accordance with another embodiment, there is provided a process of producing a composite material, the process comprising: combining a pre-polymer of a thermosetting polymer and an aqueous suspension of a nanocrystalline cellulose (NCC) to form an aqueous mixture of the pre-polymer and the nanocrystalline cellulose; and removing water from the aqueous mixture to produce the composite material. In another embodiment, there is provided a process of producing a composite material having a chiral structure, the process comprising: combining a

30

pre-polymer of a thermosetting polymer and an aqueous suspension of a nanocrystalline cellulose (NCC) to form an aqueous mixture of the pre-polymer and the nanocrystalline cellulose; and removing water from the aqueous mixture to produce the composite material having a chiral structure. In a further embodiment, the composite material may have a chiral nematic order. In another embodiment, the process may further comprise casting the aqueous mixture of the pre-polymer and the nanocrystalline cellulose before removing water from the aqueous mixture to form a cast mixture, and removing water from the cast mixture to produce the composite material. In accordance with still another embodiment, the process may further comprise curing the composite material.

As used herein, the phrase 'pre-polymer of a thermosetting polymer' may be used as it is normally understood to a person skilled in the art and often refers to a soft solid or viscous state of a thermosetting polymer that changes irreversibly into an infusible, insoluble polymer network by curing. In some embodiments, the pre-polymer may be a pre-polymer of an aldehyde-based polymer. In a further embodiment, the pre-polymer may be a pre-polymer of an amine aldehyde polymer. In another embodiment, the pre-polymer may be a pre-polymer of a phenol aldehyde polymer. In a further embodiment, the pre-polymer may be a pre-polymer of a phenol-formaldehyde (PF) polymer, a pre-polymer of a urea-formaldehyde (UF) polymer, a pre-polymer of a melamine-formaldehyde (MF) polymer, a pre-polymer of a melamine-urea-formaldehyde (MUF) polymer, a pre-polymer of a resorcinol-formaldehyde polymer, a pre-polymer of a phenol-acetaldehyde polymer, a pre-polymer of a resorcinol-acetaldehyde polymer, a pre-polymer of a urea-acetaldehyde polymer, or a pre-polymer of a melamine-acetaldehyde polymer or any combination thereof. The pre-polymer may be, for example, a pre-polymer of a phenol-formaldehyde polymer, a pre-polymer of a urea-formaldehyde polymer, a pre-polymer of a melamine-formaldehyde polymer, or a pre-polymer of a urea-melamine-formaldehyde polymer, or any combination thereof. In another embodiment, the pre-polymer may be a pre-polymer of a phenol-formaldehyde (PF) polymer. In accordance with a further embodiment, the pre-polymer may be a pre-polymer of a urea-formaldehyde (UF) polymer. In still

another embodiment, the pre-polymer may be a pre-polymer of a melamine-formaldehyde (MF) polymer. In a further embodiment, the pre-polymer may be a pre-polymer of a melamine-urea-formaldehyde (MUF) polymer. In another embodiment, the pre-polymer may be a pre-polymer of a resorcinol-formaldehyde polymer. In a further embodiment, the pre-polymer may be a pre-polymer of a phenol-acetaldehyde polymer. In another embodiment, the pre-polymer may be a pre-polymer of a resorcinol-acetaldehyde polymer. In a further embodiment, the pre-polymer may be a pre-polymer of a urea-acetaldehyde polymer. In another embodiment, the pre-polymer may be a pre-polymer of a melamine-acetaldehyde polymer. The skilled person will appreciate that other pre-polymers formed by reaction of phenol, amino and aldehyde compounds, or derivatives thereof, will also work in this procedure. Non limiting examples include pre-polymers comprising: resorcinol-formaldehyde pre-polymers, phenol-acetaldehyde pre-polymers, resorcinol-acetaldehyde pre-polymers, urea-acetaldehyde pre-polymers, melamine-acetaldehyde pre-polymers and any combinations of these. Other related pre-polymers known to those skilled in the art may also be used.

Suitable methods or procedures for preparing the pre-polymer of a thermosetting polymer would be understood to and can be determined by those of ordinary skill in the art. For example, the pre-polymer of a thermosetting polymer may be prepared by a method as described anywhere herein, including base catalyzed polymerization.

In some embodiments, the pre-polymer of a thermosetting polymer may have a molecular weight, M_w , of greater than or equal to about 50, or greater than or equal to about 100, or greater than or equal to about 200, or greater than or equal to about 300, or greater than or equal to about 400, or greater than or equal to about 500, or greater than or equal to about 600, or greater than or equal to about 700, or greater than or equal to about 800, or greater than or equal to about 900, or greater than or equal to about 1000, or greater than or equal to about 1100, or greater than or equal to about 1200, or greater than or equal to about 1300, or greater than or equal to about 1400, or greater than or equal to about 1500, or greater than or

equal to about 1600, or greater than or equal to about 1700, or greater than or
equal to about 1800, or greater than or equal to about 1900, or greater than or
equal to about 2000, or greater than or equal to about 2100, or greater than or
equal to about 2200, or greater than or equal to about 2300, or greater than or
5 equal to about 2400, or greater than or equal to about 2500, or greater than or
equal to about 2600, or greater than or equal to about 2700, or greater than or
equal to about 2800, or greater than or equal to about 2900, or greater than or
equal to about 3000, or greater than or equal to about 3100, or greater than or
equal to about 3200, or greater than or equal to about 3300, or greater than or
10 equal to about 3400, or greater than or equal to about 3500, or greater than or
equal to about 3600, or greater than or equal to about 3700, or greater than or
equal to about 3800, or greater than or equal to about 3900, or greater than or
equal to about 4000, or greater than or equal to about 4100, or greater than or
equal to about 4200, or greater than or equal to about 4300, or greater than or
15 equal to about 4400, or greater than or equal to about 4500, or greater than or
equal to about 4600, or greater than or equal to about 4700, or greater than or
equal to about 4800, or greater than or equal to about 4900, or greater than or
equal to about 5000, or greater than or equal to about 5100, or greater than or
equal to about 5200, or greater than or equal to about 5300, or greater than or
20 equal to about 5400, or greater than or equal to about 5500, or greater than or
equal to about 5600, or greater than or equal to about 5700, or greater than or
equal to about 5800, or greater than or equal to about 5900, or greater than or
equal to about 6000, or from about 400 to about 6000, or from about 400 to about
5500, or from about 450 to about 5000, or from about 500 to about 6000, or from
25 about 500 to about 5500, or from about 500 to about 5000, and including any
values within these ranges, such as about 400, or about 500, or about 600, or
about 700, or about 800, or about 900, or about 1000, or about 1100, or about
1200, or about 1300, or about 1400, or about 1500, or about 1600, or about 1700,
or about 1800, or about 1900, or about 2000, or about 2100, or about 2200, or
30 about 2300, or about 2400, or about 2500, or about 2600, or about 2700, or about
2800, or about 2900, or about 3000, or about 3100, or about 3200, or about 3300,
or about 3400, or about 3500, or about 3600, or about 3700, or about 3800, or

about 3900, or about 4000, or about 4100, or about 4200, or about 4300, or about 4400, or about 4500, or about 4600, or about 4700, or about 4800, or about 4900, or about 5000.

5 Suitable methods and procedures for preparing the nanocrystalline cellulose would be understood to and can be determined by those of ordinary skill in the art including any methods as described herein. For example, the nanocrystalline cellulose may be prepared from softwood kraft pulp fibers by sulfuric-acid hydrolysis. The person skilled in the art will appreciate that the methods described
10 herein can also be applied to nanocrystalline cellulose from other sources, given that cellulose from other plant sources, animals (e.g., tunicate), and bacterial cellulose are structurally similar to that from softwood trees.

15 In an embodiment, the nanocrystalline cellulose of the aqueous suspension has a chiral phase. In another embodiment, the nanocrystalline cellulose of the aqueous suspension has a chiral nematic phase. In some embodiments, the aqueous suspension of nanocrystalline cellulose may have a concentration of the nanocrystalline cellulose which is greater than or equal to a critical concentration. As used herein, the phrase 'critical concentration' may be used as it is normally
20 understood to a person skilled in the art and often refers to the concentration at which the nanocrystalline cellulose suspension transforms from an isotropic phase, where the nanocrystalline cellulose particles are randomly oriented in aqueous suspension, to an anisotropic chiral nematic liquid crystalline phase, having chiral nematic ordering. In another embodiment, the aqueous suspension may have a
25 concentration of the nanocrystalline cellulose of greater than or equal to about 1 wt%, or greater than or equal to about 2 wt%, or greater than or equal to about 3 wt%, or greater than or equal to about 4 wt%, or greater than or equal to about 5 wt%, or greater than or equal to about 6 wt%, or greater than or equal to about 7 wt%, or greater than or equal to about 8 wt%, or greater than or equal to about 9
30 wt%, or greater than or equal to about 10 wt%. In accordance with some embodiments, the aqueous suspension may have a concentration of the nanocrystalline cellulose of about 1 to about 10 wt%, or about 2 to about 10 wt %,

or about 3 to about 10 wt %, or about 3 to about 9 wt %, or about 3 to about 8 wt %, or about 3 to about 7 wt %, or about 3 to about 6 wt %, or about 3 to about 5 wt %, or about 3 to about 4 wt %. In accordance with some embodiments, the aqueous suspension may have a concentration of the nanocrystalline cellulose that includes
5 any value within these ranges, such as, for example, about 1 wt%, or about 1.5 wt%, or about 2 wt%, or about 2.5 wt%, or about 3 wt %, or about 3.5 wt%, or about 4 wt %, or about 4.5 wt%, or about 5 wt%, or about 5.1 wt %, or about 5.5 wt%, or about 6 wt %, or about 6.5 wt%, or about 7 wt%, or about 7.5 wt%, or about 8 wt%, or about 8.5 wt%, or about 9 wt %, or about 9.5 wt %, or about 10 wt%.

10 In some embodiments, the aqueous suspension of a nanocrystalline cellulose may have a pH of about 2.0 to about 10.0, or about 2.0 to about 7.0, or about 2.0 to about 4.0, and including any values within these ranges, such as about 2.0, or about 2.1, or about 2.2, or about 2.3, or about 2.4, or about 2.5, or about 2.6, or
15 about 2.7, or about 2.8, or about 2.9, or about 3.0, or about 3.1, or about 3.2, or about 3.3, or about 3.4, or about 3.5, or about 3.6, or about 3.7, or about 3.8, or about 3.9, or about 4.0, or about 4.1, or about 4.2, or about 4.3, or about 4.4, or about 4.5, or about 4.6, or about 4.7, or about 4.8, or about 4.9, or about 5.0, or about 5.1, or about 5.2, or about 5.3, or about 5.4, or about 5.5, or about 5.6, or
20 about 5.7, or about 5.8, or about 5.9, or about 6.0, or about 6.1, or about 6.2, or about 6.3, or about 6.4, or about 6.5, or about 6.6, or about 6.7, or about 6.8, or about 6.9, or about 7.0, or about 7.1, or about 7.2, or about 7.3, or about 7.4, or about 7.5, or about 7.6, or about 7.7, or about 7.8, or about 7.9, or about 8.0, or about 8.1, or about 8.2, or about 8.3, or about 8.4, or about 8.5, or about 8.6, or
25 about 8.7, or about 8.8, or about 8.9, or about 9.0, or about 9.1, or about 9.2, or about 9.3, or about 9.4, or about 9.5, or about 9.6, or about 9.7, or about 9.8, or about 9.9, or about 10.0.

30 In another embodiment, the ratio of the amount of the pre-polymer of a thermosetting polymer to the amount of the nanocrystalline cellulose (pre-polymer:NCC) combined in the process of producing the composite material may be from about 0.1 to 3.5 (by weight). In another embodiment, the ratio of the

amount of the pre-polymer of a thermosetting polymer to the amount of the nanocrystalline cellulose (pre-polymer:NCC) combined in the process of producing the composite material may be from about 0.2 to 2.5 (by weight).

5 In some embodiments, the ionic strength of the aqueous mixture of the pre-polymer and the nanocrystalline cellulose may be varied by adding an electrolyte to the aqueous mixture. In some embodiments, the pre-polymer of a thermosetting polymer and the aqueous suspension of nanocrystalline cellulose may be combined in the presence of an electrolyte. In accordance with some embodiments, 10 the electrolyte may comprise a salt, a base or an acid, or any combination thereof. In another embodiment, the electrolyte may comprise a salt. In a further embodiment, the electrolyte may comprise a base. In another embodiment, the electrolyte may comprise an acid. In a further embodiment, the electrolyte may comprise NaCl, KCl or HCl. In some embodiments, the electrolyte may comprise 15 NaCl. As will be appreciated by the person skilled in the art, the electrolyte may be added to the aqueous suspension of nanocrystalline cellulose, the pre-polymer of a thermosetting polymer, or the aqueous mixture of the pre-polymer and the nanocrystalline cellulose or any combination thereof. In accordance with another embodiment, the electrolyte may be added to the aqueous suspension of 20 nanocrystalline cellulose. In a further embodiment, the electrolyte may be added to the pre-polymer of a thermosetting polymer. In still another embodiment, the electrolyte may be added to the aqueous mixture of the pre-polymer and the nanocrystalline cellulose. The person skilled in the art will appreciate that the electrolyte may be added before, during or after combining of the pre-polymer of a 25 thermosetting polymer and the aqueous suspension of nanocrystalline cellulose.

In some embodiments, the pre-polymer of a thermosetting polymer and the aqueous suspension of nanocrystalline cellulose may be combined with an additive. Suitable additives would be understood to and can be determined by 30 those of ordinary skill in the art. For example, the additive may comprise a plasticizer. In another embodiment, the additive may comprise glycerol or phthalate or any combination thereof. In a further embodiment, the additive may comprise

glycerol. In still another embodiment, the additive may comprise phthalate. As will be appreciated by the person skilled in the art, the additive may be added to the aqueous suspension of a nanocrystalline cellulose, the pre-polymer of a thermosetting polymer, or the aqueous mixture of the pre-polymer and the nanocrystalline cellulose or any combination thereof. In another embodiment, the additive may be added to the aqueous suspension of nanocrystalline cellulose. In a further embodiment, the additive may be added to the pre-polymer of a thermosetting polymer. In still another embodiment, the additive may be added to the aqueous mixture of the pre-polymer and the nanocrystalline cellulose. The person skilled in the art will appreciate that the additive may be added before, during or after combining of the pre-polymer of a thermosetting polymer and the aqueous suspension of nanocrystalline cellulose.

Suitable methods for casting the aqueous mixture to form the cast mixture would be understood to and can be determined by those of ordinary skill in the art. For example, the aqueous mixture may be cast using a method or procedure as described anywhere herein.

In some embodiments, removing water from the aqueous mixture may comprise evaporating the water. Suitable conditions and lengths of time for evaporating the water would be understood to and can be determined by those of ordinary skill in the art. For example, the water may be removed from the aqueous mixture using a method or procedure as described anywhere herein, including removing water from the aqueous mixture by drying the aqueous mixture at ambient conditions at room temperature for 1 to 3 days.

In another embodiment, the composite material may be cured by heating the composite material. Suitable heating temperatures and heating lengths of time would be understood to and can be determined by those of ordinary skill in the art. For example, in an embodiment, the composite material may be heated at a temperature from about 75 to about 150 °C, and including any value within these

ranges, such as 75 °C. In some embodiments, the composite material may be heated for 24 hours.

5 In a further embodiment, there is provided a composite material produced by the process of producing the composite material as described anywhere herein.

10 In another embodiment, there is provided a porous polymer material comprising a thermosetting polymer, wherein the porous polymer material has a chiral structure. In another embodiment, the porous polymer material may have chiral nematic order. In a further embodiment, there is provided a mesoporous polymer material comprising a thermosetting polymer, wherein the mesoporous polymer material has a chiral structure. In another embodiment, the mesoporous polymer material may have chiral nematic order.

15 As used herein, the phrase 'mesoporous' may be used as it is normally understood to a person skilled in the art and often refers to a material containing pores having an average diameter in the range of from about 2 to about 50 nm. In some embodiments, the mesoporous polymer material may contain pores having an average diameter in the range of from about 2 to about 50 nm, or from about 3 to
20 about 20 nm, and including any values within this range, such as about 3 nm, or about 4 nm, or about 5 nm, or about 6 nm, or about 7 nm, or about 8 nm, or about 9 nm, or about 10 nm, or about 11 nm, or about 12 nm, or about 13 nm, or about 14 nm, or about 15 nm, or about 16 nm, or about 17 nm, or about 18 nm, or about 19 nm or about 20 nm. In some embodiments, the mesoporous polymer material may
25 have a surface area in the range of from about 50 to about 400 m²/g, and including any values within this range.

30 In a further embodiment, the mesoporous polymer material may have a left-handed helical structure. In some embodiments, the mesoporous polymer material may have a left-handed helical structure with a helical pitch ranging from about 200 nanometers to about 1000 nanometers. In another embodiment, the helical pitch may be varied by applying a mechanical stress to the mesoporous polymer

material. In a further embodiment, applying a mechanical stress may comprise applying pressure to the mesoporous polymer material. In another embodiment, applying a mechanical stress may comprise stretching the mesoporous polymer material.

5

In another embodiment, the mesoporous polymer material may reflect left-handed circularly polarized light. In a further embodiment, the mesoporous polymer material may reflect left-handed circularly polarized light with a reflection peak at a wavelength in a region of the electromagnetic spectrum that includes the visible region and the near-infrared region. In a further embodiment, the mesoporous polymer material may reflect left-handed circularly polarized light with a reflection peak at a wavelength in the region of the electromagnetic spectrum that spans from the blue region to the near-infrared region.

10

15

In another embodiment, the mesoporous polymer material may have a color that may be varied by applying a mechanical stress to the mesoporous polymer material. In a further embodiment, applying a mechanical stress may comprise applying pressure to the mesoporous polymer material. In another embodiment, applying a mechanical stress may comprise stretching the mesoporous polymer material.

20

In some embodiments, the mesoporous polymer material may have iridescence. In another embodiment, the mesoporous polymer material may have birefringence. In some embodiments, the mesoporous polymer material may have birefringence as observed by polarizing optical microscopy.

25

In an embodiment, the thermosetting polymer of the mesoporous polymer material may be an aldehyde-based polymer. In a further embodiment, the thermosetting polymer may be an amine aldehyde polymer. In another embodiment, the thermosetting polymer may be a phenol aldehyde polymer. In a further embodiment, the thermosetting polymer may be a phenol-formaldehyde (PF) polymer, a urea-formaldehyde (UF) polymer, a melamine-formaldehyde (MF)

30

polymer, a melamine-urea-formaldehyde (MUF) polymer, a resorcinol-formaldehyde polymer, a phenol-acetaldehyde polymer, a resorcinol-acetaldehyde polymer, a urea-acetaldehyde polymer, or a melamine-acetaldehyde polymer or any combination thereof. The polymer may be, for example, a phenol-formaldehyde polymer, a urea-formaldehyde polymer, a melamine-formaldehyde polymer, or a urea-melamine-formaldehyde polymer, or any combination thereof. In another embodiment, the thermosetting polymer may be a phenol-formaldehyde (PF) polymer. In a further embodiment, the thermosetting polymer may be a urea-formaldehyde (UF) polymer. In still another embodiment, the thermosetting polymer may be a melamine-formaldehyde (MF) polymer. In a further embodiment, the thermosetting polymer may be a melamine-urea-formaldehyde (MUF) polymer. In another embodiment, the thermosetting polymer may be a resorcinol-formaldehyde polymer. In a further embodiment, the thermosetting polymer may be a phenol-acetaldehyde polymer. In another embodiment, the thermosetting polymer may be a resorcinol-acetaldehyde polymer. In a further embodiment, the thermosetting polymer may be a urea-acetaldehyde polymer. In another embodiment, the thermosetting polymer may be a melamine-acetaldehyde polymer. The skilled person will appreciate that other polymers formed by reaction of phenol, amino and aldehyde compounds, or derivatives thereof, will also work in this procedure. Non limiting examples include polymers comprising: resorcinol-formaldehyde, phenol-acetaldehyde, resorcinol-acetaldehyde, urea-acetaldehyde, melamine-acetaldehyde and any combinations of these. Other related polymers known to those skilled in the art may also be used.

In an embodiment, the mesoporous polymer material may comprise a nanocrystalline cellulose in an amount of about 5-50 wt%. In another embodiment, the mesoporous polymer material may comprise a nanocrystalline cellulose in an amount of about 10-15 wt%.

In an embodiment, the mesoporous polymer material may further comprise an additive. Suitable additives would be understood to and can be determined by

those of ordinary skill in the art. For example, the additive may comprise a plasticizer. In another embodiment, the additive may comprise glycerol or phthalate or any combination thereof. In a further embodiment, the additive may comprise glycerol. In still another embodiment, the additive may comprise phthalate.

5

In some embodiments, the mesoporous polymer material may further comprise an electrolyte. In accordance with some embodiments, the electrolyte may comprise a salt, a base or an acid, or any combination thereof. In another embodiment, the electrolyte may comprise a salt. In a further embodiment, the electrolyte may
10 comprise a base. In another embodiment, the electrolyte may comprise an acid. In a further embodiment, the electrolyte may comprise NaCl, KCl or HCl. In some embodiments, the electrolyte may comprise NaCl.

10

In some embodiments, the mesoporous polymer material may be self-supporting.
15 In a further embodiment, the mesoporous polymer material may be free-standing. In some embodiments, the mesoporous polymer material may be in the form of a film.

15

In some embodiments, the mesoporous polymer material may reversibly absorb a solvent. In a further embodiment, the solvent may comprise a polar solvent. In
20 another embodiment, the solvent may comprise a nonpolar solvent. In a further embodiment, the solvent may comprise water or an alcohol or any combination thereof. In an embodiment, the solvent may comprise water. In another embodiment, the solvent may comprise an alcohol. In a further embodiment, the
25 solvent may comprise ethanol.

20

25

In some embodiments, the mesoporous polymer material may have thermal stability in air or nitrogen of up to about 350 °C.

30

In another embodiment, there is provided an article comprising the mesoporous polymer material as described anywhere herein. In an embodiment, the article may be a tunable reflective filter, a separation membrane, a lightweight reinforcement

material, a low k dielectric material, a decoration, a support for a catalyst, an adsorbent of a chemical or an adsorbent of a gas. In another embodiment, there is provided an article comprising a substrate and the mesoporous polymer material as described anywhere herein, wherein the mesoporous polymer material forms a coating on the substrate.

In another embodiment, there is provided a process of producing a mesoporous polymer material having a chiral structure, the process comprising: removing at least a portion of nanocrystalline cellulose from a composite material having a chiral structure, the composite material comprising: a thermosetting polymer; and the nanocrystalline cellulose, wherein the thermosetting polymer forms a polymeric matrix of the composite material and nanocrystals of the nanocrystalline cellulose are embedded in the polymeric matrix. In another embodiment, there is provided a process of producing a mesoporous polymer material having a chiral structure, the process comprising: combining a pre-polymer of a thermosetting polymer and an aqueous suspension of nanocrystalline cellulose (NCC) to form an aqueous mixture of the pre-polymer and the nanocrystalline cellulose; removing water from the aqueous mixture to produce a composite material, wherein the composite material has a chiral structure; and removing at least a portion of the nanocrystalline cellulose from the composite material. In accordance with another embodiment, the process may further comprise casting the aqueous mixture before removing water from the aqueous mixture to form a cast mixture, and removing water from the cast mixture to produce the composite material. In accordance with still another embodiment, the process may further comprise curing the composite material before removing at least a portion of the nanocrystalline cellulose from the composite material. In a further embodiment, the mesoporous polymer material may have chiral nematic order.

In some embodiments, the nanocrystalline cellulose may be removed from the composite material while maintaining the integrity of the polymeric matrix of the composite material. In a further embodiment, the nanocrystalline cellulose may be removed from the composite material while maintaining the chiral nematic order of

the polymeric matrix of the composite material. In another embodiment, the nanocrystalline cellulose may be removed from the composite material by hydrolyzing the nanocrystalline cellulose. In still another embodiment, the nanocrystalline cellulose may be removed from the composite material by hydrolyzing the nanocrystalline cellulose under basic conditions. In a further embodiment, hydrolyzing the nanocrystalline cellulose may comprise exposing the composite material to a basic solution. For example, the nanocrystalline cellulose may be removed from the composite material using a method or procedure as described anywhere herein, including hydrolysis using an aqueous LiOH solution or an aqueous solution of NaOH and urea cooled to -10 °C. In a further embodiment, the process further comprises washing the composite material with water to remove the basic solution. In some embodiments, the amount of the nanocrystalline cellulose removed from the composite material may be from about 50% to 95%. In some embodiments, the amount of the nanocrystalline cellulose removed from the composite material may be from about 85% to 90%.

The pre-polymer of a thermosetting polymer for the process of producing the mesoporous polymer material may be a pre-polymer of a thermosetting polymer as described anywhere herein. Suitable methods or procedures for preparing the pre-polymer of a thermosetting polymer would be understood to and can be determined by those of ordinary skill in the art. For example, the pre-polymer of a thermosetting polymer may be prepared by a method as described anywhere herein, including base catalyzed polymerization. The pre-polymer of a thermosetting polymer for the process of producing the mesoporous polymer material may have a molecular weight, M_w , as described anywhere herein.

The nanocrystalline cellulose for the process of producing the mesoporous polymer material may be prepared by a method or procedure as described anywhere herein. Suitable methods or procedures for preparing the nanocrystalline cellulose would be understood to and can be determined by those of ordinary skill in the art. In an embodiment, the nanocrystalline cellulose of the aqueous suspension has a chiral phase. In another embodiment, the nanocrystalline cellulose of the aqueous

suspension has a chiral nematic phase. The aqueous suspension of nanocrystalline cellulose polymer for the process of producing the mesoporous polymer material may have a concentration of the nanocrystalline cellulose as described anywhere herein. The aqueous suspension of the nanocrystalline cellulose for the process of producing the mesoporous polymer material may have a pH as described anywhere herein. In another embodiment, the ratio of the amount of the pre-polymer of a thermosetting polymer to the amount of the nanocrystalline cellulose (pre-polymer:NCC) combined in the process of producing the polymer material may be a ratio as described anywhere herein.

In some embodiments, the ionic strength of the aqueous mixture of the pre-polymer and the nanocrystalline cellulose may be varied by adding electrolyte to the aqueous mixture. In some embodiments, the pre-polymer of a thermosetting polymer and the aqueous suspension of nanocrystalline cellulose may be combined in the presence of an electrolyte. The electrolyte for the process of producing the mesoporous polymer material may be an electrolyte as described anywhere herein. As will be appreciated by the person skilled in the art, the electrolyte may be added to the aqueous suspension of nanocrystalline cellulose, the pre-polymer of a thermosetting polymer, or the aqueous mixture of the pre-polymer and the nanocrystalline cellulose or any combination thereof. In accordance with another embodiment, the electrolyte may be added to the aqueous suspension of nanocrystalline cellulose. In a further embodiment, the electrolyte may be added to the pre-polymer of a thermosetting polymer. In still another embodiment, the electrolyte may be added to the aqueous mixture of the pre-polymer and the nanocrystalline cellulose. The person skilled in the art will appreciate that the electrolyte may be added before, during or after combining of the pre-polymer of a thermosetting polymer and the aqueous suspension of nanocrystalline cellulose.

The composite material for the process of producing the mesoporous polymer material may be cured by using a method or procedure as described anywhere

herein. Suitable methods or procedures for curing the composite material would be understood to and can be determined by those of ordinary skill in the art.

5 Suitable methods for casting the aqueous mixture to form the cast mixture would be understood to and can be determined by those of ordinary skill in the art. For example, the aqueous mixture may be cast using a method or procedure as described anywhere herein.

10 In some embodiments, removing water from the aqueous mixture comprises evaporating the water. Suitable conditions and lengths of time for evaporating the water would be understood to and can be determined by those of ordinary skill in the art. For example, the water may be removed from the aqueous mixture using a method or procedure as described anywhere herein, including removing water from the aqueous mixture by drying the aqueous mixture at ambient conditions at room
15 temperature for 1 to 3 days.

20 In some embodiments, the pre-polymer of a thermosetting polymer and the aqueous suspension of nanocrystalline cellulose may be combined with an additive. Suitable additives would be understood to and can be determined by those of ordinary skill in the art. In an embodiment, the additive may be an additive as described anywhere herein. As will be appreciated by the person skilled in the art, the additive may be added to the aqueous suspension of nanocrystalline cellulose, the pre-polymer of a thermosetting polymer, or the aqueous mixture of the pre-polymer and the nanocrystalline cellulose or any combination thereof. In
25 another embodiment, the additive may be added to the aqueous suspension of nanocrystalline cellulose. In a further embodiment, the additive may be added to the pre-polymer of a thermosetting polymer. In still another embodiment, the additive may be added to the aqueous mixture of the pre-polymer and the nanocrystalline cellulose. The person skilled in the art will appreciate that the
30 additive may be added before, during or after combining of the pre-polymer of a thermosetting polymer and the aqueous suspension of nanocrystalline cellulose.

In a further embodiment, there is provided a mesoporous polymer material produced by the process of producing the mesoporous polymer material as described anywhere herein.

5 Chromatographic separation may be carried out using films of the materials (e.g., stacked or rolled films) or by using beads or particles of the materials as a chromatographic matrix. Materials that can be synthesized as beads, or formed into beads after they are synthesized, may be incorporated into a column and applied in, for example, a high-performance liquid chromatography (HPLC) column or in a
10 similar column where a solution containing the mixture of analytes is flowed over the bed of material. The separations may be used for analytical purposes (e.g., determining the concentration or identity of analytes within a sample) or for purification of substances (e.g., pharmaceuticals or agricultural chemicals), including the separation of mixtures of enantiomers into separate enantiomers
15 (molecules that have non-superimposable mirror images).

All materials described herein show a chiral organization with positive ellipticity by CD, which is characteristic of a left-handed helical structure. Besides the described polymer composites and compositions, various related materials with varying ratios
20 of polymer precursor and additives will also work. Below we provide a series of specific examples that illustrate the method of our invention. These examples are illustrative of the procedures that yield the novel chiral nematic composite materials, but other ways to prepare the materials may also exist and be used to make PF-, MUF-, MF-, and UF-based composites with chiral nematic order.
25

EXAMPLES

Example 1. Preparation of nanocrystalline cellulose

Preparation 1 Preparation of nanocrystalline cellulose

30 Nanocrystalline cellulose (NCC) obtained from FPIInnovations was prepared according to the method described in reference 22 from fully-bleached commercial kraft softwood pulp. Sonication was typically applied to ensure complete dispersion

of the NCC particles in aqueous suspension. A sonication time of 10 – 15 minutes was typically applied prior to addition of the resin pre-polymer

Example 2. PF-NCC composites

These composite materials may be made of PF resin obtained by the thermopolymerization of resol pre-polymer in presence of NCC. By way of example, resol pre-polymers work as a polymerizable precursor giving a thermoset resin matrix with NCC incorporated in it with chiral nematic organization.

Preparation 2. Preparation of the resol pre-polymer

Base-catalysed phenol-formaldehyde resins may be made with a formaldehyde to phenol ratio of greater than one (usually around 1.5). These resins are called resols. Phenol, formaldehyde, water and catalyst may be mixed in the desired amount, depending on the resin to be formed, and then heated.

A base catalyzed polymerization method was employed to synthesize a soluble, low-molecular-weight polymer, resol ($M_w = 500 - 5000$) derived from phenol and formaldehyde. In a typical preparation procedure, phenol (0.61 g, 6.50 mmol) was melted at 40 – 42°C followed by the addition of 20% NaOH (aq) (0.13 g, 0.65 mmol) slowly over 10 min with stirring. 1.05 g of formalin (36.5 wt%) containing formaldehyde equivalent to 13.0 mmol was added drop wise, and the reaction mixture was stirred at 70 – 75 °C for 1 h. After cooling to room temperature, the pH of the reaction mixture was adjusted to that of a neutral solution (7.0) using 0.6 M HCl solution. Water was then removed under vacuum below 50 °C. The resulting product was redissolved in ethanol and the precipitate was removed by filtration. The final product was dissolved in a calculated amount of water/ethanol (85/15 v/v%) solvent mixture to make a 35 wt% resol solution.

A resol type pre-polymer may be used as phenol-formaldehyde resin precursor. NCC suspension with concentration ranging from about 3 – 5 wt% at about pH 2.4 can be homogeneously mixed with an aqueous solution of the resin precursor, and allowed to dry at ambient conditions, e.g. at room temperature over 1 – 2 days, until

free-standing films are obtained. The composite films may then be cured at temperatures ranging from 75 – 150 °C (preferably at 75 °C for most of the experiments), e.g. for 24 h.

5 Preparation 3. Resin-NCC composite

Synthesis of resin-NCC composite

20 mL of a 3.5 wt% aqueous NCC suspension was sonicated for 10 – 15 min using an Aquasonic 50T sonicator. 500 µL (35 wt %) PF resin precursor solution was added to the NCC suspension and was stirred at room temperature for 30 min. The homogenous solution was then transferred in 5 mL portion to each 60 mm polystyrene Petri dish and allowed to dry for 48 h at ambient conditions until free-standing films (Fig. 1) were obtained. The resulting free-standing composite films were then thermo-polymerized in an oven at 75 °C for 24 h yielding 660 mg of composite films. The films turned slightly pink after thermal curing. Observation of the films by polarizing optical microscopy reveals strong birefringence and, in some regions of the film, fingerprint textures (Fig. 2a) indicating chiral nematic ordering is not hampered by the presence of resin pre-polymer. SEM images (Fig. 9 a, b and Fig. 10 b) of cross sections of the composite films show layered structure having rod-like morphology with twisting in a counter-clockwise direction indicating left-handed helical organization. Infrared spectra showed characteristic peaks of both the NCC and the PF resin. CP/MAS ¹³C ssNMR spectra (Fig. 5) and the PXRD pattern (Fig. 6) show the characteristic peaks mostly corresponding to NCC owing to its high relative concentration (75%) with respect to the resin precursor in the composite films. TGA (Fig. 12) under both nitrogen and air showed that the film is stable up to ~165 °C and beyond that temperature the composite film thermally degrades resulting in ~22.5% char content and ~3.0% ash content at 900 °C under nitrogen and air, respectively.

Removal of NCC:

30 200 mg of the composite films were placed in a beaker containing 100 mL solution mixture having 4.2% LiOH and 12% urea precooled to -10 °C. The films were gently swirled intermittently while keeping in and taking out (to prevent freezing) of

-36-

a freezer at -10 to -15 °C for 12 h resulting in a transparent film. The films were then periodically washed with copious amount of de-ionized water to remove LiOH/urea solution and were allowed to dry yielding 65 mg of resin film. Optical microscopy showed strong birefringence and a fingerprint texture (Fig. 2b) in some regions, indicating chiral nematic ordering. SEM images (Fig. 10 c, d) of cross sections of the resin films show layered structure having rod-like morphology with twisting in a counter-clockwise direction indicating left-handed helical organization is retained in the resin films after removal of NCC. CP/MAS ^{13}C ssNMR spectra (Fig. 5) and PXRD pattern (Fig. 6) show substantial changes after this procedure that correspond to partial removal of NCC from the composite and an amorphous structure for any remaining NCC. TGA (Fig. 12) under both nitrogen and air showed that the film is stable up to ~300 °C and beyond that temperature the composite film thermally degrades resulting in ~ 19.3% char content and ~ 3.5% ash content at 900 °C under nitrogen and air respectively.

Preparation 4. Resin-NCC composite

Synthesis of resin-NCC composite:

20 mL of a 3.5 wt% aqueous NCC suspension was sonicated for 10 – 15 min using an Aquasonic 50T sonicator. 700 μL (35 wt %) PF resin precursor solution was added to the NCC suspension and was stirred at room temperature for 30 min. The homogenous solution was then transferred in 5 mL portion to each 60 mm polystyrene Petri dish and allowed to dry for 48 h at ambient conditions giving a nearly transparent film with slightly reddish tinge (Fig. 1). The resulting free-standing composite films were then thermo-polymerized in an oven at 75 °C for 24 h yielding 890 mg of composite films. The films turned slightly pink after thermal curing. Optical microscopy showed strong birefringence and finger print texture indicating chiral nematic ordering. UV-Vis spectra (Fig. 4) showed a reflection peak at ~890 nm. CD spectroscopy showed a reflection peak almost at the same position with a positive ellipticity indicating left-handed chiral nematic ordering.

Removal of NCC:

250 mg of the composite films were placed in a beaker containing 100 mL solution mixture having 4.2% LiOH and 12% urea precooled to -10 °C. The films were gently swirled intermittently while keeping in and taking out of a freezer at -10 to -15 °C for 12 h resulting in a transparent film. The films were then periodically washed with copious amount of de-ionized water to remove LiOH/urea solution and were allowed to dry yielding ~95 mg of resin film.

Preparation 5. Resin-NCC compositeSynthesis of resin-NCC composite:

15 mL of a 3.5 wt% aqueous NCC suspension was sonicated for 10 – 15 min using an Aquasonic 50T sonicator. 675 µL (35 wt %) PF resin precursor solution was added to the NCC suspension and was stirred at room temperature for 30 min. The homogenous solution was then transferred in 5 mL portion to each 60 mm polystyrene Petri dish and allowed to dry for 48 h at ambient conditions. The resulting free-standing composite films were then thermo-polymerized in an oven at 75 °C for 24 h yielding 720 mg of composite films. The films turned slightly pink after thermal curing. Optical microscopy showed birefringence and a fingerprint texture indicating chiral nematic ordering. UV-Vis spectra showed a reflection peak at ~1110 nm.

Removal of NCC:

200 mg of the composite films were placed in a beaker containing 100 mL solution mixture having 4.2% LiOH and 12% urea precooled to -10 °C. The films were gently swirled intermittently while keeping in a freezer at -10 to -15 °C for 12 h resulting in a transparent film. The films were then periodically washed with copious amount of de-ionized water to remove LiOH/urea solution and were allowed to air-dry yielding ~101 mg of resin film. UV-Vis spectra showed a reflection peak at ~1005 nm (Fig. 7).

Preparation 6. Resin-NCC compositeSynthesis of resin-NCC composite without chiral nematic ordering:

5 mL of a 3.5 wt% aqueous NCC suspension was sonicated for 10 – 15 min using an Aquasonic 50T sonicator. 350 μ L (35 wt %) resin precursor solution was added to the NCC suspension and was stirred at room temperature for 30 min. The homogenous solution was then transferred to a 60 mm polystyrene Petri dish and allowed to dry for 48 h at ambient conditions giving a transparent film. The resulting free-standing composite film was then thermo-polymerized in an oven at 75 °C for 24 h yielding 290 mg of composite films. The films turned slightly pink after thermal curing. The film did not show any iridescence. Optical microscopy showed neither birefringence nor a fingerprint texture that would suggest chiral nematic ordering in the films. The lack of chiral nematic ordering was further confirmed with SEM (Fig. 9 c and d).

Preparation 7. Resin-NCC compositeSynthesis of resin-NCC composite:

150 μ L of 0.1 M NaCl (aq) solution was added to 15 mL of 3.5 wt% aqueous NCC suspension and was sonicated for 10 – 15 min using an Aquasonic 50T sonicator. Then 375 μ L (35 wt %) PF resin precursor solution was added to the NCC suspension and was stirred at room temperature for 30 min. The homogenous solution was then transferred in 5 mL portion to each 60 mm polystyrene Petri dish and allowed to dry for 48 h at ambient conditions giving red iridescent films. The resulting free-standing composite films were then thermo-polymerized in an oven at 75 °C for 24 h to obtain 520 mg of films. Optical microscopy showed strong birefringence and finger print texture indicating chiral nematic ordering.

The same procedure was followed with 300 μ L and 450 μ L of 0.1 M NaCl (aq) solution to obtain 540 mg of 2 mM and 565 mg of 3 mM NaCl films respectively.

Removal of NCC of these films was performed using the same procedure described above.

Preparation 8. Resin-NCC compositeSynthesis of resin-NCC composite:

150 μ L of 0.1 M NaCl (aq) solution was added to 15 mL of a 3.5 wt% aqueous NCC suspension and was sonicated for 10 – 15 min using an Aquasonic 50T sonicator. Then 525 μ L (35 wt %) PF resin precursor solution was added to the NCC suspension and was stirred at room temperature for 30 min. The homogenous solution was then transferred in 5 mL portion to each 60 mm polystyrene Petri dishes and allowed to dry for 48 h at ambient conditions giving yellow-red films. The resulting free-standing composite films were then thermo-polymerized in an oven at 75 °C for 24 h to obtain 713 mg of films. Optical microscopy showed strong birefringence and a fingerprint texture indicating chiral nematic ordering in the composite films. UV-Vis spectra (Fig. 4) showed a reflection peak at ~660 nm.

The same procedure was followed with 300 μ L and 450 μ L of 0.1 M NaCl (aq) solution to obtain 740 mg of 2 mM (greenish yellow film; Fig. 5b) and 764 mg of 3 mM (greenish blue film; Fig. 5a) NaCl films respectively. UV-Vis spectra (Fig. 4) showed a reflection peak at ~610 and ~540 nm for 2 mM and 3 mM films respectively.

Removal of NCC of these films was performed using the same procedure described above.

Preparation 9. Resin-NCC compositeSynthesis of resin-NCC composite:

150 μ L of 0.1 M NaCl (aq) solution was added to 15 mL of a 3.5 wt% aqueous NCC suspension and was sonicated for 10 – 15 min using an Aquasonic 50T sonicator. Then 675 μ L (35 wt %) PF resin precursor solution was added to the NCC suspension and was stirred at room temperature for 30 min. The homogenous solution was then transferred in 5 mL portion to each 60 mm polystyrene Petri dishes and allowed to dry for 48 h at ambient conditions. The resulting free-standing composite films were then thermo-polymerized in an oven at 75 °C for 24 h to obtain 745 mg of 1 mM NaCl films. Optical microscopy showed birefringence

and a fingerprint texture indicating chiral nematic ordering. UV-Vis spectra showed a reflection peak at ~865 nm.

The same procedure was followed with 300 μL and 450 μL of 0.1 M NaCl (aq) solution to obtain 767 mg of 2 mM and 794 mg of 3 mM NaCl films respectively.

Removal of NCC of these films was performed using the same procedure described above. The resulting films showed reflection peaks both in UV-Vis (Fig. 7) and CD spectra (Fig 8).

Results for NCC/resin composites

Dry composite films show strong iridescence in the visible region. The composite films have chiral nematic order as confirmed by circular dichroism (CD) spectroscopy and UV-visible / near-IR spectroscopy. They reflect at a wavelength that can be tuned by both varying the resin-NCC composition (Fig. 3) as well as changing the ionic strength of the solution by addition of salts at different concentrations (Fig. 4). The colors of the composite films can be varied from blue to the near infrared by varying ionic strength and/or the ratio of NCC/resin precursor in the suspensions.

Dissolution and selective partial removal of NCC from the composite films were achieved with 4.2% LiOH(aq) (alternatively 7% NaOH(aq))/12% urea(aq) solution cooled to -10 °C. The composite films were soaked in the above solution for 12 h with intermittent slow swirling or mixing resulting in transparent films while wet that became iridescent films after drying. The partial removal of NCC was confirmed by solid-state NMR spectroscopy (ssNMR) and powder X-ray diffraction (PXRD) of the mesoporous resins. Solid-state ^{13}C CP/MAS NMR spectra (Fig. 5) of the resin-NCC composite film shows peaks corresponding mostly to the cellulose at 105 ppm (C1), 89 ppm (C4), around 73 ppm (C2,3,5) and 65 ppm (C6).²⁴ These peaks appear with similar peak profiles and relative peak intensities compared to those of neat cellulose²⁵ or cellulose in organosilica/NCC composite materials²³. In the ^{13}C CP-MAS NMR spectrum of the composite after partial NCC removal, the intensity of the peaks associated with NCC is diminished relative to those originating from the

resin. New peaks appear at 129 ppm (various substituted and non-substituted aromatic carbons), and 152 ppm (aromatic carbon attached to hydroxyl group). In addition, very low intensity peaks at around 190, 30-40 and 15 ppm can be assigned to the CHO, various methylene linkages and methyl groups, respectively, of the cross-linked PF resin. Although ^{13}C CP-MAS NMR spectroscopy is not a quantitative method, the two spectra shown were obtained under the same conditions and so the relative intensities of the peaks is an estimate of the quantities of the components present. Based on the extent of diminution of the peaks associated with cellulose, we estimate that ~85% of the NCC was removed. Removal of NCC was further confirmed by PXRD analysis (Fig. 6). The PXRD pattern of the composite film shows strong reflection peaks at $2\theta = 22.8^\circ$ and at $2\theta = 15.0^\circ$ (with a shoulder at $2\theta = 16.8^\circ$) that can be assigned to the (002) and (101) planes, respectively, of crystalline cellulose.²⁶ After NCC removal, the PXRD pattern of the resin film shows only two very low intensity amorphous halos centered at $2\theta = 12^\circ$ and 21° , with no evidence of crystalline cellulose remaining in the resin. Taken together, these data show that most of the cellulose can be removed from the PF-NCC composite film.

The dried resin films thus obtained show strong birefringence and fingerprint textures under POM (Fig. 2b) that are very similar to those of resin-NCC composite films (Fig. 2a) and pure NCC films. The peak reflectance of the mesoporous resin films is blue-shifted relative to the corresponding composite films by ~100 nm as discerned from the UV-Vis-NIR spectra. UV-Vis-near-IR transmittance spectra (Fig. 7) and CD spectroscopy confirmed that the mesoporous resin films selectively reflect left circularly polarized light (Fig. 8) and hence prove that the helical ordering of NCC is replicated and preserved in the resin films. It is thus possible to synthesize mesoporous resin films reflecting left-handed circularly polarized light with reflection peaks spanning from blue to near-infrared region.

The replication of the chiral nematic organization of the NCC template in the mesoporous resin films was confirmed with scanning electron microscopy (SEM). Cross sections perpendicular to the surface of the films show layered structures

with repeating distance of several hundreds of nanometers. This layered structure arises from the helical pitch of the chiral nematic structure and is responsible for the reflection of light from the materials. Imprinting of chiral nematic ordering in the resin films is limited by a range of NCC:resin ratio. Films prepared with about 50 wt% or less of resin pre-polymer with respect to the weight of NCC in the suspension show chiral nematic ordering. Beyond that concentration chiral nematic ordering is not seen in PF composites or their corresponding resin films (Fig. 9). Imprinting of chiral nematic structures of NCC in the resin films occurred over various length scales. SEM of the resin films reveals domain structures in the relatively smooth surface of the films (Fig. 10a) while higher magnification SEM of cross sections show rod-like morphology with twisting in a counter-clockwise direction indicating left-handed helical organization (Fig. 10b). Defects associated with LCs are seen in some locations throughout the films (Fig. 10c). The structures of the resin films (Fig. 10d) resemble overall structures of corresponding composite films and neat NCC films providing direct evidence of replication of the chiral nematic organization of NCC into the resin films which is preserved even after removal of NCC.

The chiral nematic PF resin films obtained after partial NCC removal did not show any significant porosity by N_2 adsorption measurements when wet films were air-dried under ambient conditions. This could be due to the strong capillary action of the hydrophilic pores resulting in pore collapse during drying.²⁷ However, critical point drying of the wet films using supercritical carbon dioxide ($scCO_2$) leads to substantial porosity of the films as measured by nitrogen adsorption analysis. All of the resin films analysed (after partial NCC removal) showed type IV adsorption isotherms with large hysteresis loops (Fig. 11a). The calculated BET (Brunauer-Emmett-Teller model) surface areas of the resin films ranged from 300 – 400 m^2/g depending on the NCC/resin ratio. The BJH (Barrett-Joyner-Halenda model) pore size distributions calculated from the adsorption branch of the isotherm give average diameter of about 6 nm (Fig. 11b) which is on the order of the diameter of individual nanocrystals. Hence the calculated adsorption average pore diameter

indicates replication of individual cellulose nanocrystals instead of bundles in the pore structures.

5 Thermogravimetric analysis (TGA) was performed to study the thermal stability of the resin films both under air and nitrogen. TGA of the materials run under both air and nitrogen show that the resin films after partial NCC removal have very different degradation profiles than their corresponding composite films (Fig 12). The composite films start degrading at ~165 °C. In contrast, after NCC removal, the resin films are stable up to about 300 °C. The char content of the resin films is about 19% at 900 °C under nitrogen.

10 The chiral nematic resin films are mechanically robust and flexible. They can be cut into shapes using scissors and can be bent and straightened several times without any visible structural damage (Fig. 13).

15 Adsorption of water and consequent swelling of the mesoporous PF resins demonstrate interesting properties of the chiral nematic mesoporous resin films. These films rapidly adsorb water and become transparent. Under POM, a significant reduction in the birefringence is observed when the film is infiltrated with water. The films regain their iridescence and birefringence after drying, indicating that these changes are reversible. It is found that the swelled films show reflection peaks by UV-visible and CD spectroscopy that are red-shifted relative to the unswollen films, indicating an increase in the helical pitch of the chiral nematic structure after swelling. Swelling of the composite film results in a red shift of the reflection peak by ~50 nm, whereas the corresponding resin film shows a much larger red shift in the reflection peak (>400 nm in some cases) (Fig. 14). This difference in the shifting of the reflection peak can be attributed to the lower swellability of the PF-NCC resins probably because of the highly crystalline nature of cellulose in the nanocrystals and also interactions between the cellulose and the PF resin. The resin films obtained after NCC removal swell more in polar solvent than in nonpolar ones as observed by UV-Vis spectroscopy (Fig. 15). This is a

unique property that enables these resin films to be used as a sensor based on spectrophotometric measurements.

While the chiral nematic mesoporous resin described above were prepared from PF-NCC composites, a person skilled in the art will understand that other phenol derivative formaldehyde resins are stable in basic conditions relative to NCC, and can be used to produce chiral nematic mesoporous resins. These include, but are not limited to, resorcinol, phloroglucinol, and aldehyde derivatives thereof. A person skilled in the art may further understand that other mild drying conditions other than supercritical CO₂ may be sufficient to maintain the porosity of the resins. A person skilled in the art will understand that other strong hydroxide bases of alkali metals and alkaline earth metals, may be useful for removing the NCC from the PF polymer, including LiOH, NaOH, CsOH, RbOH, Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂. Ammonia solution or group 1 salts of amides and hydrides may also be useful.

Example 3. UF-NCC composites

Preparation of UF Composite Materials

Figure 16 shows a typical precursor employed and the structure of the polymer obtained in the presence of NCC. A typical procedure to obtain UF-NCC composites uses an acidic urea-formaldehyde precursor solution (preparation 10, Fig. 16) that is subsequently mixed with an aqueous suspension of NCC (for example, #1: pH = 2.4, 3.0 wt%). After 48 – 72 h drying under ambient conditions highly iridescent polymer composite films are obtained (preparation 11). Various ratios of polymer precursor and NCC suspension as well as the addition of different amounts of aqueous sodium chloride solution (0.25 N) can be used in order to modify the color of the iridescent composite films. After 48 – 72 h drying under ambient conditions highly iridescent polymer composite films are obtained (preparation 11).

Preparation 10. Preparation of the UF precursor

1.00 g of urea was dissolved in 10.0 g of a formaldehyde solution in water (37 wt%). To the clear solution, 1 drop of a solution of hydrochloric acid in water (37

wt%) was added. After 3-5 minutes, the solution turns opaque and a white solid starts to precipitate. By heating the reaction mixture to 100 °C a clear solution is observed. The precursor solution is stirred with continued heating for 30 minutes. After cooling to room temperature a clear solution was obtained. This clear solution was used as the UF precursor solution in Preparations 11 and 12.

Preparation 11

Synthesis of the UF/NCC composite (samples 4A – C)

A) To 5.0 mL of a stirred NCC suspension in water (#1: pH = 2.4, 3.0 wt%), 250 µL of the UF precursor solution (preparation 10) was added. The mixture was stirred for 5 min and then poured into a 5 cm polystyrene Petri dish. After drying under ambient conditions for 48 h, a highly iridescent composite film was obtained. In order to remove the film from the polystyrene dish the edge of the Petri-dish was removed and the bottom was heated for 5-10 sec on a hot plate (at approx. 250 °C). Afterward, the free-standing composite films detached from the polystyrene layer. After drying, a red iridescent film (sample 4A) was obtained. The UV-Vis spectrum shows a minimum in transmission at 750 nm and the CD spectrum exhibits a maximum at 730 nm (positive ellipticity).

B) To 5.0 mL of a stirred NCC suspension in water (#1: pH = 2.4, 3.0 wt%), 500 µL of the UF precursor solution (preparation 10) was added. The mixture was stirred for 5 min and then poured into a 5 cm polystyrene Petri dish. After drying under ambient conditions for 48 h a highly iridescent composite film was obtained. In order to remove the film from the polystyrene dish the edge of the Petri dish was removed and the bottom was heated for 5-10 s on a hot plate (at approx. 250°C). Afterward, the composite film (sample 4B) detached from the polystyrene layer.

The composite materials were obtained as slightly red iridescent films. The UV-Vis spectrum shows a reflection at 790 nm and the CD spectrum exhibits a peak at 750 nm. The IR spectrum shows characteristic signals for UF as well as for NCC: 3650-3100 cm⁻¹ (OH/NH), 2970-2840 cm⁻¹ (CH), 1640 cm⁻¹

(C=O), 1500 cm^{-1} ($-\text{CH}_2\text{-OH}$). The thermogravimetric analysis of the composite sample shows the start of decomposition at $320\text{ }^{\circ}\text{C}$.

5 C) To 5.0 mL of a stirred NCC suspension in water (#1: pH = 2.4, 3.0 wt%), 750 μL of the UF precursor solution (preparation 10) was added. The mixture was stirred for 5 min and then poured into a 5 cm polystyrene Petri dish. After drying under ambient conditions for 48 h, a highly iridescent composite film was obtained. In order to remove the film from the polystyrene dish the edge of the Petri dish was removed and the bottom was heated for 5-10 s on a hot plate (at approx. $250\text{ }^{\circ}\text{C}$). Afterward, the composite films detached from the polystyrene layer.

10 The polymer composite (sample 4C) was obtained as a nearly colorless iridescent film with a reflection signal at 830 nm in the UV-Vis spectrum and at 830 nm in the CD spectrum (positive ellipticity).

15 Preparation 12.

Synthesis of the UF-NCC composite with salt addition

20 Samples 5A – D were prepared by the same procedure, but using different amounts of 0.25 M aqueous NaCl solution. In a typical procedure, an aqueous sodium chloride solution (0.25 M; 20 μL for preparation A, 40 μL for preparation B, 80 μL for preparation C, or 120 μL for preparation D) was added to 5.0 mL of a suspension of NCC in water (#1: pH = 2.4, 3.0 wt.%). After sonicating the mixture for 10 min and stirring for an additional 10 min, 500 μL of UF precursor solution (preparation 10) were added. The suspension was stirred for 5 min and then poured into a 5 cm polystyrene Petri dish. After drying under ambient conditions for 25 72 h, a highly iridescent composite film was obtained. The composite films were detached from the polystyrene substrate by removing the edge of the Petri dish and heating on a hot plate (at approx. $250\text{ }^{\circ}\text{C}$) for 5-10 s.

30 A) The polymer composite (sample 5A) was obtained as a slightly red iridescent film with a reflection signal at 780 nm in the UV-Vis spectrum and at 740 nm in the CD spectrum.

B) The polymer composite (sample 5B) was obtained as a red iridescent film with a maximum reflectance signal at 690 nm in the UV-Vis spectrum and at 680 nm in the CD spectrum.

C) The sample (5C) was obtained as green/yellow iridescent film with an absorption signal at 600 nm in the UV-Vis spectrum and at 580 nm in the CD spectrum.

D) The sample (5D) was obtained as blue/green iridescent film with an absorption signal at 530 nm in the UV-Vis spectrum and at 520 nm in the CD spectrum.

This sample was used to investigate the swelling behavior of the material. UV-Vis as well as CD-data confirm the change in color by swelling under preservation of the chiral nematic order (original film: UV-Vis: 530 nm, CD: 520 nm, swollen film: 630 nm, CD: 670 nm; dry film: UV-Vis: 490 nm, CD: 380 nm).

Results

For demonstration, three different ratios of polymer precursor to NCC mixtures (4A – C) were used ending in UF-NCC composites with 20 wt%, 45 wt% and 60 wt% of urea-formaldehyde with respect to NCC (calculated by amount of precursor employed). The color of the composite films is red-shifted from 740 nm to 825 nm with increasing proportion of polymer in the composition. The different colors arise from a change in the helical pitch. Fig. 17 shows the UV-Visible spectra (Fig. 17a) and CD spectra (Fig. 17b) of the different composite samples. The CD spectra as well as SEM images confirm the chiral nematic order of the composite films (Fig. 18 shows the SEM image of sample 4A as a representative example). Fig. 19 shows the IR spectrum of UF-NCC composite 4B as a representative example. The carbonyl C=O stretching signal at 1640 cm^{-1} confirms the formation of the UF polymer. The thermal stability of the polymer composites was investigated by TGA. Compared to pure NCC films, the UF-NCC composite shows enhanced thermal stability. Whereas the NCC starts to decompose at $200\text{ }^{\circ}\text{C}$, the composite sample 4B is stable to $320\text{ }^{\circ}\text{C}$ (see Fig. 20).

The effect of salt addition on the chiral nematic order of the UF-NCC composite films was investigated in a series of four different composite samples (5A – D) with various salt concentrations. The different amounts of salt cause varying hydrodynamic radii of NCC during the self-organization in solution and therefore lead to varying helical pitches in the final polymer composite films. The color of the UF-NCC composites ranges from red to yellow/green to blue (see fig. 21). The addition of salt to the composites results in a strong blue shift from 780 nm to 500 nm. The change in the helical pitch was verified by CD spectroscopy of the UF-NCC composite films. The UV-Vis (Fig. 22a) and CD spectra (Fig. 22b) of the films prepared with variation in the amount of sodium chloride added during synthesis are shown in Fig. 22.

In order to investigate the properties of the UF-NCC composites in full detail, their swelling behavior in water and ethanol was investigated. Swelling the films for 12 h in water causes a visible color change from blue (dry films) to red (wet films). UV-Vis spectral analysis (Fig. 23a) of the swelling behavior shows a shift of the peak wavelength reflected from 490 nm to 630 nm which was confirmed by CD spectroscopy (Fig. 23b) as well. Fig. 23c shows a photograph of UF-NCC sample before and after swelling in water as well as the corresponding UV-Vis spectra. The UF-NCC composites thus show solvent-dependent responses and iridescence that could be used for sensing applications, among others.

Example 4. MF-NCC composites

Figure 16 shows a typical MF precursor employed and the structure of the polymer obtained in the presence of NCC. Composite films were synthesized by mixing a NCC suspension (#2: pH = 6.9, 5.1 wt%) with various amounts of MF precursor solution (preparations 15A – C). After drying for 72 h on a polystyrene Petri dish, iridescent films were obtained.

Preparation 13. Preparation of the MF precursor

1.00 g of melamine was dissolved in 10.0 g of a 37% aqueous formaldehyde solution and heated to 100 °C. The resulting clear solution was heated for 15 min

then cooled to room temperature. The clear solution was immediately used as MF precursor solution in Preparation 14.

Preparation 14. Synthesis of the MF-NCC composite

Samples 6A – C were prepared by the same general procedure, but changing the quantity of MF precursor solution (preparation 13) employed (in preparation A, 0.25 mL of MF precursor solution was used, in preparation B, 0.50 mL of MF precursor solution was used, and in preparation C, 0.75 mL of MF precursor solution was used). The given quantity of MF precursor solution was added to 5.0 mL of an aqueous suspension of NCC (#2: pH = 6.9, 5.1 wt%). The cloudy suspension was stirred for 15 min and then poured into a 5 cm diameter polystyrene Petri dish. The samples were dried under ambient conditions for 72 h. The free-standing iridescent films were separated from the polystyrene layer by heating the Petri dish for 5-10 s at 250 °C. The samples all showed reflection signals in the UV-visible spectrum and peaks in the CD spectrum that confirmed the chiral nematic structure of the materials.

A) The sample (6A) was obtained as red iridescent film with a reflection signal at 570 nm in the UV-Vis spectrum and a peak with positive ellipticity at 600 nm in the CD spectrum.

B) The sample (6B) was obtained as a reddish iridescent film with a reflection signal at 600 nm in the UV-Vis spectrum and a peak at 650 nm in the CD spectrum. The IR spectrum shows characteristic signals for MF as well as for NCC: 3650-3070 cm^{-1} (OH/NH), 3030 – 2840 cm^{-1} (CH), 1550 cm^{-1} (-C=N-), 1370 cm^{-1} (-CH₂-OH). The solid-state ¹³C CP/MAS NMR (100 MHz, 33921 scans, spinning rate: 6 kHz, contact time: 2 msec, recycle delay: 5 sec): 165 ppm (C₃H₃N₃), 120 – 60 ppm (NCC), 60 – 80 ppm (CH₂MF; overlapped by NCC signals). The thermogravimetric analysis of the composite sample shows the start of decomposition at ~380 °C.

C) The sample (6C) was obtained as a slightly red iridescent film with a reflection signal at 640 nm in the UV-Vis spectrum and a peak at 660 nm in the CD spectrum.

Results

Three different samples with varying ratios of NCC-suspension and MF-precursor were prepared. The characterization by UV-Vis (Fig. 24a) and CD spectroscopy (Fig. 24b) shows a shift of the reflected wavelength to higher wavelengths with increasing amount of melamine-formaldehyde polymer in the composites (see Fig. 24). Additionally the samples become less transparent. The CD spectra confirm the chiral nematic structure and SEM images reveal a layered structure that is typical of this organization (see Fig. 25). The IR spectrum for representative sample 6B is shown in Fig. 26. The signal at 1550 cm^{-1} is assigned to the C-N stretching of the triazine group.²⁸ A representative solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) ssNMR spectrum for 6B is shown in Fig. 27. The signal at 165 ppm is characteristic of the carbon atom in the triazine unit.²⁹ The signal at 223 ppm is due to a spinning side band.²⁹ The remaining signals belong to the NCC and overlap with the methylene carbon signal of the MF-resin at 60 – 80 ppm.

The thermal stability of the composite films was investigated by TGA (see Fig. 28). The NCC films start to decompose at temperatures around 200 °C, while the MF-NCC composite shows a significantly improved thermal stability, with decomposition occurring above about 380 °C.

Example 5. MUF-NCC composites

Figure 16 shows a typical MF precursor employed and the structure of the polymer obtained in the presence of NCC. Mixing a suspension of NCC in water (e.g. #2: pH = 6.9, 5.1 wt.%) with an aqueous MUF precursor and drying, e.g. for 72 h at room temperature (preparations 16 and 17), leads to iridescent, flexible MUF-NCC composite films.

Preparation 15. Preparation of the MUF precursor

1.00 g of urea was dissolved in 10.0 g of a 37 wt.% aqueous formaldehyde solution and stirred for 10 min. After adding 1.00 g of melamine, the mixture was heated to 100 °C and stirred for 15 min. The solution was then cooled to room temperature 10 drops of an aqueous ammonium hydroxide solution (28 wt%) were added. The

mixture was stirred for 4 h at ambient temperature. The colorless, clear solution obtained from this procedure was used in Preparation 16.

Preparation 16. Synthesis of the MUF-NCC composite with salt addition

5 Preparations 16A – D were carried out using the same procedure, but varying the amount of 0.25 M NaCl solution added. 0, 35, 140, and 280 μ L of 0.25 M NaCl solution were added in Preparations 16A, 16B, 16C, and 16D, respectively. The indicated quantity of 0.25 M NaCl was added to 5.0 mL of a suspension of NCC in water (#2: pH = 6.9, 5.1 wt%). The mixture was sonicating for 10 minutes, and then
10 0.50 mL of the aqueous MUF precursor solution (preparation 12) was added. The mixture was stirred for 5 min and then poured into a 5 cm diameter polystyrene Petri dish. After drying under ambient conditions for 72 h, the polymer film was carefully detached from the polystyrene dish.

15 A) The sample (7A) was obtained as a red iridescent film with a reflection signal at 690 nm in the UV-Vis spectrum and a peak at 670 nm in the CD spectrum. Sample 7A was also used to show the change in color by applying pressure on the composite film. The UV-Vis signal was shifted from 690 nm (original film) to 510 nm (pressed sample).

20 B) The sample (7B) was obtained as a red iridescent film with a reflection signal at 690 nm in the UV-Vis spectrum and a peak at 670 nm in the CD spectrum. The IR spectrum shows characteristic signals for UF as well as for NCC: 3600 – 3150 cm^{-1} (OH/NH), 2970 – 2840 cm^{-1} (CH), 1670 cm^{-1} (C=O), 1550 cm^{-1} (-C=N-). The thermo gravimetric analysis of the composite sample
25 shows the start of decomposition at 220 °C.

C) The sample (7C) was obtained as a red iridescent film with a reflection signal at 590 nm in the UV-Vis spectrum and a peak at 610 nm in the CD spectrum.

30 D) The sample (7D) was obtained as a red iridescent film with a reflectance signal at 490 nm in the UV-Vis spectrum and a peak at 480 nm in the CD spectrum.

Preparation 17. Synthesis of the MUF-NCC and imprinting

For the synthesis of appropriate films for imprinting experiments a slightly different precursor solution was used: 1.50 g of urea was dissolved in 10.00 g of 37 wt.% aqueous formaldehyde solution and stirred for 10 minutes. After adding 1.00 g of melamine, the mixture was heated to 100 °C and stirred for 15 min at that temperature. After cooling to room temperature, 10 drops of 28 wt.% aqueous ammonium hydroxide solution were added. The mixture was stirred for 4 h at ambient temperature, giving a clear and colorless precursor solution.

To 10.0 mL of a suspension of NCC in water (#2: pH = 6.9, 5.1 wt.%), 1.00 mL of the aqueous MUF precursor solution was added. The mixture was stirred for 5 min and then poured into a 5 cm diameter polystyrene Petri dish. After drying under ambient conditions for 72 h, the polymer film was carefully detached from the polystyrene dish. The composite material was obtained as a nearly colorless film. For imprinting the UBC crest into the polymer composite film, the stamp was covered with the polymer film and pressure was applied by rubbing a solid metal object carefully over the surface of the film.

Results

Fig. 29 shows samples 7A – D as representative examples for the obtained films. The color of the films can be controlled by changing the amount of polymer precursor incorporated into the preparation, or by adding an aqueous solution of sodium chloride or other salt (increasing the amount of salt causes a blue shift of the reflection peak observed by UV-Vis spectroscopy). The UV-Vis spectra (Fig. 30a) and the CD spectra (Fig. 30b) of the resulting polymer composite samples are shown in Fig. 30. The chirality of the polymer composite was demonstrated by CD spectroscopy (Fig. 30b), which showed a peak with positive ellipticity. An IR spectrum of the representative sample 7B is shown in Fig. 31. The signals at 1670 cm^{-1} (C=O) and 1550 cm^{-1} (CN of triazine) confirm the presence of the MUF resin in the composites. The thermal stability of the composite films was investigated by TGA and shows a comparable thermal stability to the corresponding NCC films (Fig. 32).

The optical properties of the composite materials can be influenced by mechanical stress. Applying pressure to a region of the film or stretching the composite material leads to a color change. This change in color arises from a change in the helical pitch of the chiral nematic polymer composite. Pressure and stretching causes a contraction of the material and a change of the helical pitch that leads to the change in color. UV-Vis spectroscopic studies show a blue shift of the signal from 690 nm to 510 nm after applying pressure on sample 7A (Fig. 33). The CD spectra of the samples and SEM images confirm that chiral nematic order is present in the composite films (Fig. 34 and Fig. 35).

The ability of the material to change color with applied pressure or stretching may be useful for applications in pressure sensing, security features, or imprinted designs. To test this, a film was prepared that was twice as thick as the previously-prepared samples (see preparation 17). The film prepared according to Preparation 17 was removed from the polystyrene petri dish and obtained as a nearly colorless film (only the edges are red colored). A metal stamp with the UBC crest was used for imprinting studies. Therefore the metal stamp was covered with the polymer composite film from preparation 17 and then pressure was carefully applied by using a wrench. During pressure application, the previously colorless film changed color to red or blue depending on the amount of pressure applied on the regions. In front of black velvet the colored iridescence is obvious, but the film remains highly transparent on a white background. The photographs in Figure 36 demonstrate the ability to imprint a pattern on the chiral nematic films by applying pressure.

All of the MUF-NCC composite films were obtained as free-standing, flexible films. However, after 2 – 3 weeks at ambient conditions the composite films become more brittle and further attempts to change the helical pitch by applying pressure failed. By addition of glycerol during the synthesis the films stay flexible for months. Other additives (such as phthalates) that are known to behave as plasticizers may be added to improve the flexibility of the films and to extend their lifetimes.

Example 5. Chiral nematic mesoporous cellulose (CNMC)

Composites as described above may be treated to remove resin to provide chiral nematic NCC. Such chiral nematic NCCs may further be treated to result in a mesoporous NCC, i.e., a chiral nematic mesoporous cellulose (CNMC). Such CNMCs may provide a chiral nematic order, enhanced stability, flexibility, and mesoporosity.

Preparation 18. Synthesis of UF-NCC precursor to CNMC

To synthesize the CNMC, UF-NCC composites were prepared as precursors to the preparation of a CNMC. UF-NCCs prepared according to process 11 or 12 were used. With the object of further increasing the structural flexibility and mesoporosity of the films, UF content was increased for a further composite material. Briefly, a further UF precursor solution was prepared by mixing urea (2 g, 66.6 mmol) and formaldehyde (10 g of a 37 wt% formaldehyde solution stabilized with 10 – 15% MeOH) and letting it stir until everything was dissolved. One drop of an HCl solution (37% in H₂O) was added and the opaque solution was heated to 100 °C for 30 min until it became clear. Next, 1 mL of the UF precursor solution was added to 5 mL of a NCC suspension (NCC-Na, pH= 6.9, 3 wt. %) and stirred for 10 min at room temperature. The mixture was transferred to a cellulose acetate surface (5 cm diameter) and allowed to dry for 48 h under ambient conditions. To terminate the polymerization these films were cured at 120 °C for 16 h in an oven to give UF-NCC composites suitable for making CNMC. Elemental analysis: %C: 41.05; %H: 6.08, %N: 17.48.

Preparation 19. Synthesis of CNMC

The films of UF-NCC described above were heated to 70 °C in an aqueous solution of KOH (15%) for 16 h. These films were then washed with water and ethanol and finally dried under ambient conditions. To obtain the mesoporous CNMC, the films were washed and soaked in EtOH and dried with supercritical CO₂. Elemental Analysis for CNMC: %C: 40.45; %H: 6.09, %N: not detected, %S: not detected. For comparison, a typical analysis of the NCC-Na films gives: %C: 40.30; %H: 6.32,

%N: not detected, %S: 0.66. The CNMC material prepared from the UF-NCC prepared with greater UF content is referred to herein as "A4"

Results

5 UF resins could be removed from the composite material with aqueous potassium hydroxide or sodium hydroxide at about 70 °C. With respect to A4, solid-state ^{13}C CP-MAS NMR spectroscopy of the UF-NCC film before the treatment showed signals associated with both the UF resin and cellulose (Fig. 37a). After the
10 treatment, the resonances associated with the UF resin have nearly completely disappeared and the resonances from cellulose I remain (both spectra were obtained with the same experimental parameters). However, signal broadening as well as new peaks at ~84 and ~62 ppm assigned to amorphous or surface cellulose (C4' and C6', respectively) indicate significant loss in crystallinity.

15 The diagnostic carbonyl C=O stretching vibration of CNC-UF composites found at about 1664 cm^{-1} in the UF-CNC composite is absent in CNMC after the treatment with base, supporting loss of the resin. Most importantly, although nitrogen is easily detected in the UF-NCC composites by elemental (combustion) analysis, no nitrogen was detected in the CNMC materials (< 0.2% N). Furthermore, powder X-
20 ray diffraction (PXRD) patterns indicate that the cellulose films obtained from this procedure have a substantially lower degree of crystallinity (~70%) than pure NCC (>90%), but maintain the natural cellulose I structure. It is notable that a control experiment where pristine NCC was treated with 15% $\text{KOH}_{(\text{aq})}$ solution under identical conditions led to mercerization (conversion from cellulose I to cellulose II)
25 of the cellulose. These results show that the product is a cellulosic material with the UF resin removed.

Nitrogen adsorption measurements indicate that chiral nematic NCC films and UF-NCC composites are both nonporous. This also applies to CNMC films dried under
30 ambient conditions from water or ethanol. However, ethanol-soaked CNMC samples dried from supercritical CO_2 show significant mesoporosity. Thus, effective removal of the space-filling UF co-template imparts mesopores between the

cellulose nanocrystals. The water dried films show a significant surface area after reswelling them in EtOH and subsequent supercritical drying. Moreover, N₂ adsorption shows a type IV isotherm with Brunauer-Emmett-Teller (BET) surface areas as high as 252 m² g⁻¹ and an average pore volume of 0.6 cm³ g⁻¹. The calculated Barrett-Joyner-Halenda (BJH) pore-size distributions are about 8 nm.

In contrast to regular NCC films, however, which disperse in one to two hours in water, CNMC is stable in water for weeks, and even boiling the water does not result in any decomposition. The enhanced stability of the CNMC in water arises from desulfation of the CNC surface proven by CHNS analysis, which showed no sulfur (<0.2%) in CNMC samples. Desulfation, resulting from the co-templating process, leads to uncharged and non-dispersible CNMC films. Desulfated NCC does not naturally self-assemble into a chiral nematic structure, however, the method disclosed herein provides a novel, desulfated NCC material in which the chiral nematic structure is preserved. Without wishing to be bound by theory, this may be due to concomitant desulfation and destruction of the UF resin.

The CNMC materials prepared in this way can be tuned to reflect light across the spectrum (including in the visible region) by appropriate choice of the UF-NCC composite. The materials appear iridescent and show a CD signal with positive ellipticity by CD spectroscopy. Furthermore, SEM images of the CNMS materials show a layered, twisting structure similar to other chiral nematic structures prepared from NCC templates (Fig. 38).

Based on IR, solid-state NMR spectroscopy, CHNS analysis, gas adsorption and PXRD data, it appears that CNMCs are made solely of cellulose I, or native cellulose (i.e. exactly the same form as that for starting NCC material). CNMC shows similar thermal stability to sodium salts of NCC and the UF-NCC composite films (Figure 39). In terms of the characteristic mechanical behavior, CNMC shows an ultimate tensile strength of 42 ± 5 MPa (Figure 40), which is substantially higher than the tensile strength reported for graphene paper (8.8 MPa) or graphene / polyaniline paper (12.6 MPa).³⁰

Retention of the chiral nematic structure in the composite and derived films was deduced by a combination of polarized optical microscopy (POM), UV-vis spectroscopy, circular dichroism (CD) spectroscopy and scanning electron microscopy (SEM). In general, chiral nematic structures reflect light with a wavelength ($\lambda_{\max}$) that depends on the helical pitch (P), the angle of incident light (θ) and the average refractive index (n_{avg}) of the material according to the following equation:³¹

$$\lambda_{\max} = n_{\text{avg}} \cdot P \cdot \sin(\theta)$$

Thus, the color reflected by a chiral nematic structure may be modulated by manipulating the pitch or the refractive index. With increasing polymer content, a red shift is observed, while salt addition causes a blue shift with increasing ionic strength. Coloration of the films can be varied in the range 500 to 1300 nm.

The composite used to produce A4 provides a good basis for a flexible and mesoporous CNMC and appears nearly transparent and colorless (reflecting at 1300 nm; Figure 41). However, after removal of the UF, the resulting films dried from water experience a significant blue shift with a peak reflectance at 330 nm in the UV-vis spectrum (Figure 41; "PnP dried from H₂O"). In contrast, films dried with supercritical CO₂ appear visibly iridescent and UV-vis spectroscopy shows that they reflect light at ~500 nm (Figure 41; "PnP dried from EtOH (scCO₂)"). The red-shifted reflectance compared to the water-dried samples indicates that the pitch, P , of the chiral nematic structure is increasing with the introduction of mesoporosity. The translucent appearance of the films is also indicative of their underlying mesoporous structure. SEM images of water-dried films and supercritically-dried CNMC films show a layered structure that is characteristic of a chiral nematic order (Figure 38a and Figure 38B). The microstructure of CMNC after supercritical drying seems less ordered than the other samples, and this heterogeneity may contribute to the opacity of this sample.

The CNMC materials swell in solvents, and the degree of swelling depends on the nature of the solvent. When the films swell, the color at which they reflect light changes. Thus, these materials can be used to sense liquids that penetrate the pores of the CNMC. Furthermore, the materials respond to pressure. It was possible to press a sample of CNMC that was placed between microscope slides and observe a visible color change. CNMC materials may prove useful for chromatography, especially for separation of enantiomers of chiral substances, for pressure sensing, for chemical sensing, for separation membranes, for drug delivery, for catalyst substrates, and as precursors to carbon materials upon pyrolysis.

To investigate the sensing performance of the composites and the derived films, swelling behavior in different polar solvents was studied. Whereas UF-NCC composites take several hours to swell in water, reaching equilibrium after ~12 h (Figure 23a and 23b), the CNMC shows a rapid red-shift of its reflection peak from 330 nm (dry film) to 820 nm when immersed in polar solvents (Figure 42a and 42b), which is easily observable by the naked eye. This response is significantly faster than previously reported for hydrogel materials, and especially remarkable due to the simplicity of the synthesized material. The degree of swelling is dependent on the solvent, and by varying the solvent mixture (ethanol/water), the visible colors can be tuned from 430 nm in pure ethanol to 840 nm in pure water (Figure 42a,b). Due to the hydrophilicity and the mesoporosity of these CNMC films, they rapidly swell to the greatest extent in pure water. During swelling, the chiral nematic order of the composite film is not affected, which is confirmed by CD measurements. It takes 5 h to fully swell the composite films to the red color, and 3 h to dry them again. As ethanol and water have similar refractive indices, the color change may be mainly attributed to a change in the helical pitch upon swelling detectable either by UV-vis or CD spectroscopy, which may allow the development of new sensors.

Surprisingly, the water-soaked chiral nematic NCC samples show a high flexibility and piezochromic behavior. When inserted between two glass slides, the films exhibit a distinctive color change upon manually pressing the films. The

macroscopically applied pressure is transferred to the nanoscale level leading to a compression of the layers and, thus, the helical pitch of the chiral nematic structure is reduced. The blue-shift was observed in a reflectivity range of about 100 nm, from 630 nm to 520 nm (Figure 42c), and the change in photonic color was quantified as a function of applied pressure (Figure 42d). The coloration is completely reversible: after the applied stress was removed, the material relaxed and returned to its initial colorless state.

While the CNMC embodiments described above were created from UF-NCC, the inventors have made a further CNMC from MUF-NCC. A person skilled in the art will understand that CNMC may be made from other composites comprising amino-formaldehyde resins, including MF-NCC, which are more labile in basic conditions than NCC. Moreover, the person skilled in the art will understand that the conditions for removing the resin could be modified.

For example, the person skilled in the art will understand that other strong hydroxide bases of alkali metals and alkaline earth metals, may be useful, including LiOH, NaOH, CsOH, RbOH, Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂. Ammonia solution or group 1 salts of amides and hydrides may also be useful. Base concentrations of between about 10 and about 30 wt%, and temperature ranges between about 60 °C and about 90 °C, may be used, with reaction times adjusted accordingly to remove the resin from the NCC.

The critical drying of the chiral nematic NCCs to form CNMC may also be modified. For example, any samples swollen in solvents compatible with supercritical CO₂ drying such as alcohols (methanol, ethanol and iso-propanol) and acetone are may be used in the process. A person skilled in the art may further understand that other mild drying conditions other than supercritical CO₂ may be sufficient to maintain the porosity of the CNMC.

Although various embodiments of the invention are disclosed herein, many adaptations and modifications may be made within the scope of the invention in

-60-

accordance with the common general knowledge of those skilled in this art. Such modifications include the substitution of known equivalents for any aspect of the invention in order to achieve the same result in substantially the same way. Numeric ranges are inclusive of the numbers defining the range. The word "comprising" is used herein as an open-ended term, substantially equivalent to the phrase "including, but not limited to", and the word "comprises" has a corresponding meaning. As used herein, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a thing" includes more than one such thing. Citation of references herein is not an admission that such references are prior art to the present invention. Any priority document(s) and all publications, including but not limited to patents and patent applications, cited in this specification are incorporated herein by reference as if each individual publication were specifically and individually indicated to be incorporated by reference herein and as though fully set forth herein. The invention includes all embodiments and variations substantially as hereinbefore described and with reference to the examples and drawings.

References:

1. *Chem. Rev.* **2010**, *110*, 3479–3500.
2. *Biomacromolecules* **2005**, *6*, 1055-1061.
3. *Angew. Chem. Int. Ed.* **2011**, *50*, 5438 – 5466.
4. *Macromol. Rapid Commun.* **2004**, *25*, 771–787.
5. *Phys. Rev. Lett.* **1987**, *58*, 2059 – 2062.
6. *Nature*, **1997**, *386*, 143 – 149.
7. *J. Mater. Chem.*, **2008**, *18*, 3040–3043.
8. *Nature Mater.* **2002**, *1*, 111 – 113.
9. *Chem. Mater.* **2008**, *20*, 649–666.
10. *Adv. Mater.* **2009**, *21*, 3915–3918.
11. *Appl. Phys. Lett.* **2007**, *90*, 093102-1-3.
12. *Macromol. Res.*, **2006**, *14*, 155-165.
13. *J. Mater. Chem.*, **2009**, *19*, 3998–4003.

14. *Chem. Mater.* **2009**, *21*, 4993–4999.
15. *Soft Matter*, **2012**, *8*, 6280–6290.
16. *Adv. Mater.* **2007**, *19*, 207–210.
17. *Macromolecules* **2009**, *42*, 1817–1823.
- 5 18. *Macromolecules* **2009**, *42*, 3715–3720.
19. *Nature*, **2003**, *424*, 852 – 855.
20. *PNAS*, **2012**, *109*, 15712 – 15715.
21. *J. Mater. Chem.*, **2010**, *20*, 1277–1284.
22. *Nature*, **2010**, *468*, 422 - 425.
- 10 23. *J. Am. Chem. Soc.*, **2012**, *134*, 867 - 870.
24. *J. Am. Chem. Soc.*, **1980**, *102*, 3249–3251.
25. *J. Am. Chem. Soc.* **2002**, *124*, 7506–7511.
26. *Can. J. Chem. Eng.* **2010**, *88*, 392 – 402.
27. *Soft Matter*, **2012**, *8*, 2087–2094.
- 15 28. *J. Adhesion Sci. Technol.* **2006**, *20*, 209–219.
29. *Macromol. Chem. Phys.* **2007**, *208*, 2204–2214.
30. *ACS Nano* **2009**, *3*, 1745–1752.
31. *Acta Crystallogr.* **1951**, *4*, 219–226.

What is claimed is:

1. A composite material comprising:
a thermosetting polymer; and
a nanocrystalline cellulose (NCC),
5 wherein the thermosetting polymer forms a polymeric matrix and nanocrystals of the nanocrystalline cellulose are embedded in the polymeric matrix.
2. The composite material according to claim 1, which has a chiral structure.
10
3. The composite material according to claim 1 or 2, which has chiral nematic order.
4. The composite material according to any one of claims 1 to 3, which
15 has a left-handed helical structure having a helical pitch of from about 300 nanometers to about 1500 nanometers.
5. The composite material according to any one of claims 1 to 4, wherein the thermosetting polymer is an aldehyde based polymer.
20
6. The composite material according to any one of claims 1 to 5, wherein the thermosetting polymer is a phenol-formaldehyde (PF) polymer, a urea-formaldehyde (UF) polymer, a melamine-formaldehyde (MF) polymer, a melamine-urea-formaldehyde (MUF) polymer, a resorcinol-formaldehyde
25 polymer, a phenol-acetaldehyde polymer, a resorcinol-acetaldehyde polymer, a urea-acetaldehyde polymer, or a melamine-acetaldehyde polymer or a combination thereof.
7. The composite material according to any one of claims 1 to 6, which
30 further comprises an additive.
8. The composite material according to claim 7, wherein the additive comprises a plasticizer.

9. A process of producing a composite material, the process comprising:
combining a pre-polymer of a thermosetting polymer and an aqueous
suspension of a nanocrystalline cellulose (NCC) to form an aqueous mixture
of the pre-polymer and the nanocrystalline cellulose; and
5 removing water from the aqueous mixture to produce the composite
material.
10. The process according to claim 9, wherein the composite material
comprises a chiral structure.
- 10 11. The process according to claim 9 or 10, wherein the composite
material comprises has chiral nematic order.
12. The process according to any one of claims 9 to 11, which further
15 comprises casting the aqueous mixture of the pre-polymer and the
nanocrystalline cellulose before removing water from the aqueous mixture to
form a cast mixture, and removing water from the cast mixture to produce the
composite material.
13. The process according to any one of claims 9 to 12, which further
20 comprises curing the composite material.
14. The process according to claim 13, wherein the composite material is
cured by applying heat to the composite material.
- 25 15. The process according to any one of claims 9 to 14, wherein the pre-
polymer of a thermosetting polymer is a pre-polymer of an aldehyde based
polymer.
16. The process according to any one of claims 9 to 15, wherein the pre-
30 polymer of a thermosetting polymer is a pre-polymer of a phenol-
formaldehyde (PF) polymer, a pre-polymer of a urea-formaldehyde (UF)
polymer, a pre-polymer of a melamine-formaldehyde (MF) polymer, a pre-
polymer of a melamine-urea-formaldehyde (MUF) polymer, a pre-polymer of a

resorcinol-formaldehyde polymer, a pre-polymer of a phenol-acetaldehyde polymer, a pre-polymer of a resorcinol-acetaldehyde polymer, a pre-polymer of a urea-acetaldehyde polymer, or a pre-polymer of a melamine-acetaldehyde polymer or a combination thereof.

5

17. The process according to any one of claims 9 to 16, wherein the aqueous suspension of a nanocrystalline cellulose has a concentration of nanocrystalline cellulose of about 1 to about 10 wt%.

10

18. The process according to any one of claims 9 to 17, wherein the aqueous suspension of a nanocrystalline cellulose has a concentration of nanocrystalline cellulose of about 3 to about 5 wt%.

15

19. The process according to any one of claims 9 to 18, wherein the aqueous suspension of a nanocrystalline cellulose has a pH of about 2 to about 4.

20

20. The process according to any one of claims 9 to 19, wherein a ratio of the amount of the pre-polymer of a thermosetting polymer to the amount of the nanocrystalline cellulose combined is from 0.2 to 2.5 (by weight).

25

21. The process according to any one of claims 9 to 20, wherein the pre-polymer of a thermosetting polymer and the aqueous suspension of a nanocrystalline cellulose are combined in the presence of an electrolyte.

30

22. The process according to claim 21, wherein the electrolyte comprises a salt.

23. The process according to any one of claims 9 to 22, wherein the pre-polymer of a thermosetting polymer and the aqueous suspension of a nanocrystalline cellulose may be combined with an additive.

24. The process according to claim 23, wherein the additive comprises a plasticizer.

25. A composite material produced by the process as defined in any one of claims 9 to 24.

5 26. A mesoporous polymer material comprising a thermosetting polymer, wherein the mesoporous polymer material has a chiral order.

27. The mesoporous polymer material according to claim 26, which has a chiral nematic order.

10

28. The mesoporous polymer material according to claim 26 or 27, which has a surface area in the range of from about 50 to about 400 m²/g.

15

29. The mesoporous polymer material according to any one of claims 26 to 28, which has a left-handed helical structure having a helical pitch of from about 200 nanometers to about 1000 nanometers.

30. The mesoporous polymer material according to any one of claims 26 to 29, wherein the thermosetting polymer is an aldehyde based polymer.

20

25

31. The mesoporous polymer material according to any one of claims 26 to 30, wherein the thermosetting polymer is a phenol-formaldehyde (PF) polymer, a urea-formaldehyde (UF) polymer, a melamine-formaldehyde (MF) polymer, a melamine-urea-formaldehyde (MUF) polymer, a resorcinol-formaldehyde polymer, a phenol-acetaldehyde polymer, a resorcinol-acetaldehyde polymer, a urea-acetaldehyde polymer, or a melamine-acetaldehyde polymer or a combination thereof.

30

32. The mesoporous polymer material according to any one of claims 26 to 31, which further comprises an additive.

33. The mesoporous polymer material according to claim 32, wherein the additive comprises a plasticizer.

34. A process of producing a mesoporous polymer material, the process comprising: combining a pre-polymer of a thermosetting polymer and an aqueous suspension of a nanocrystalline cellulose (NCC) to form an aqueous mixture of the pre-polymer and the nanocrystalline cellulose; removing water from the aqueous mixture to produce a composite material; and removing at least a portion of the nanocrystalline cellulose from the composite material.
35. The process according to claim 34, wherein the mesoporous polymer material has a chiral structure.
36. The process according to claim 34 or 35, wherein the mesoporous polymer material has chiral nematic order.
37. The process according to any one of claims 34 to 36, which further comprises casting the aqueous mixture of the pre-polymer and the nanocrystalline cellulose before removing water from the aqueous mixture to form a cast mixture, and removing water from the cast mixture to produce the composite material.
38. The process according to any one of claims 34 to 37, which further comprises curing the composite material.
39. The process according to claim 38, wherein the composite material is cured by applying heat to the composite material.
40. The process according to any one of claims 34 to 39, wherein at least a portion of the nanocrystalline cellulose is removed from the composite material by hydrolyzing the nanocrystalline cellulose under basic conditions.
41. The process according to any one of claims 34 to 40, wherein the pre-polymer of a thermosetting polymer is a pre-polymer of an aldehyde based polymer.

42. The process according to any one of claims 34 to 41, wherein the pre-polymer of a thermosetting polymer is a pre-polymer of a phenol-formaldehyde (PF) polymer, a pre-polymer of a urea-formaldehyde (UF) polymer, a pre-polymer of a melamine-formaldehyde (MF) polymer, a pre-polymer of a melamine-urea-formaldehyde (MUF) polymer, a pre-polymer of a resorcinol-formaldehyde polymer, a pre-polymer of a phenol-acetaldehyde polymer, a pre-polymer of a resorcinol-acetaldehyde polymer, a pre-polymer of a urea-acetaldehyde polymer, or a pre-polymer of a melamine-acetaldehyde polymer or a combination thereof.

43. The process according to any one of claims 34 to 42, wherein the aqueous suspension of a nanocrystalline cellulose has a concentration of nanocrystalline cellulose of about 1 to about 10 wt%.

44. The process according to any one of claims 34 to 43, wherein the aqueous suspension of a nanocrystalline cellulose has a concentration of nanocrystalline cellulose of about 3 to about 5 wt%.

45. The process according to any one of claims 34 to 44, wherein the aqueous suspension of a nanocrystalline cellulose has a pH of about 2 to about 4.

46. The process according to any one of claims 34 to 45, wherein a ratio of the amount of the pre-polymer of a thermosetting polymer to the amount of the nanocrystalline cellulose combined is from 0.2 to 2.5 (by weight).

47. The process according to any one of claims 34 to 46, wherein the pre-polymer of a thermosetting polymer and the aqueous suspension of a nanocrystalline cellulose are combined in the presence of an electrolyte.

48. The process according to claim 47, wherein the electrolyte comprises a salt.

49. The process according to according to any one of claims 34 to 48, wherein the pre-polymer of a thermosetting polymer and the aqueous suspension of a nanocrystalline cellulose may be combined with an additive.

5 50. The process according to claim 49, wherein the additive comprises a plasticizer.

51. A mesoporous polymer material produced by the process as defined in any one of claims 34 to 50.

10

52. An article comprising a substrate and the mesoporous polymer material as defined in any one of claims 26 to 33, wherein the mesoporous polymer material forms a coating on the substrate.

15 53. A desulfated nanocrystalline cellulose (NCC) having chiral nematic order.

54. The NCC of claim 53, wherein the NCC is partially desulfated.

20 55. The NCC of claim 53, wherein the NCC is substantially or completely desulfated.

56. The NCC of claim 53, 54, or 55, wherein the NCC is mesoporous.

25 57. A method of making a nanocrystalline cellulose having chiral nematic order, the method comprising combining a pre-polymer of a thermosetting polymer and an aqueous suspension of a nanocrystalline cellulose (NCC) to form an aqueous mixture of the pre-polymer and the NCC; removing water from the aqueous mixture to produce a composite material; and removing at least a portion of the thermosetting polymer from the composite material.

30

58. The method of claim 57, wherein removing at least a portion of the thermosetting polymer from the composite material comprises hydrolyzing the thermosetting polymer under basic conditions.

5 59. The method of claim 58, wherein the basic conditions hydrolyzing the thermosetting polymer under basic conditions includes treatment with a hydroxide base.

10 60. The method of claim 57, 58, or 59, further comprising, after removing at least a portion of the thermosetting polymer from the composite material, critical point drying of the wet films using supercritical carbon dioxide.

15 61. A nanocrystalline cellulose having chiral nematic order, wherein the nanocrystalline cellulose is produced according to a method as defined in any one of claims 57 to 60.

62. A chromatographic matrix comprising a composite as defined in any one of claims 1 to 8.

20 63. A chromatographic matrix comprising a desulfated nanocrystalline cellulose having chiral nematic order as defined in any one of claims 53 to 56 and 61.

25 64. A chromatographic column comprising a chromatographic matrix as defined in claim 62 or 63.

65. Use of a composite as defined in any one of claims 1 to 8 for the separation of enantiomers from an enantiomeric mixture.

30 66. Use of a desulfated chiral nematic nanocrystalline cellulose having chiral nematic order for the separation of enantiomers from an enantiomeric mixture.

1/33

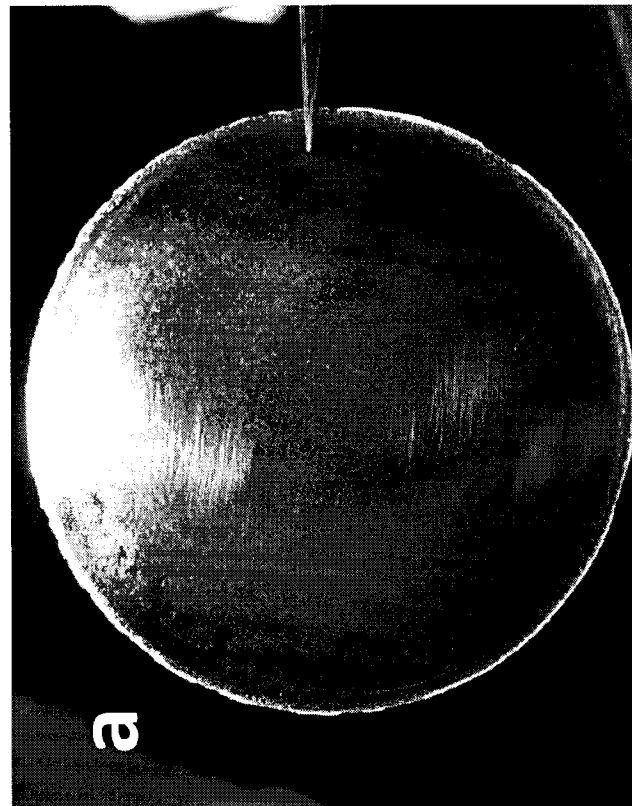
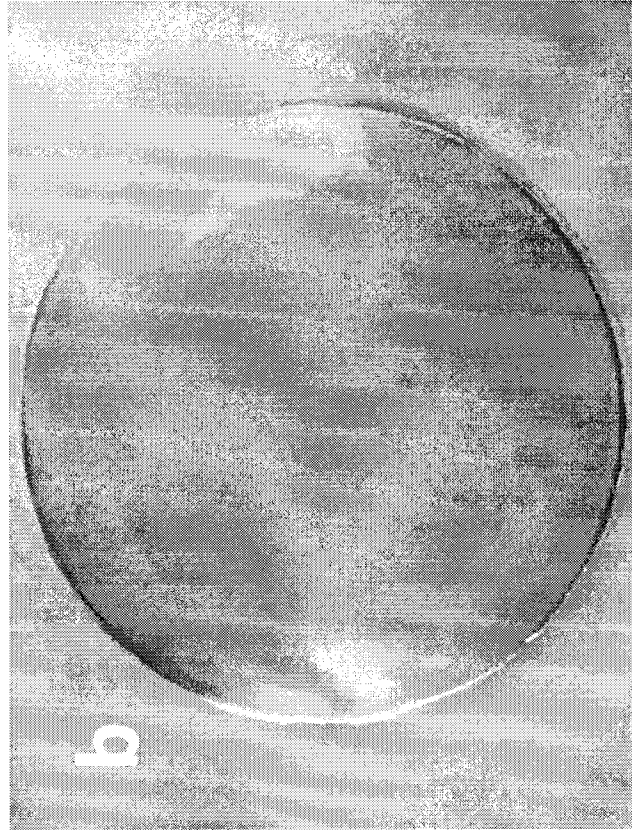


FIG. 1

2/33

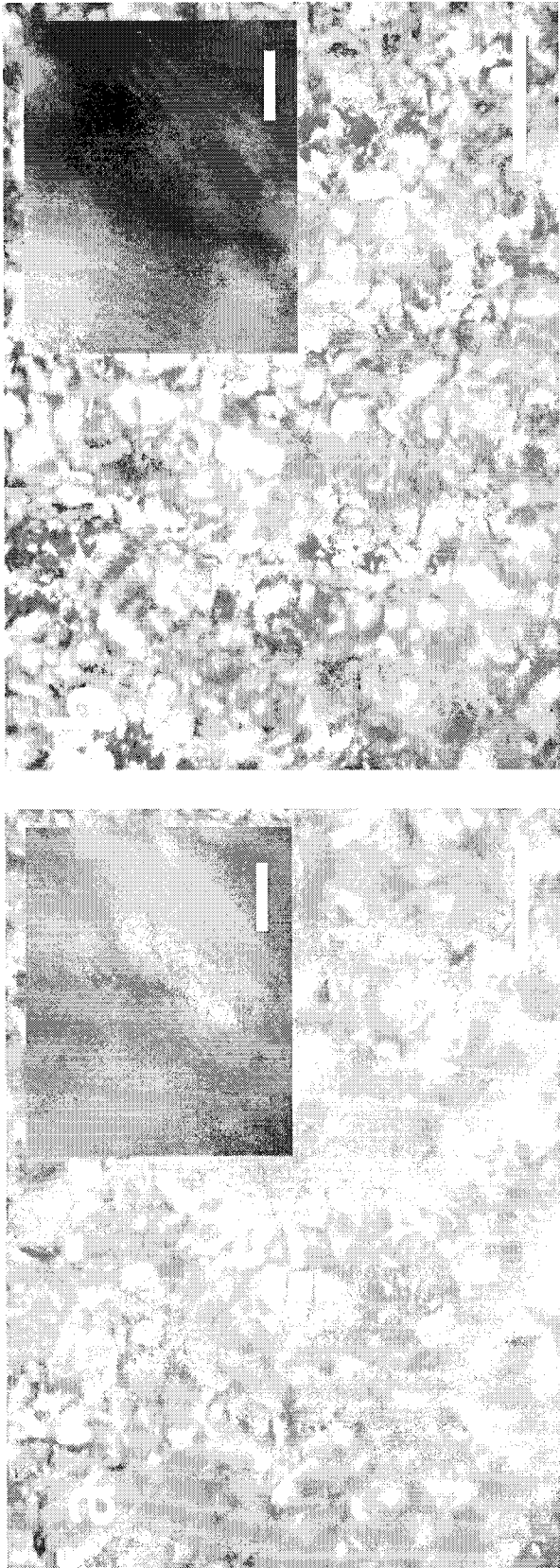
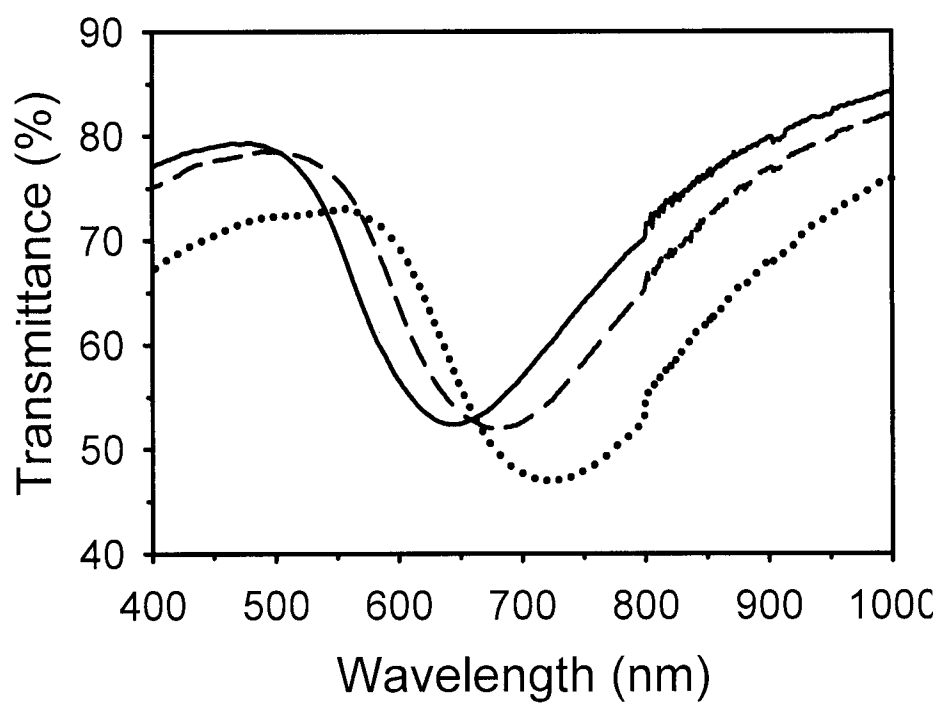
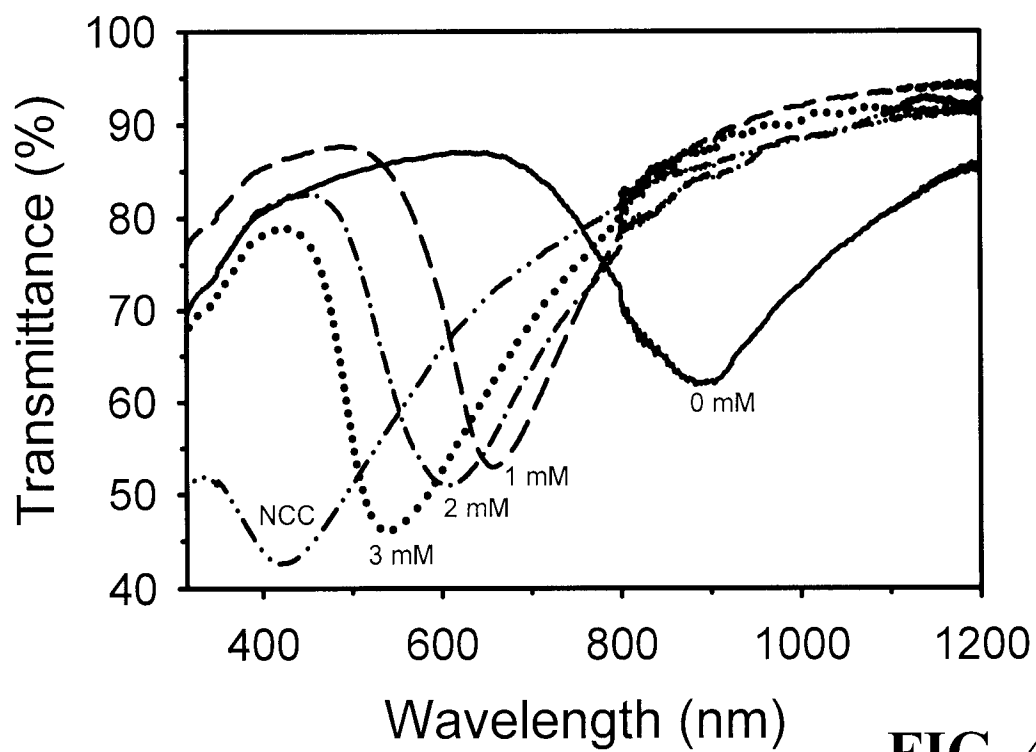
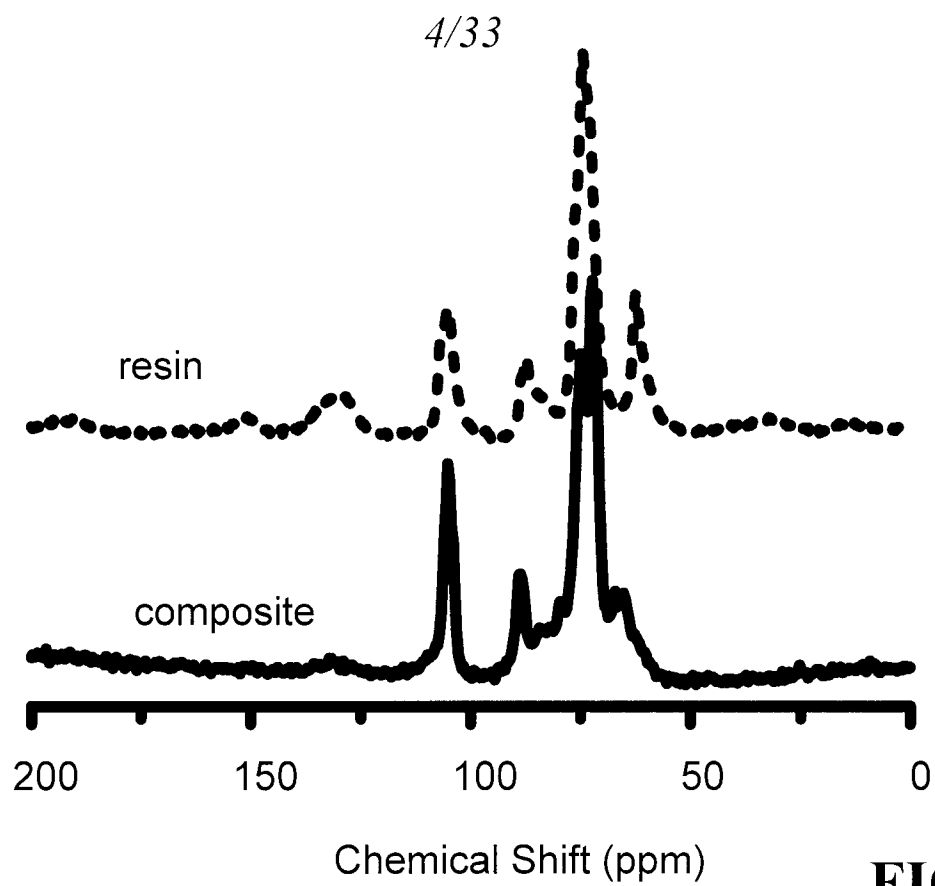
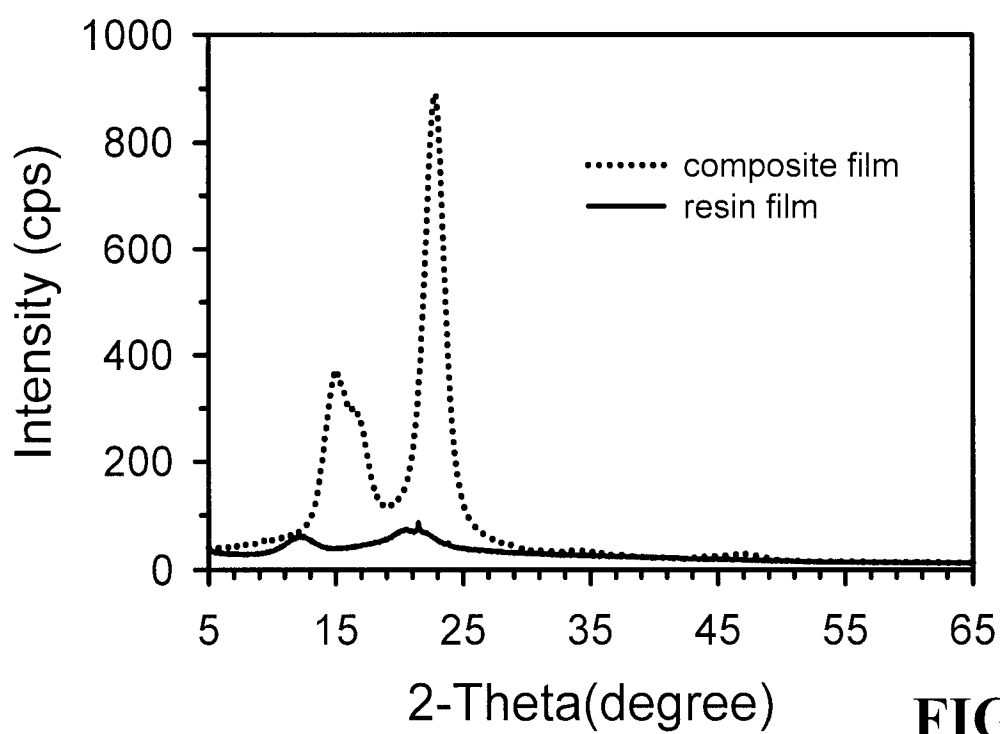


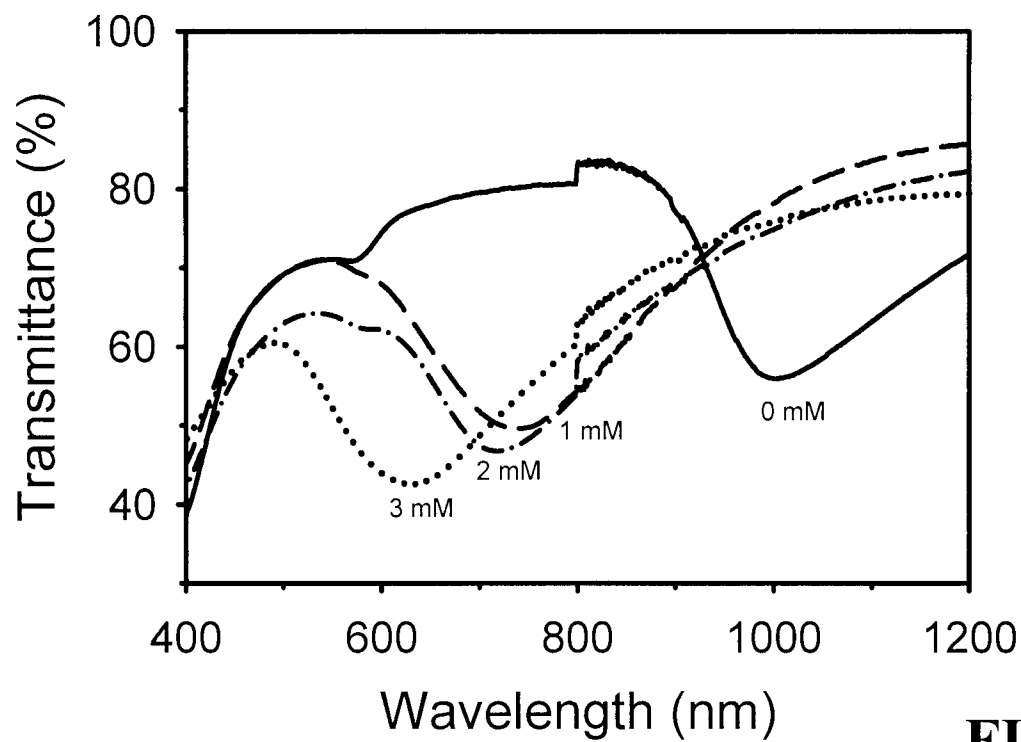
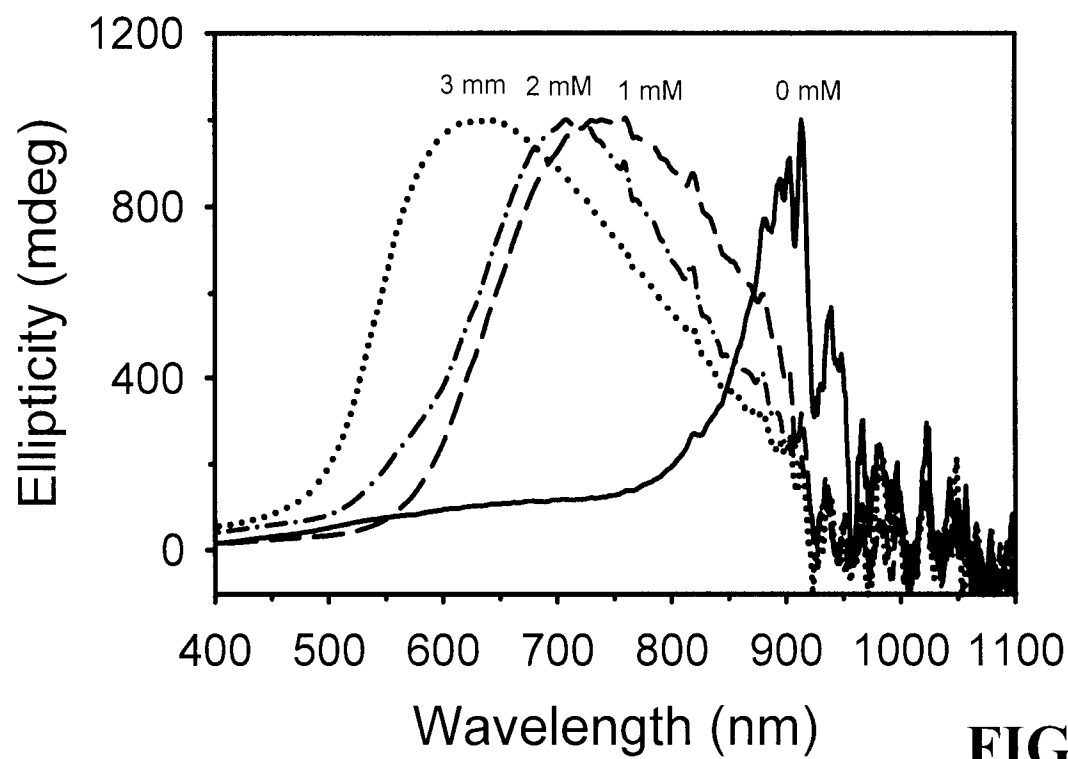
FIG. 2

3/33

**FIG. 3****FIG. 4**

**FIG. 5****FIG. 6**

5/33

**FIG. 7****FIG. 8**

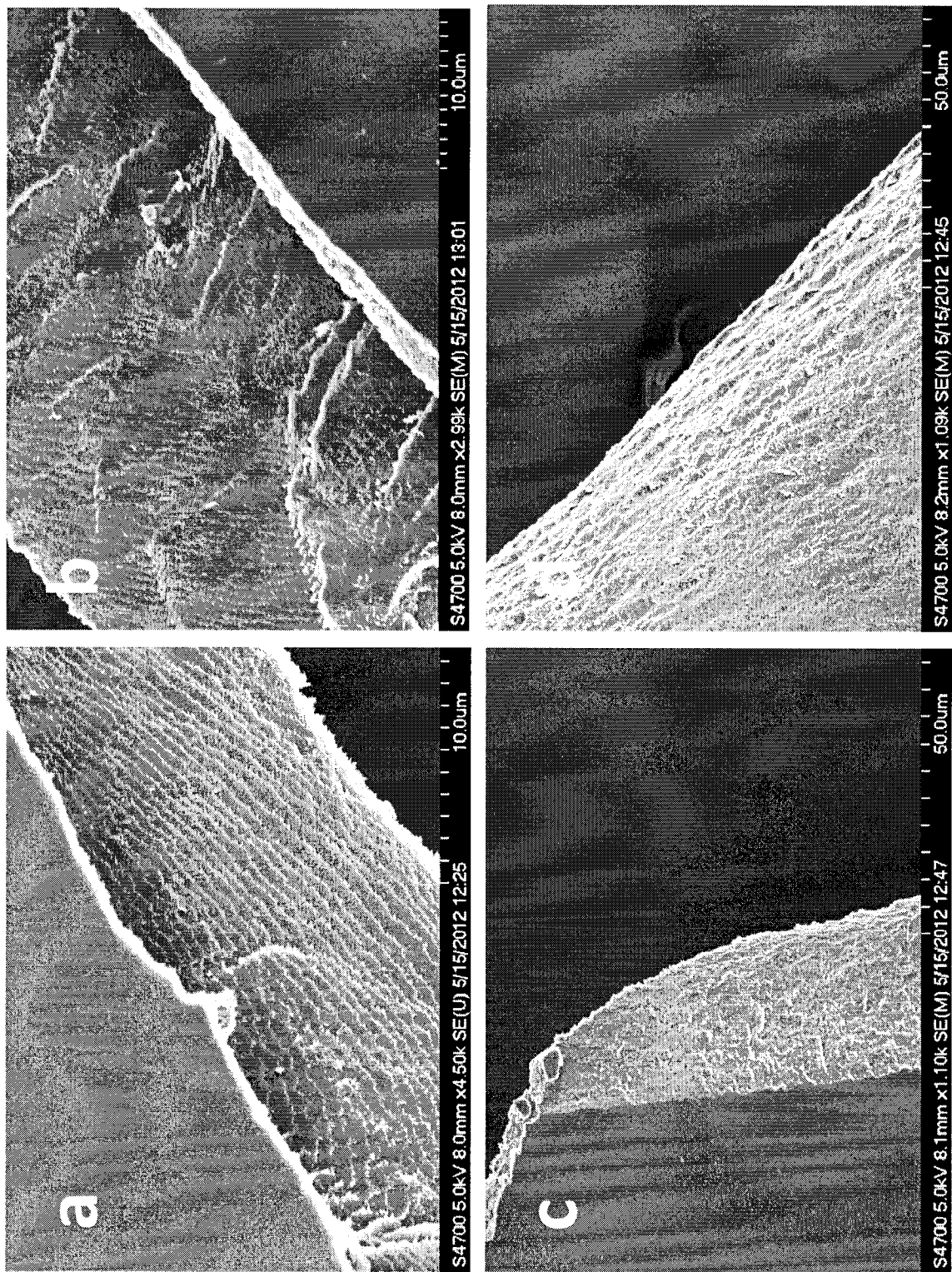


FIG. 9

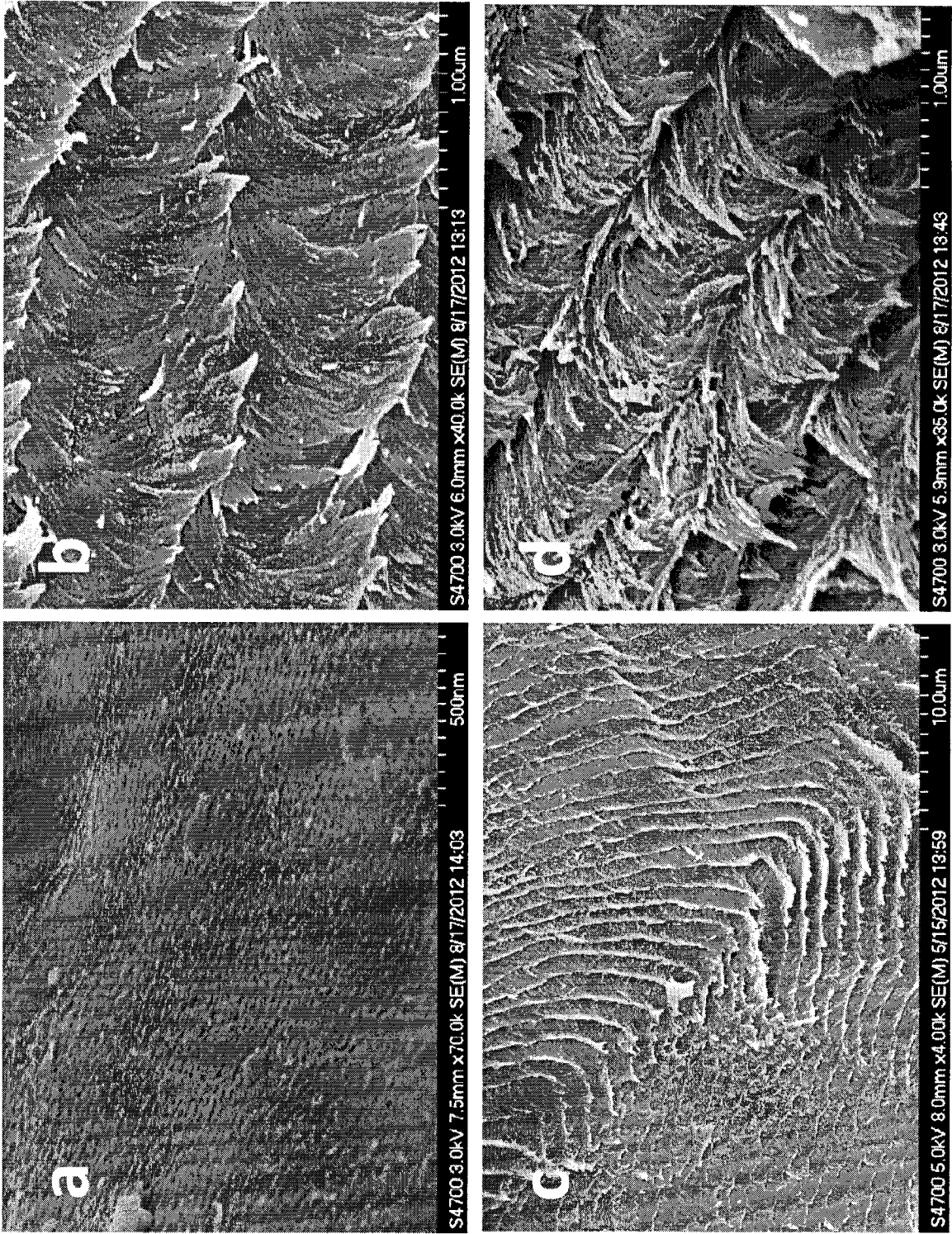


FIG. 10

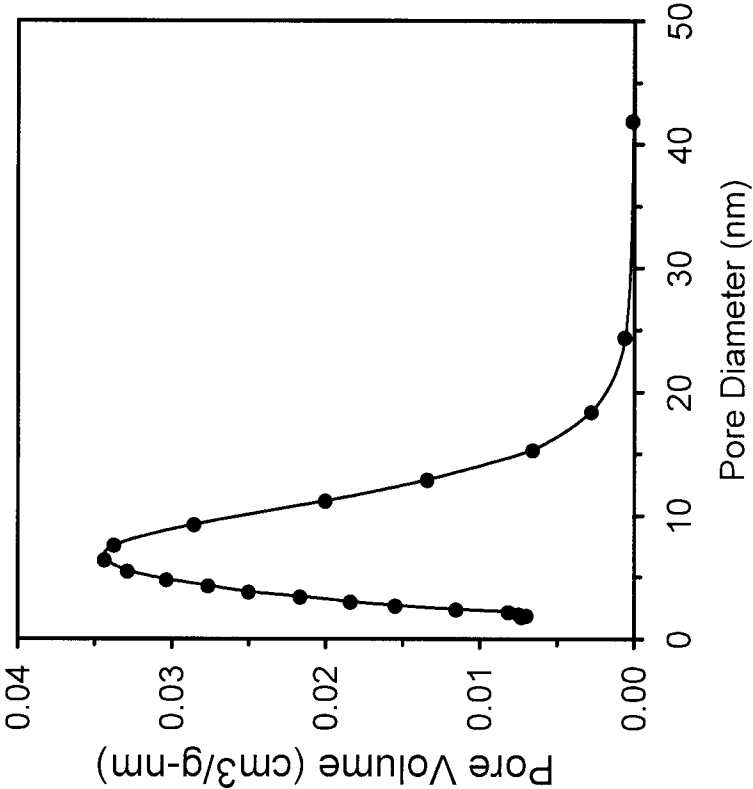


FIG. 11B

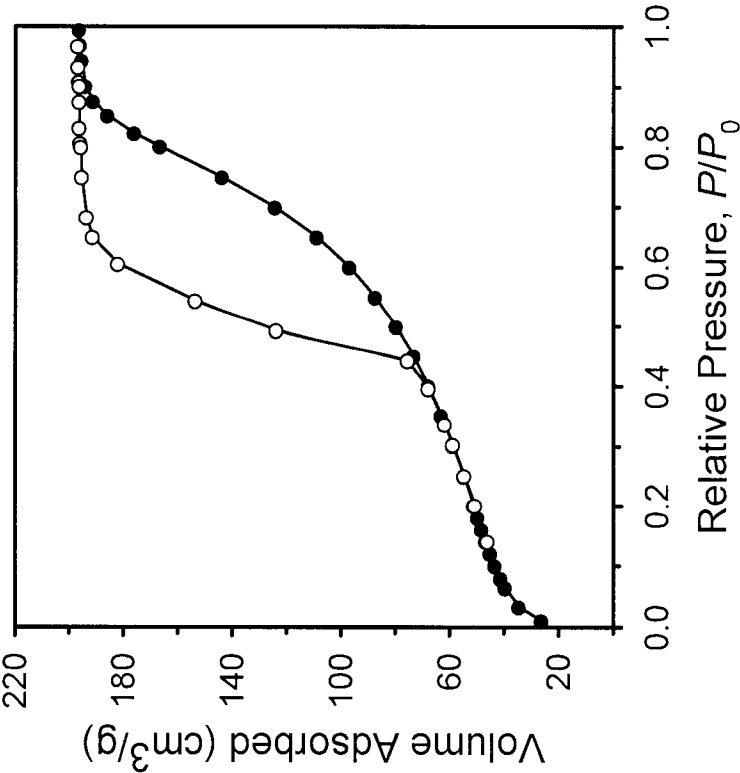


FIG. 11A

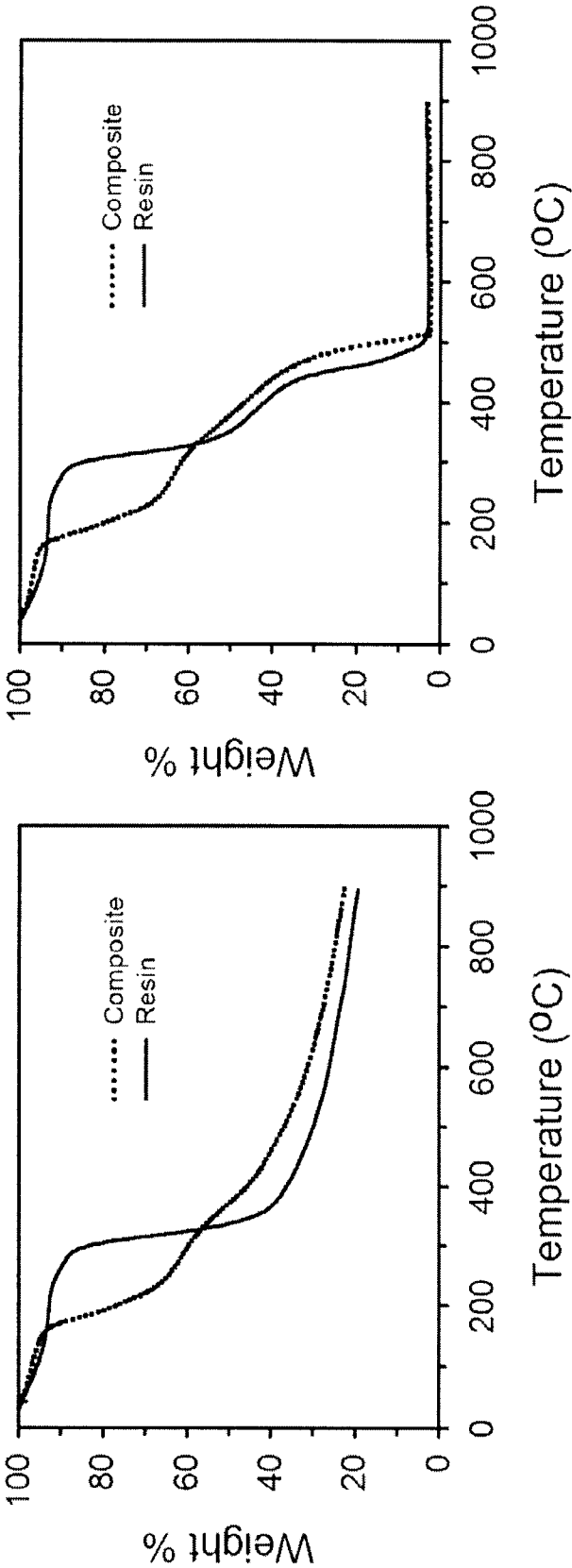


FIG. 12B

FIG. 12A

10/33

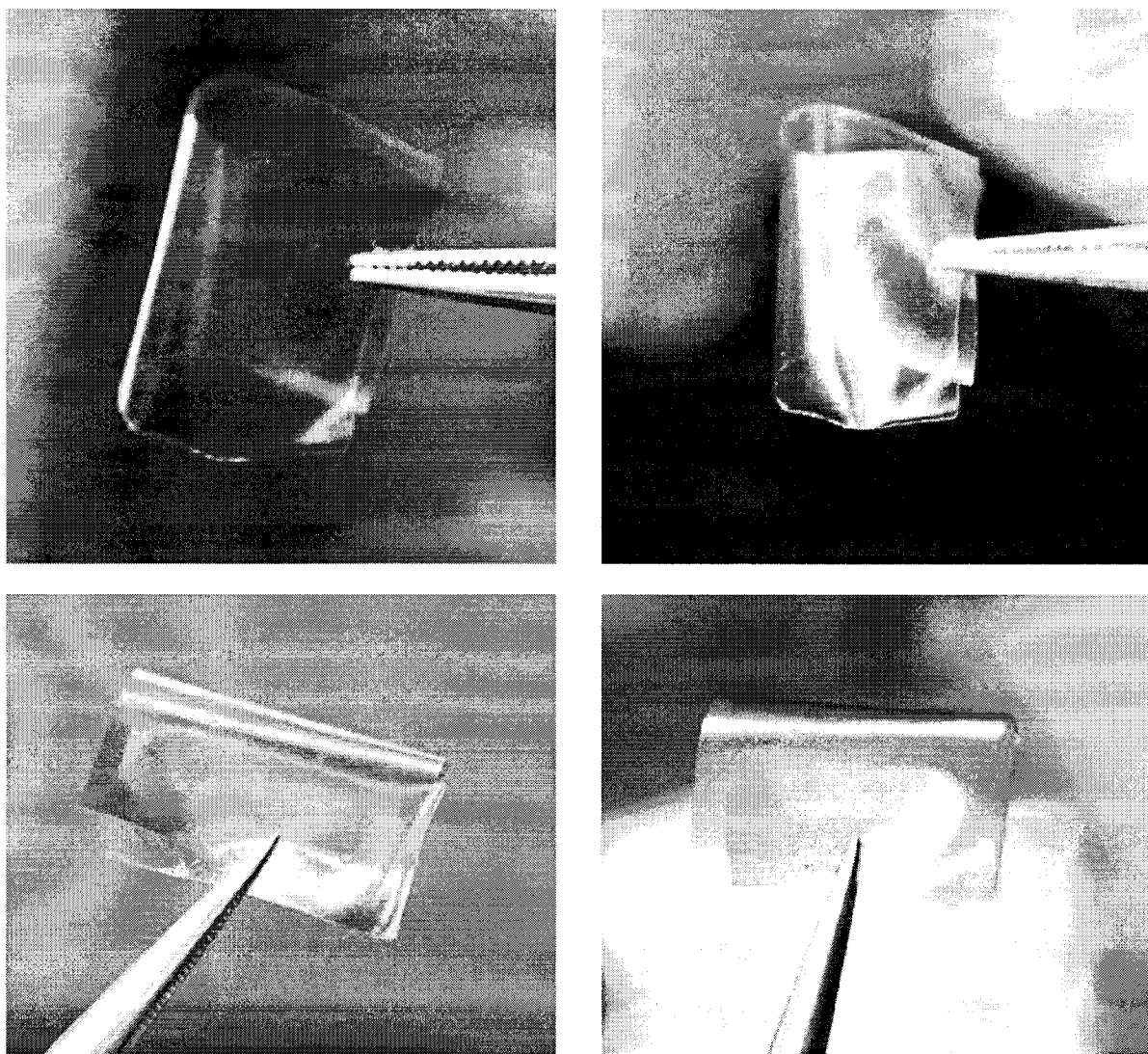


FIG. 13

11/33

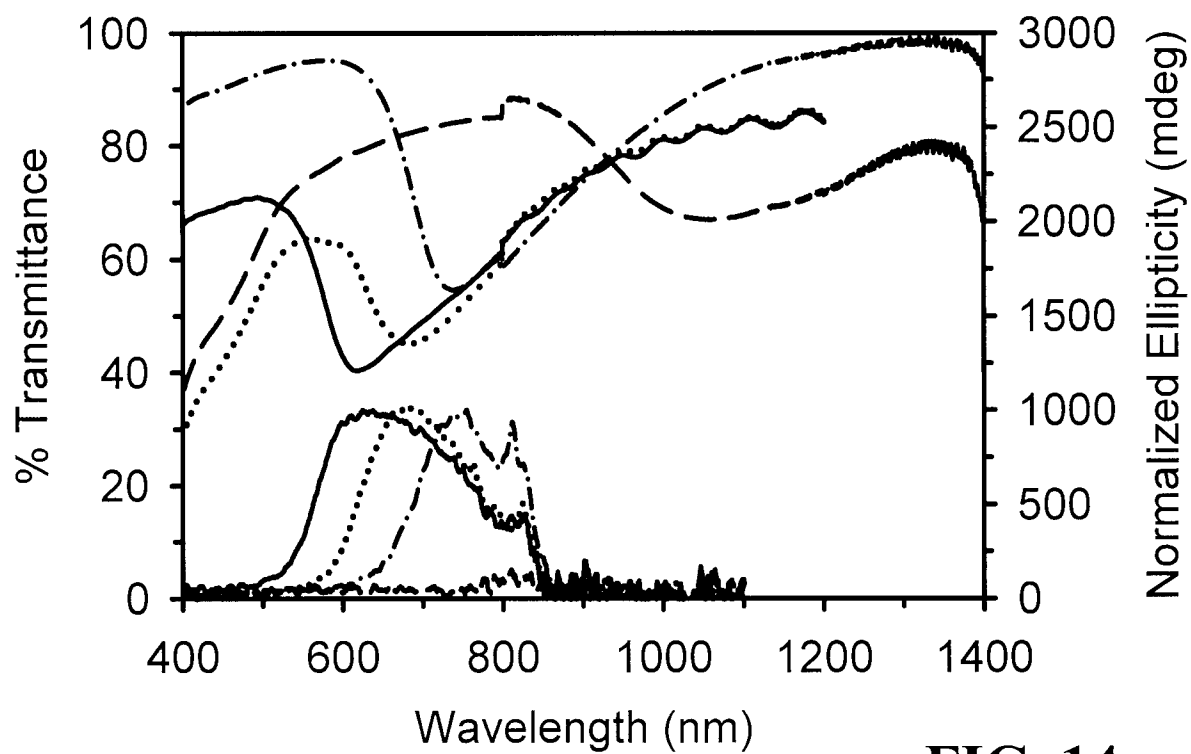


FIG. 14

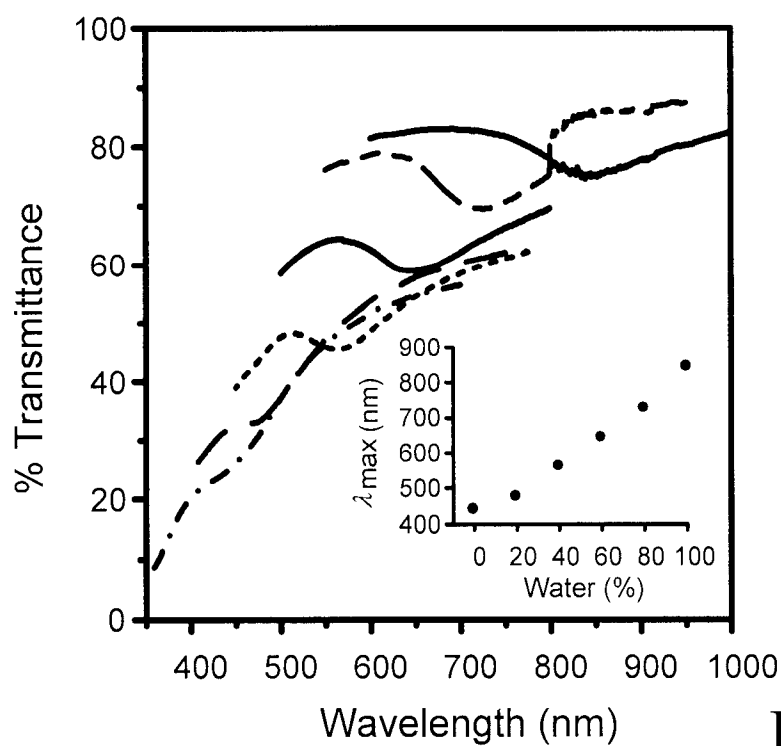


FIG. 15

12/33

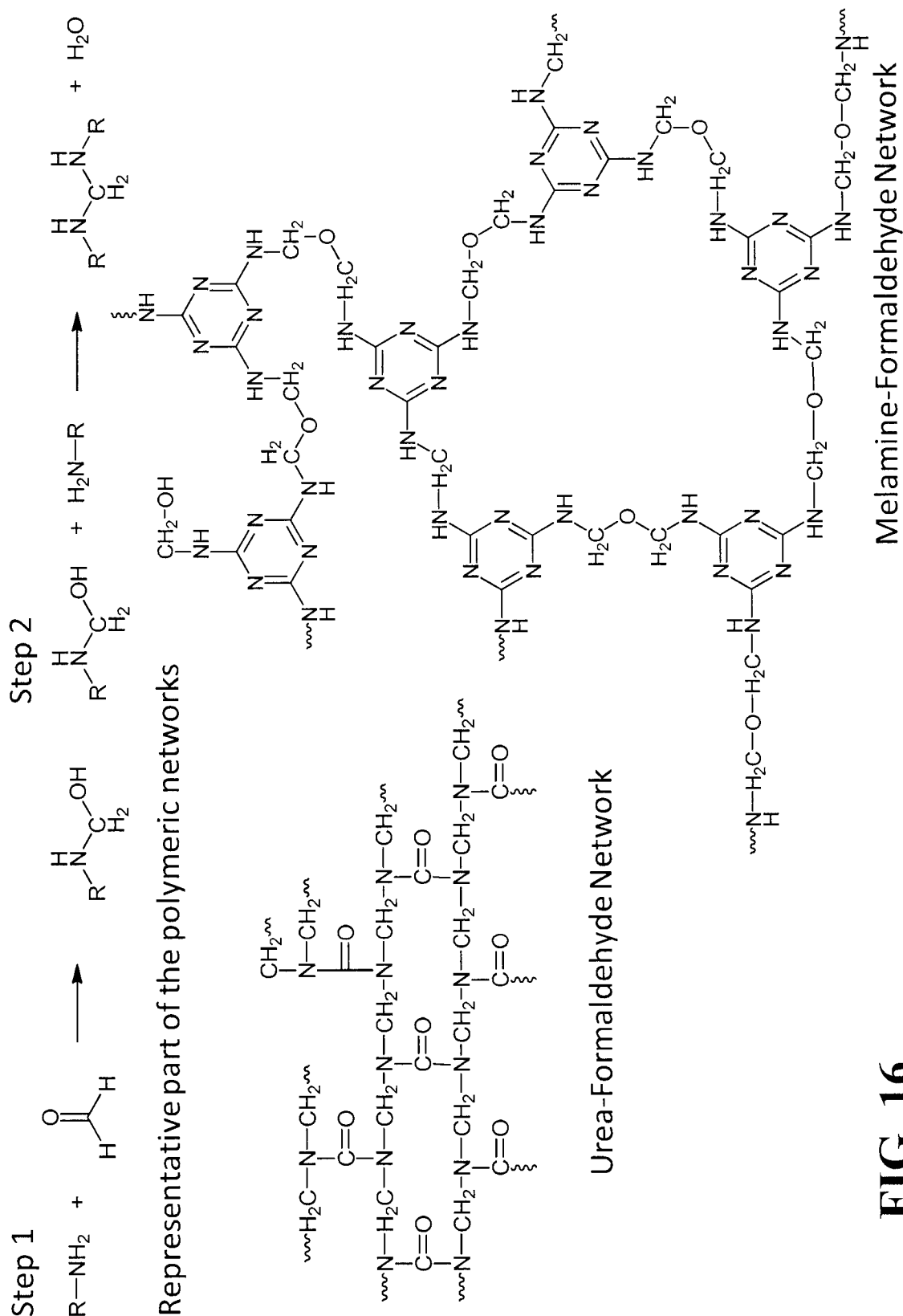


FIG. 16

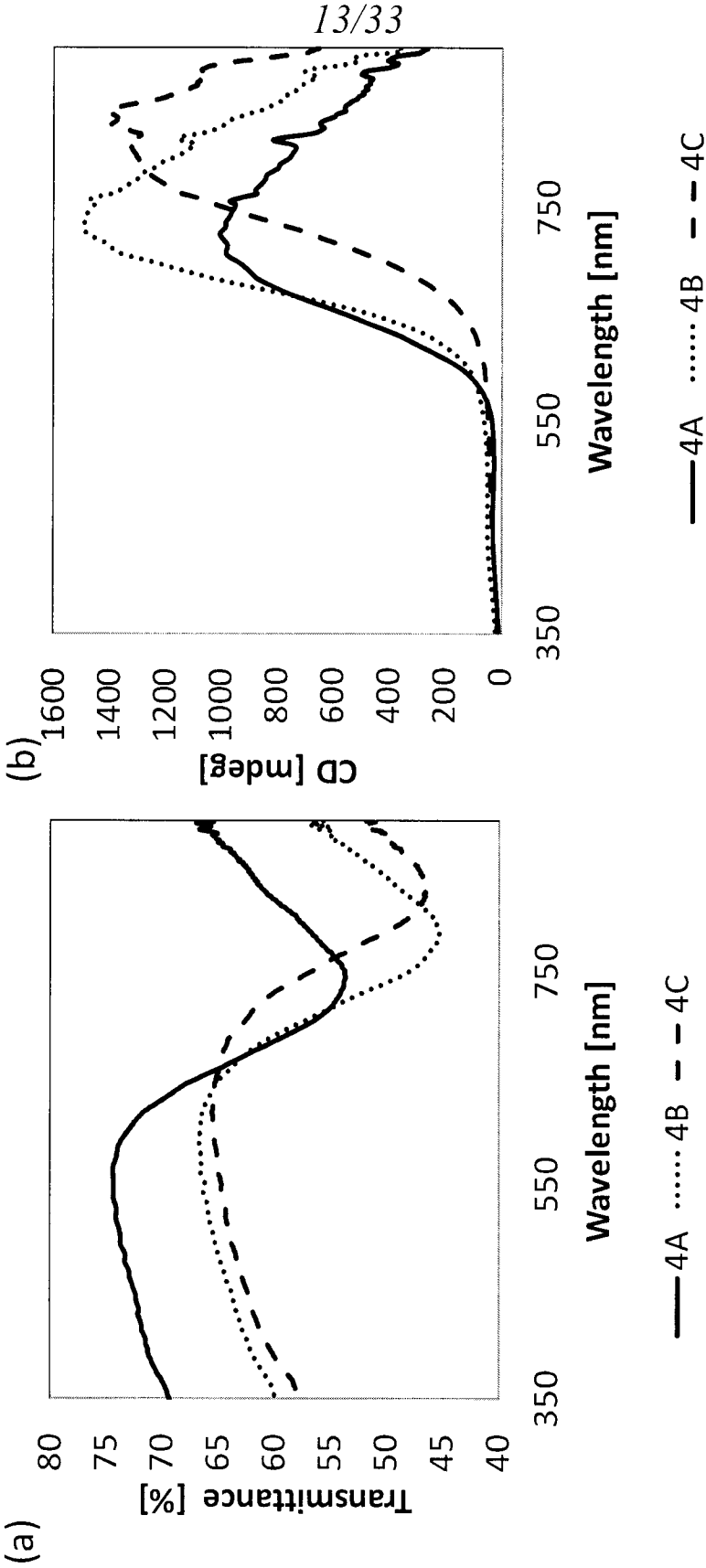


FIG. 17

14/33

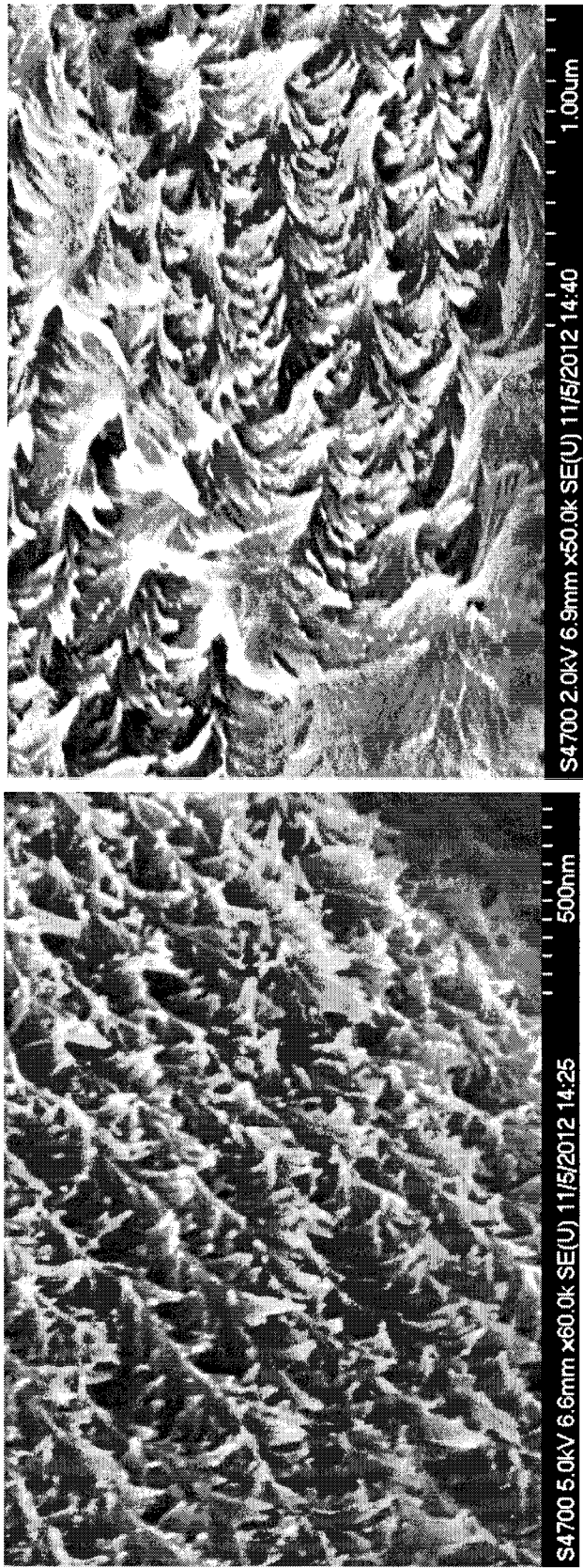
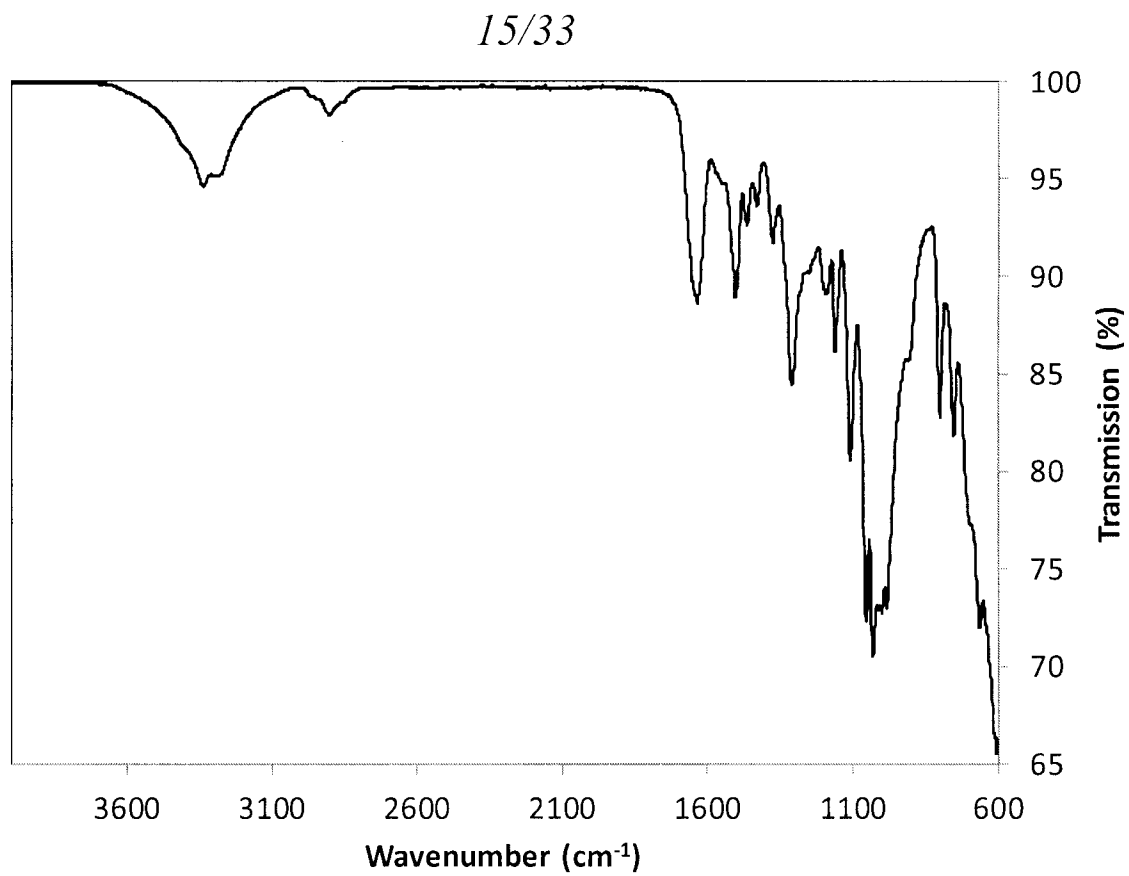
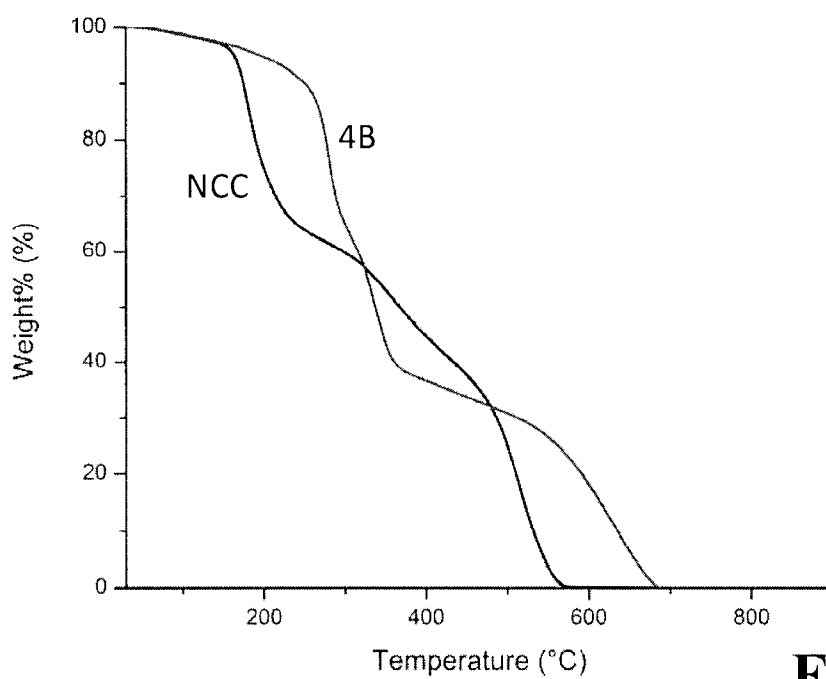


FIG. 18

**FIG. 19****FIG. 20**

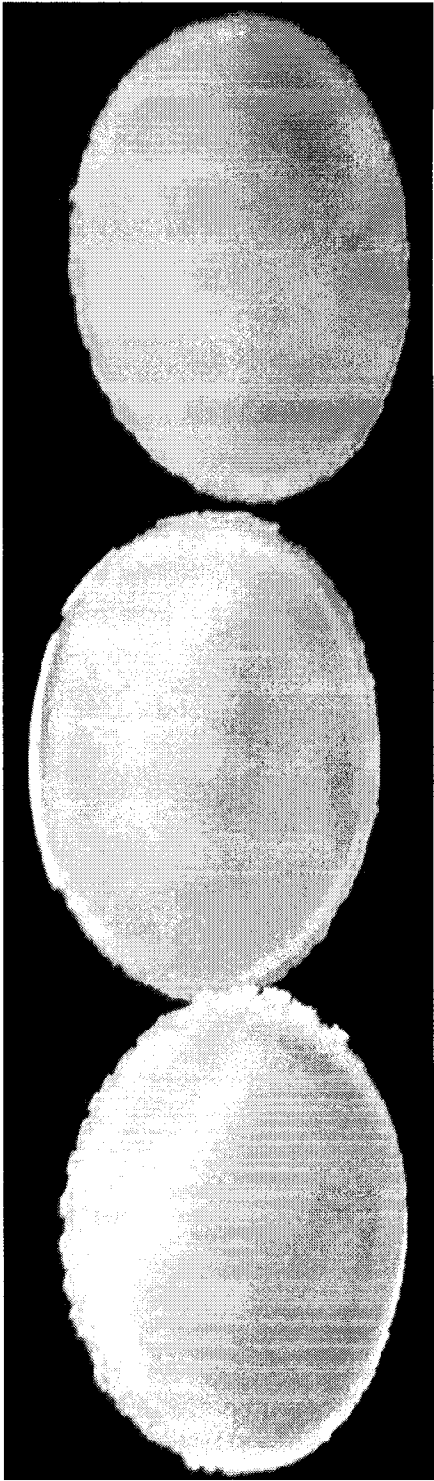
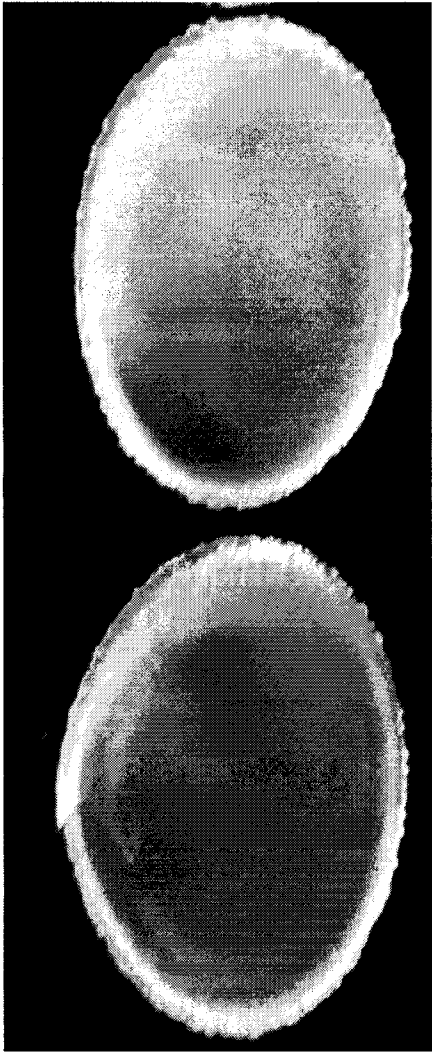


FIG. 21

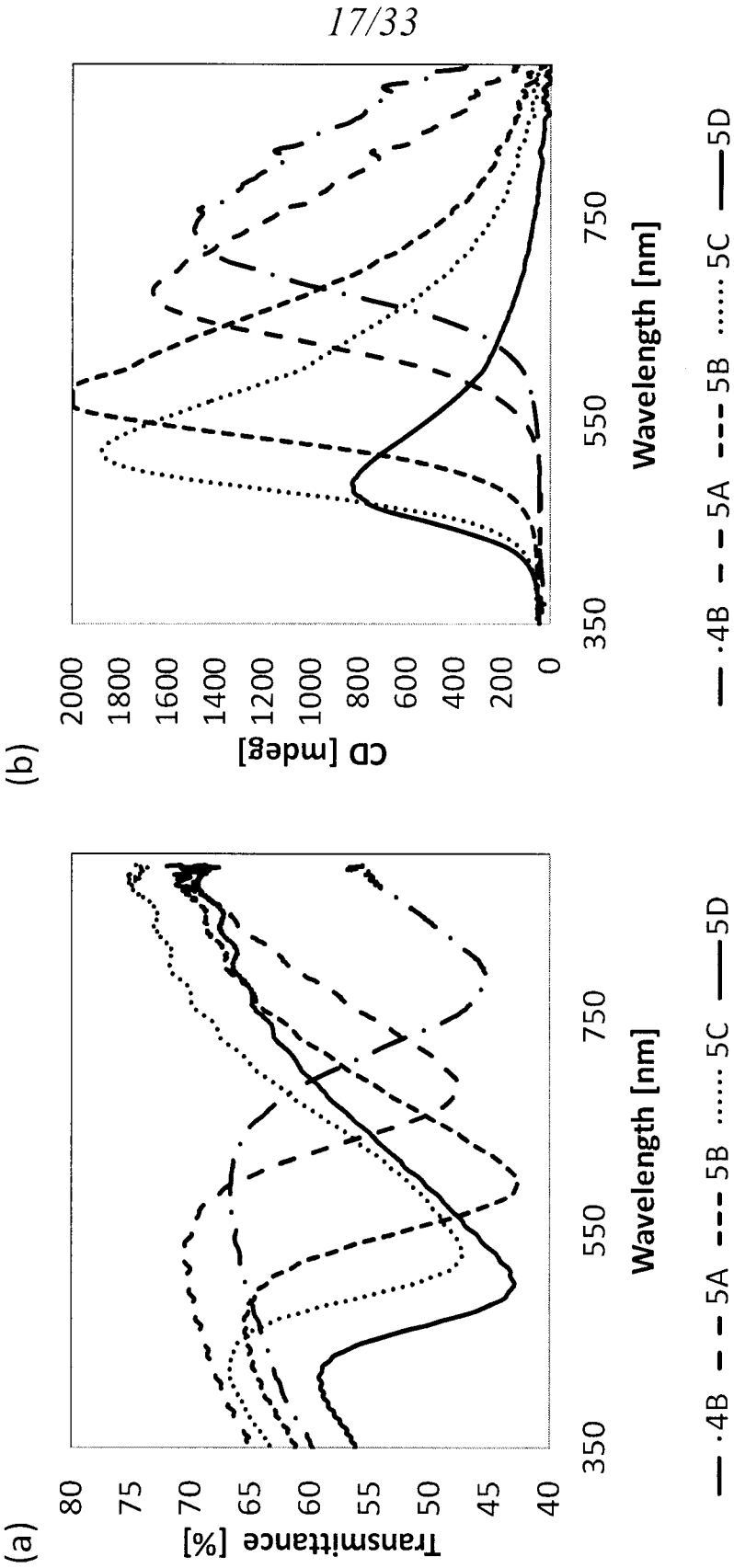


FIG. 22

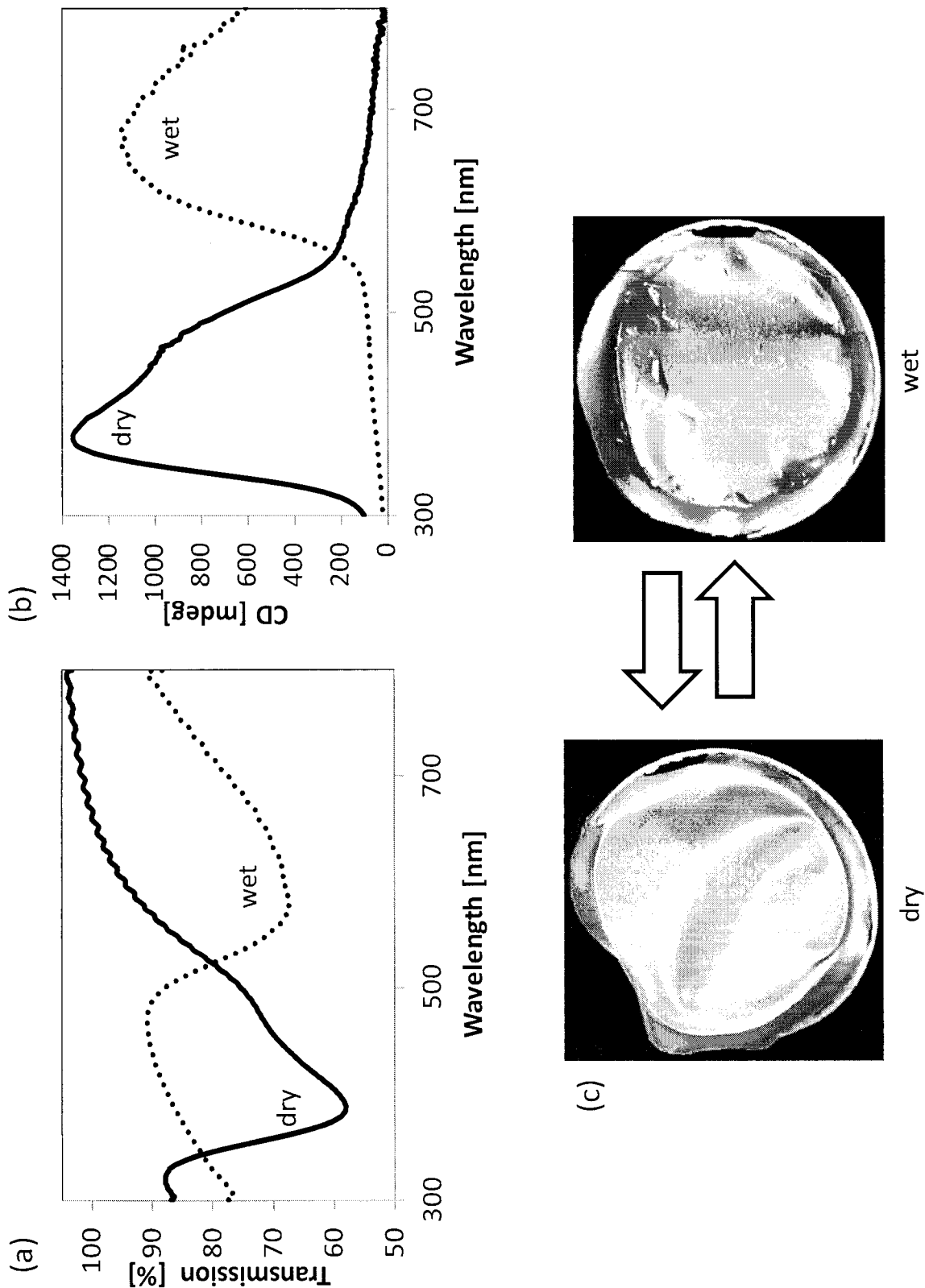


FIG. 23

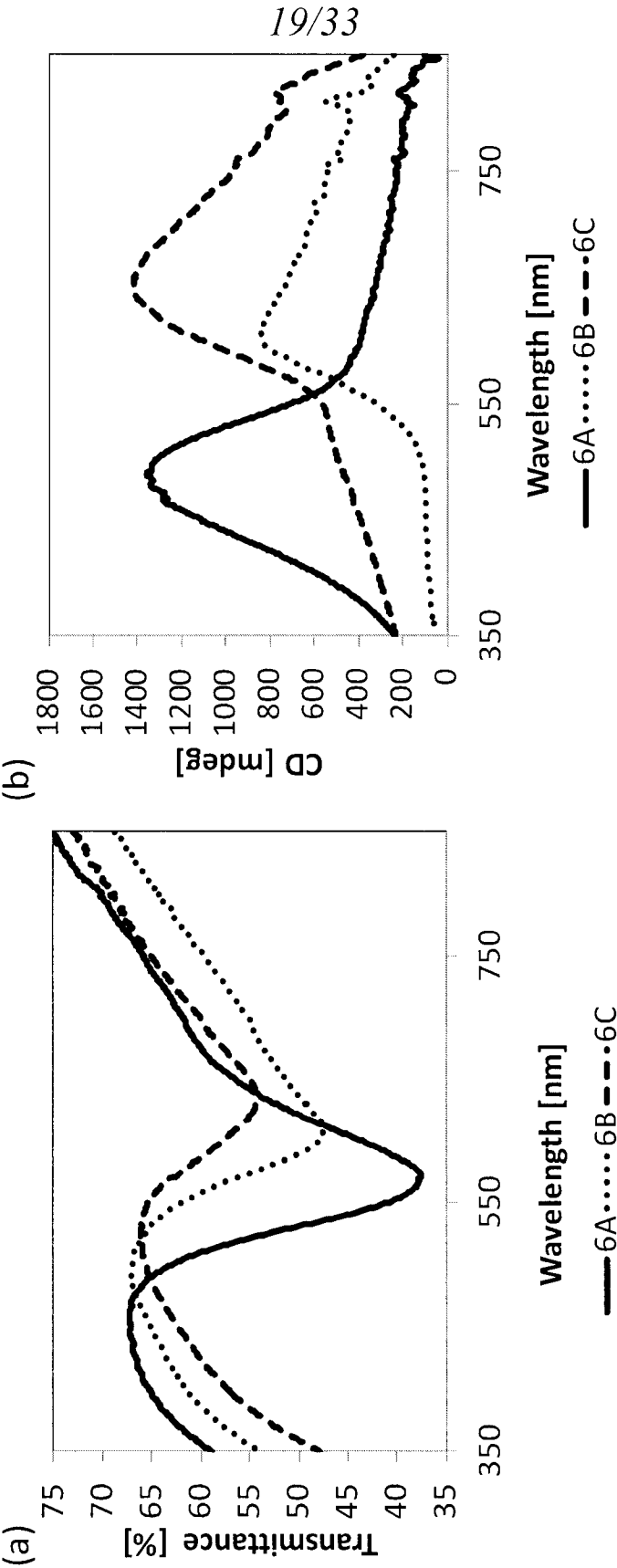


FIG. 24

20/33

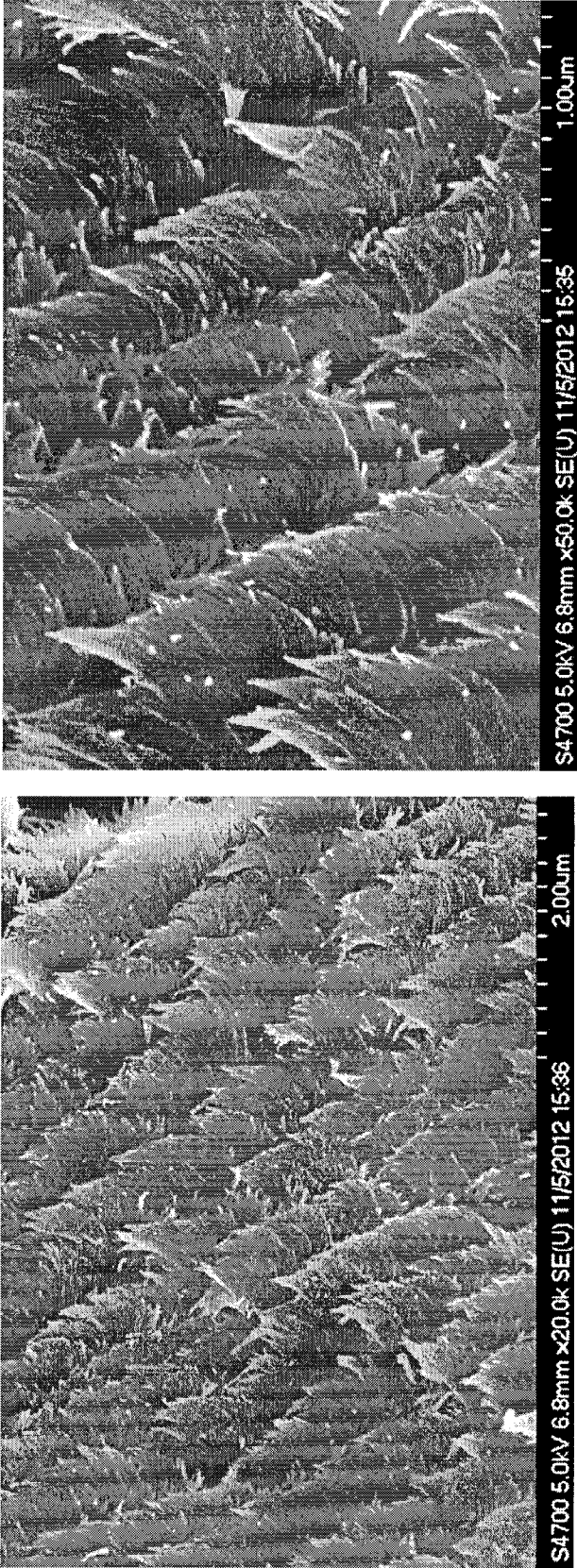


FIG. 25

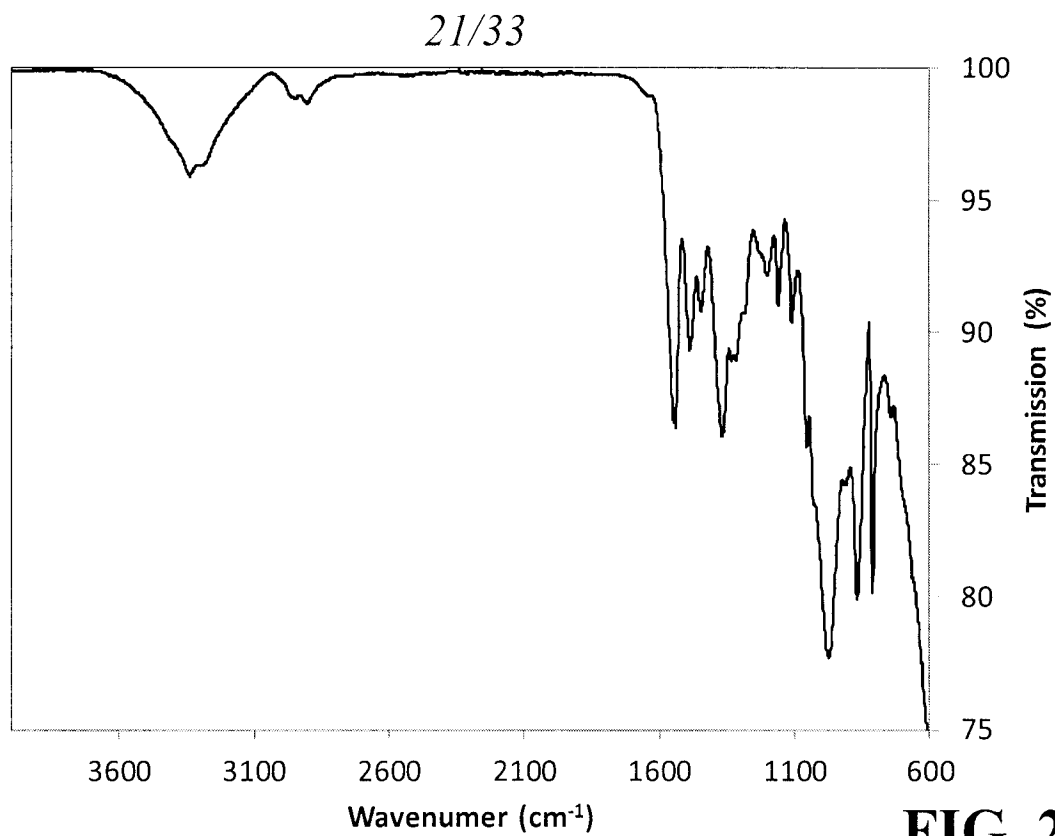


FIG. 26

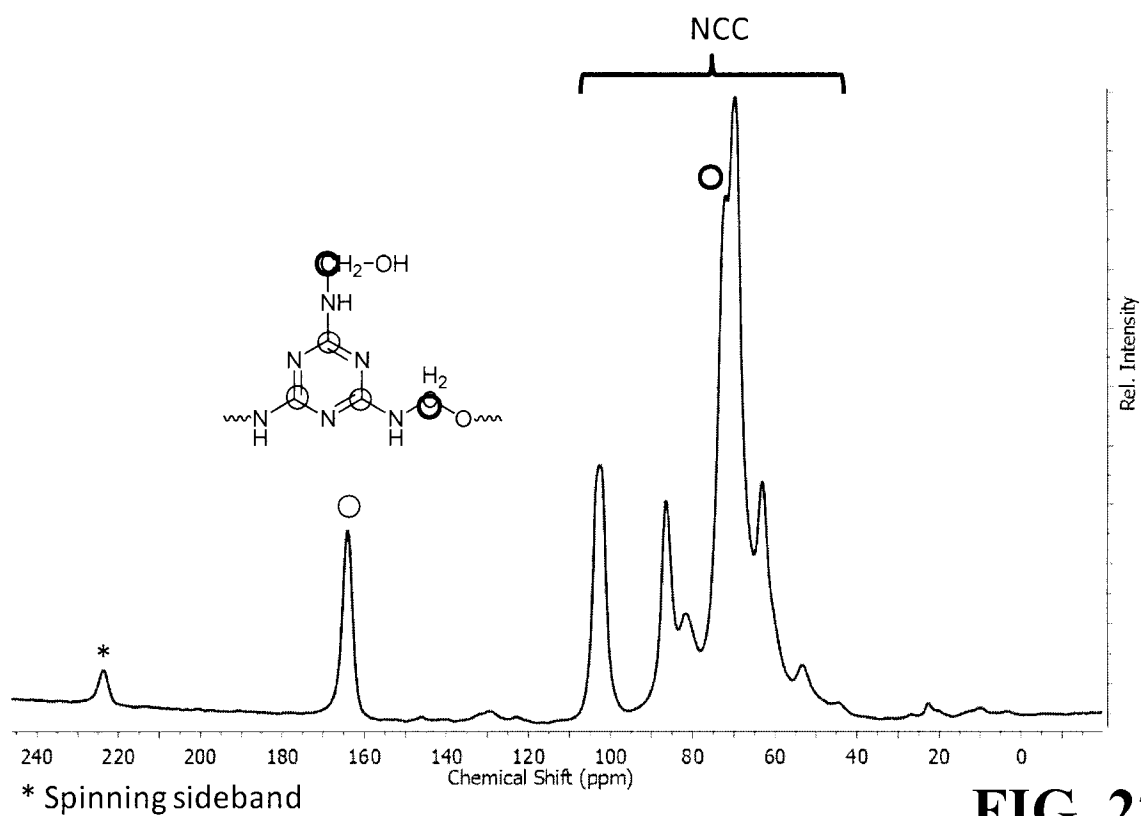
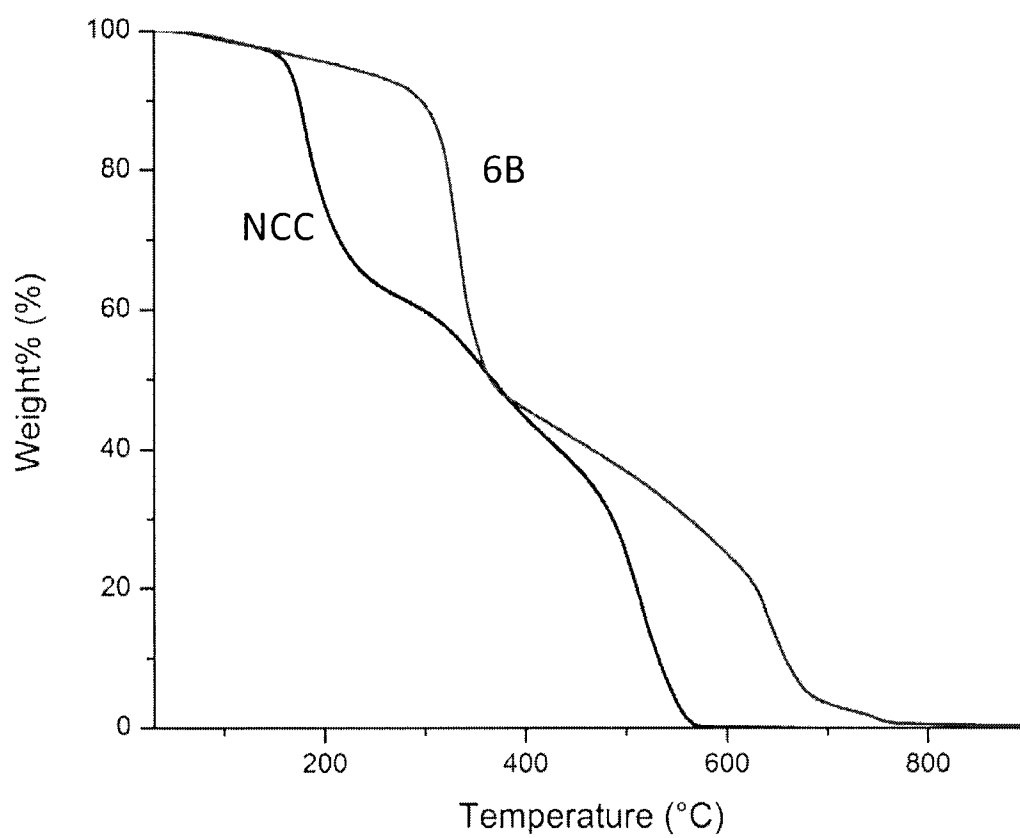


FIG. 27

22/33

**FIG. 28**

23/33

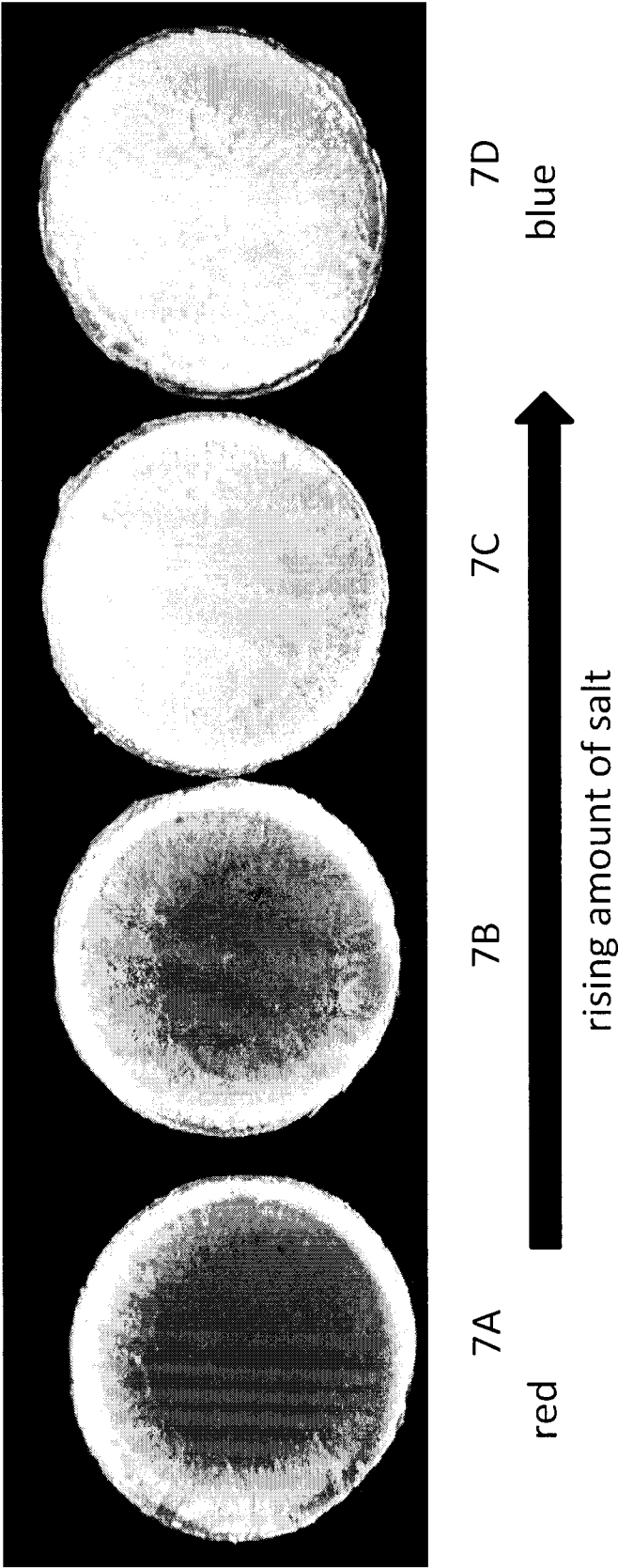


FIG. 29

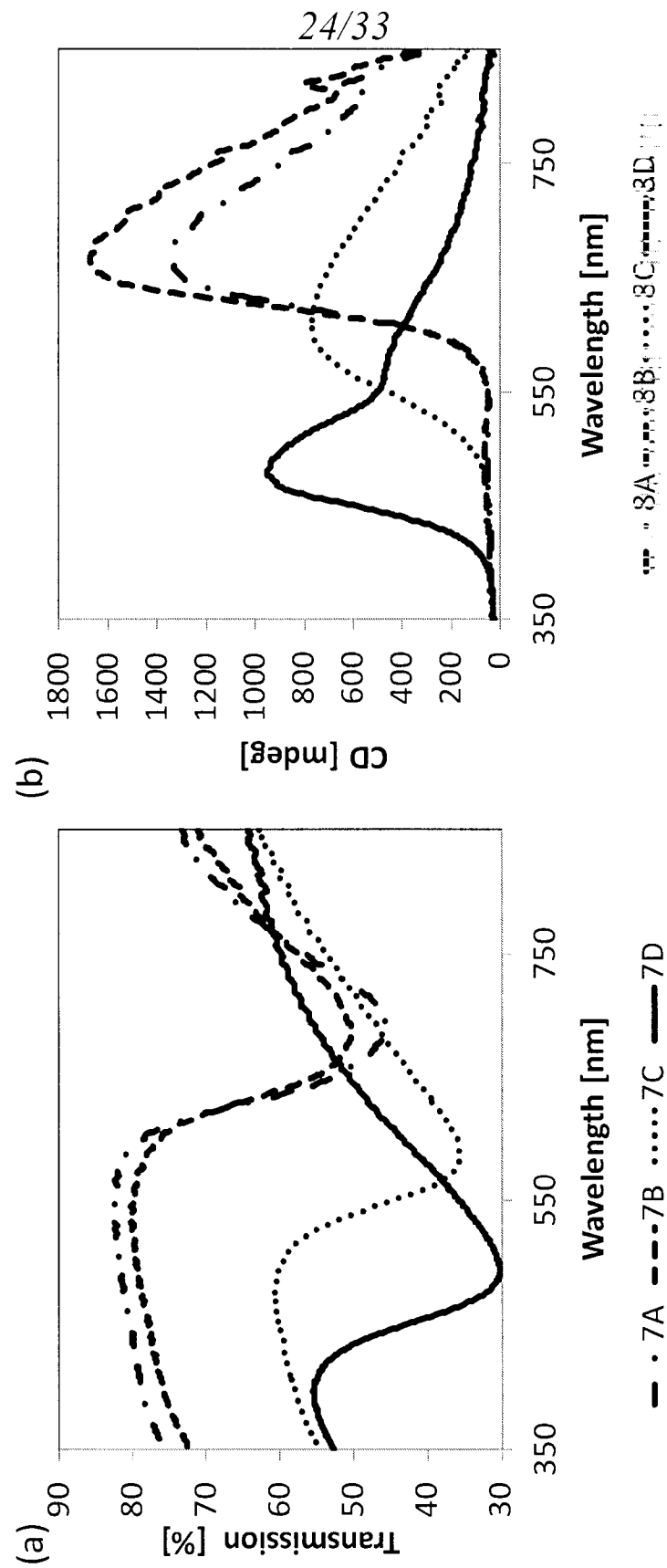


FIG. 30

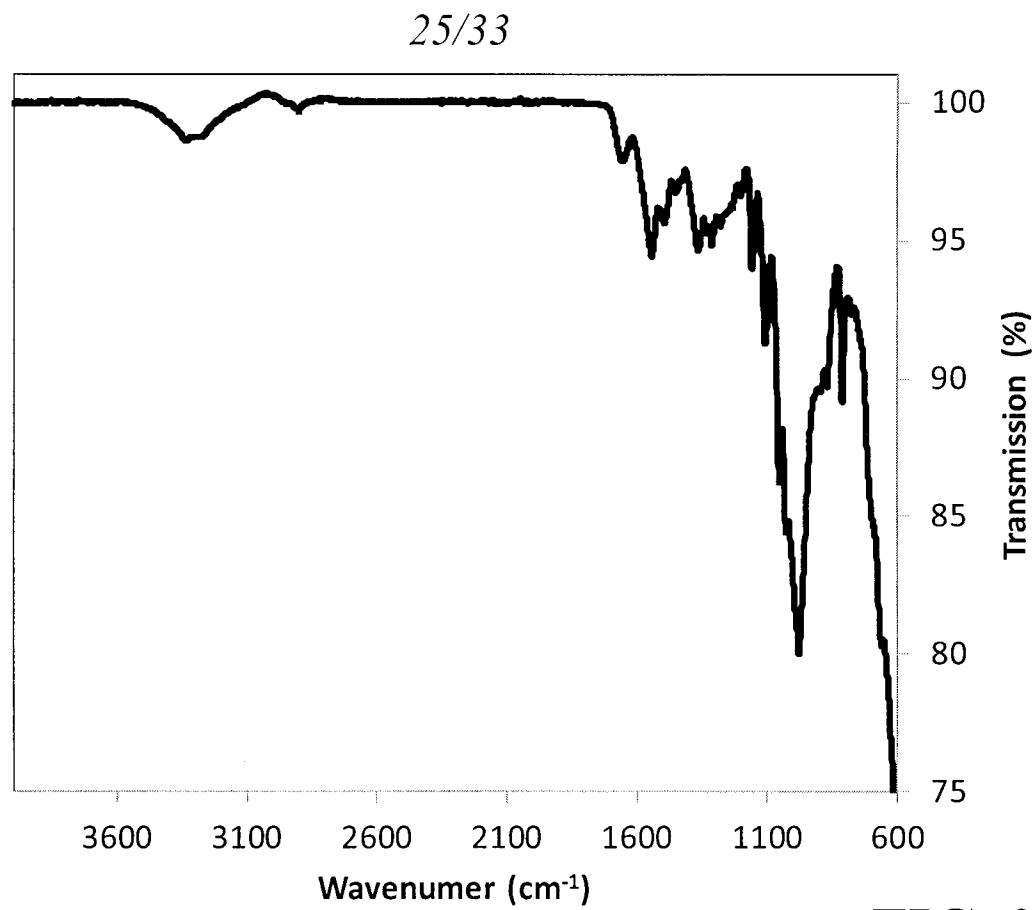


FIG. 31

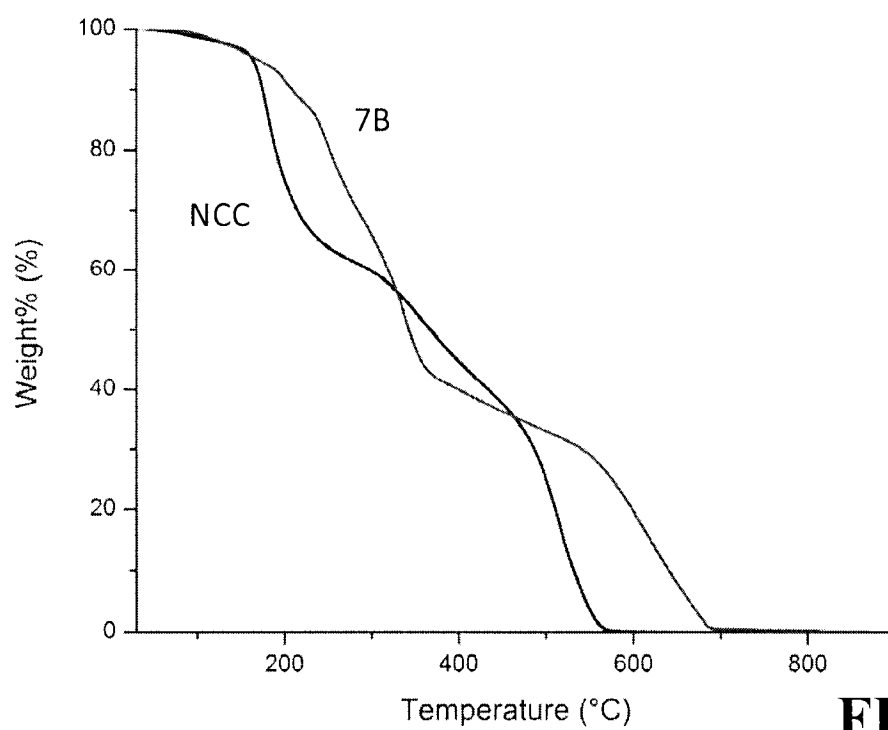
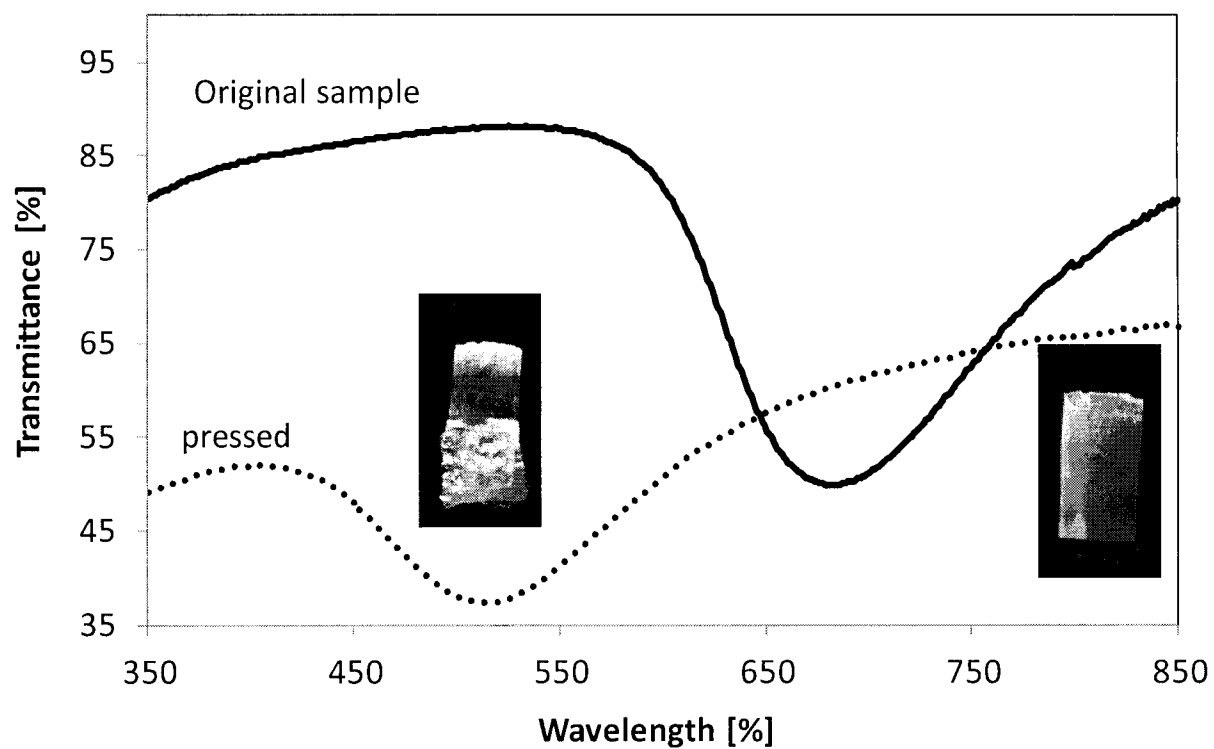
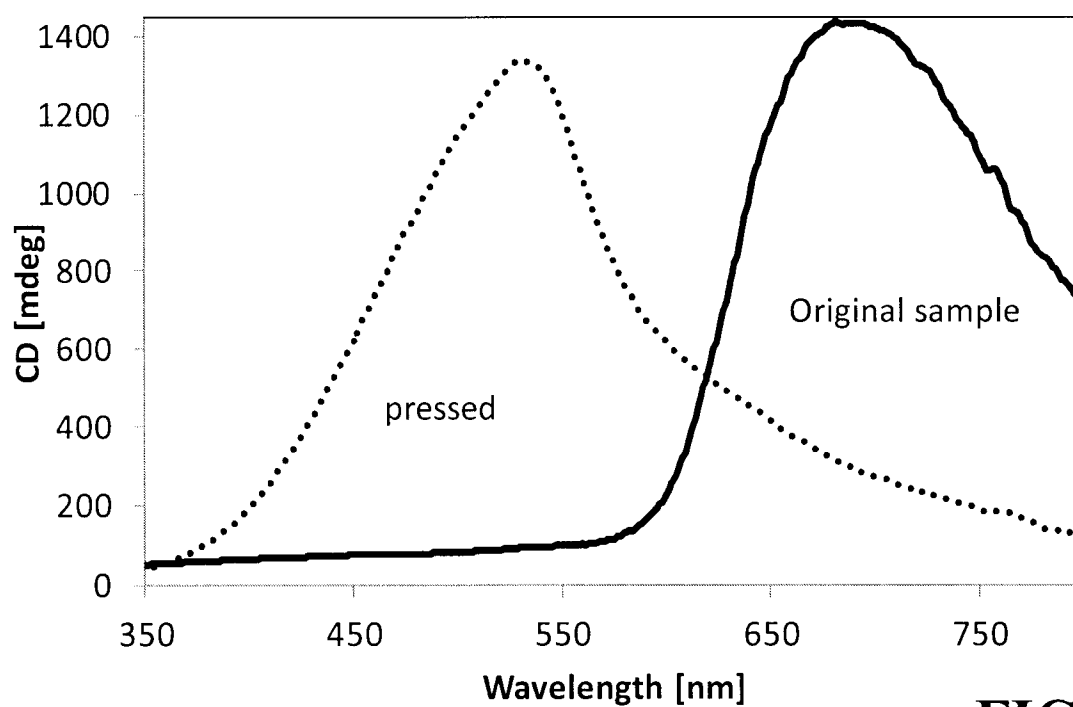


FIG. 32

26/33

**FIG. 33****FIG. 34**

27/33

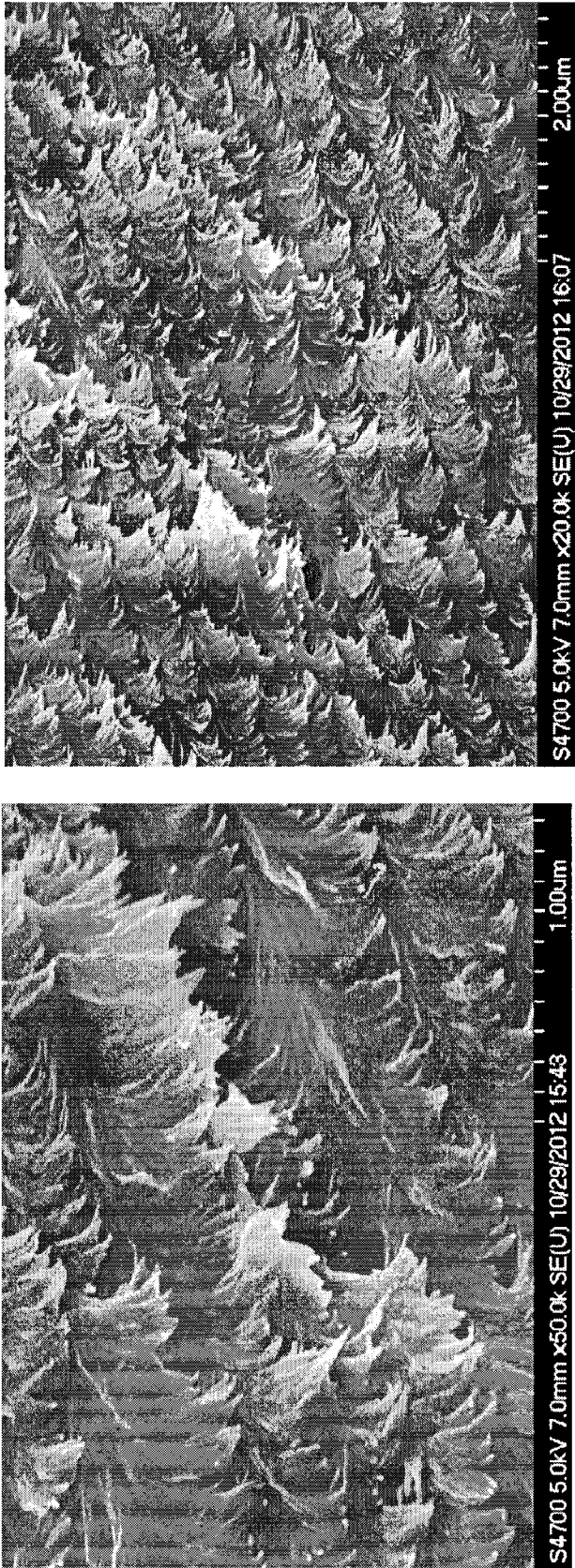


FIG. 35

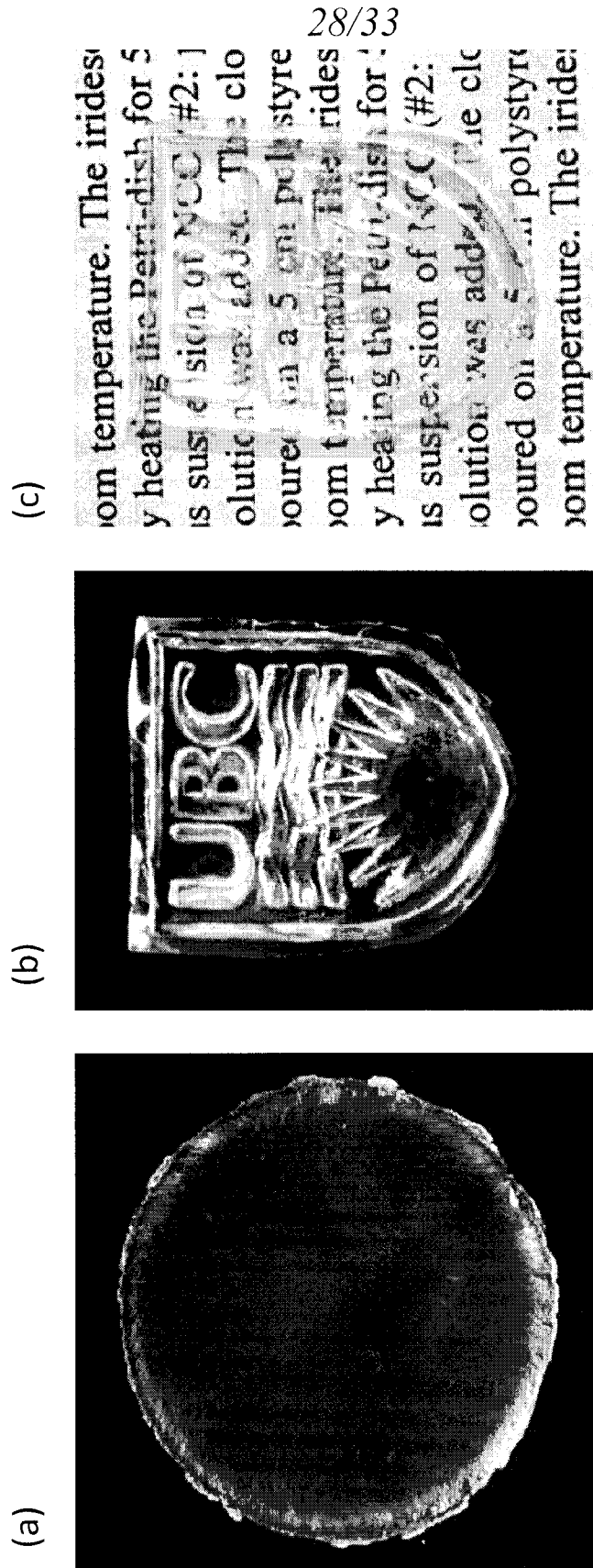


FIG. 36

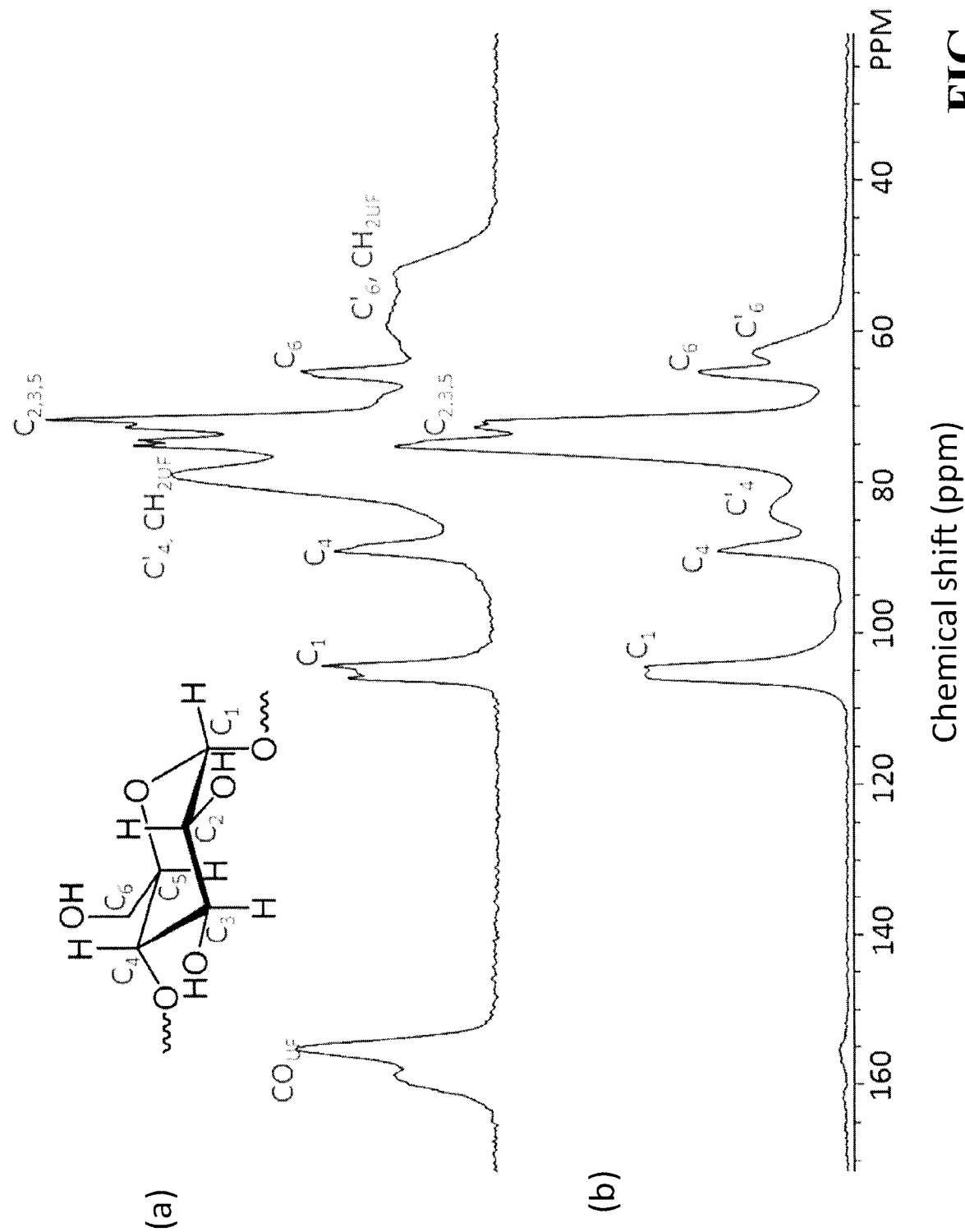
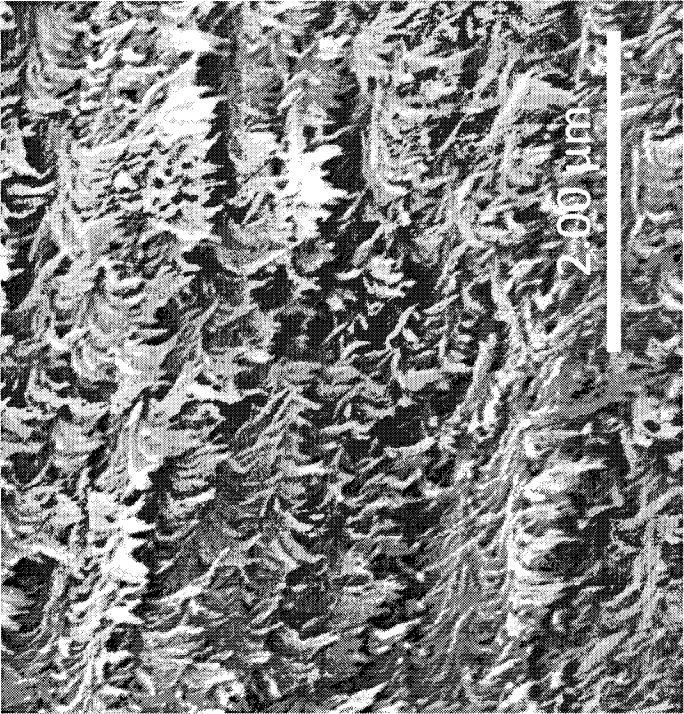
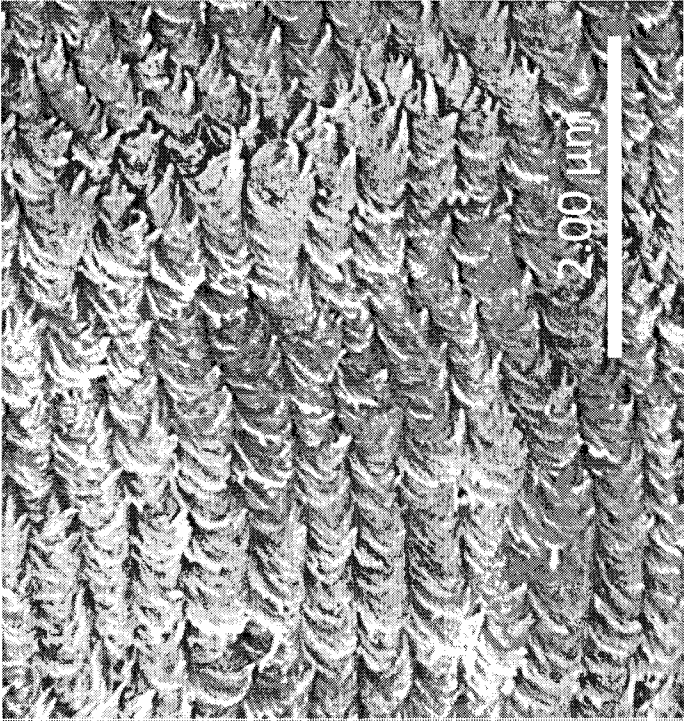


FIG. 37

30/33

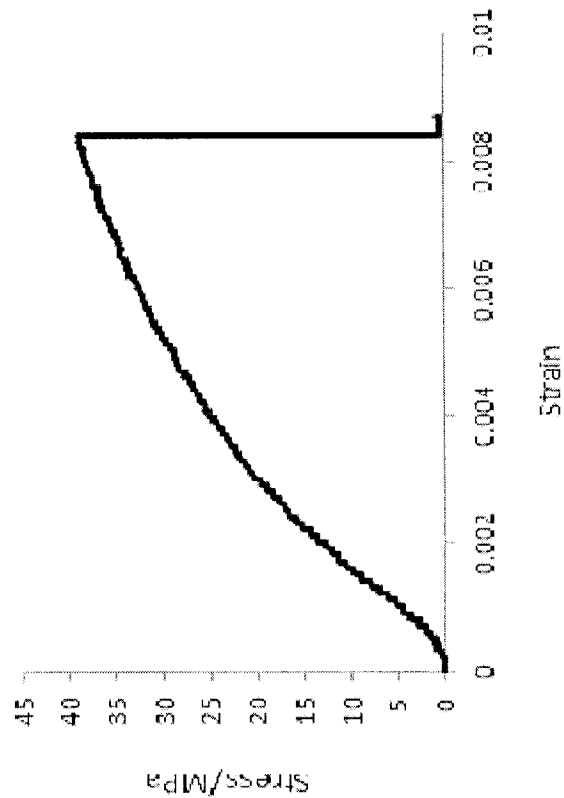
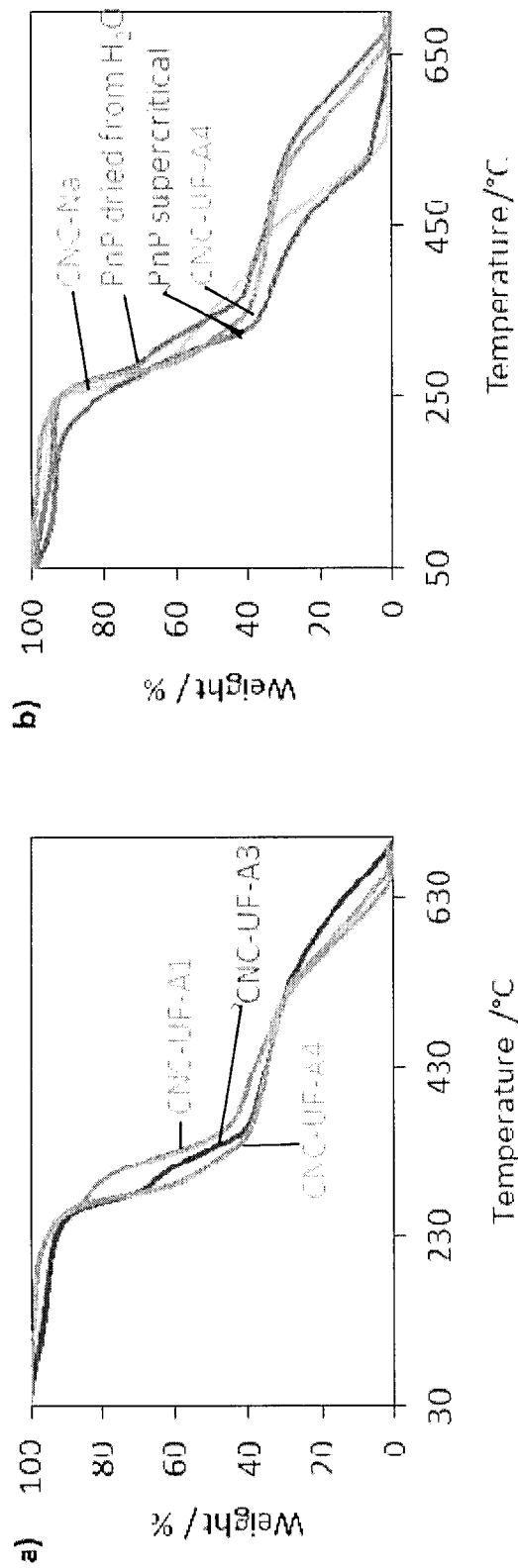


(b)



(a)

FIG. 38



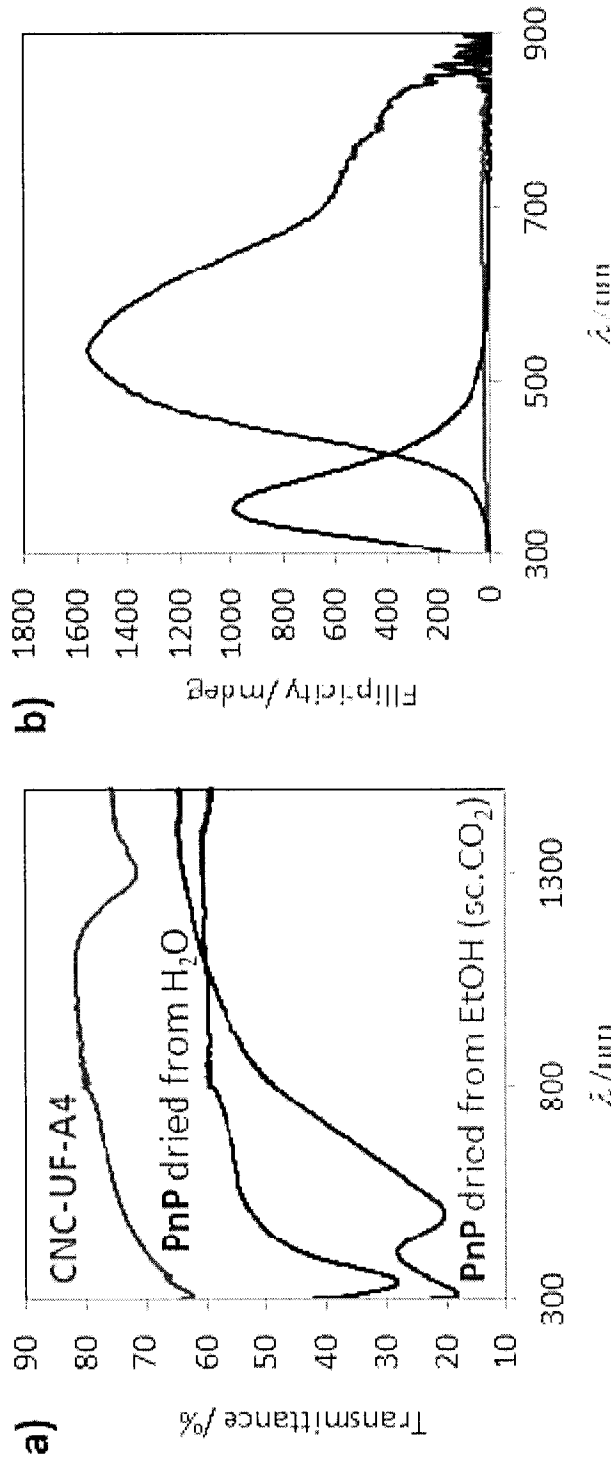


FIG. 41

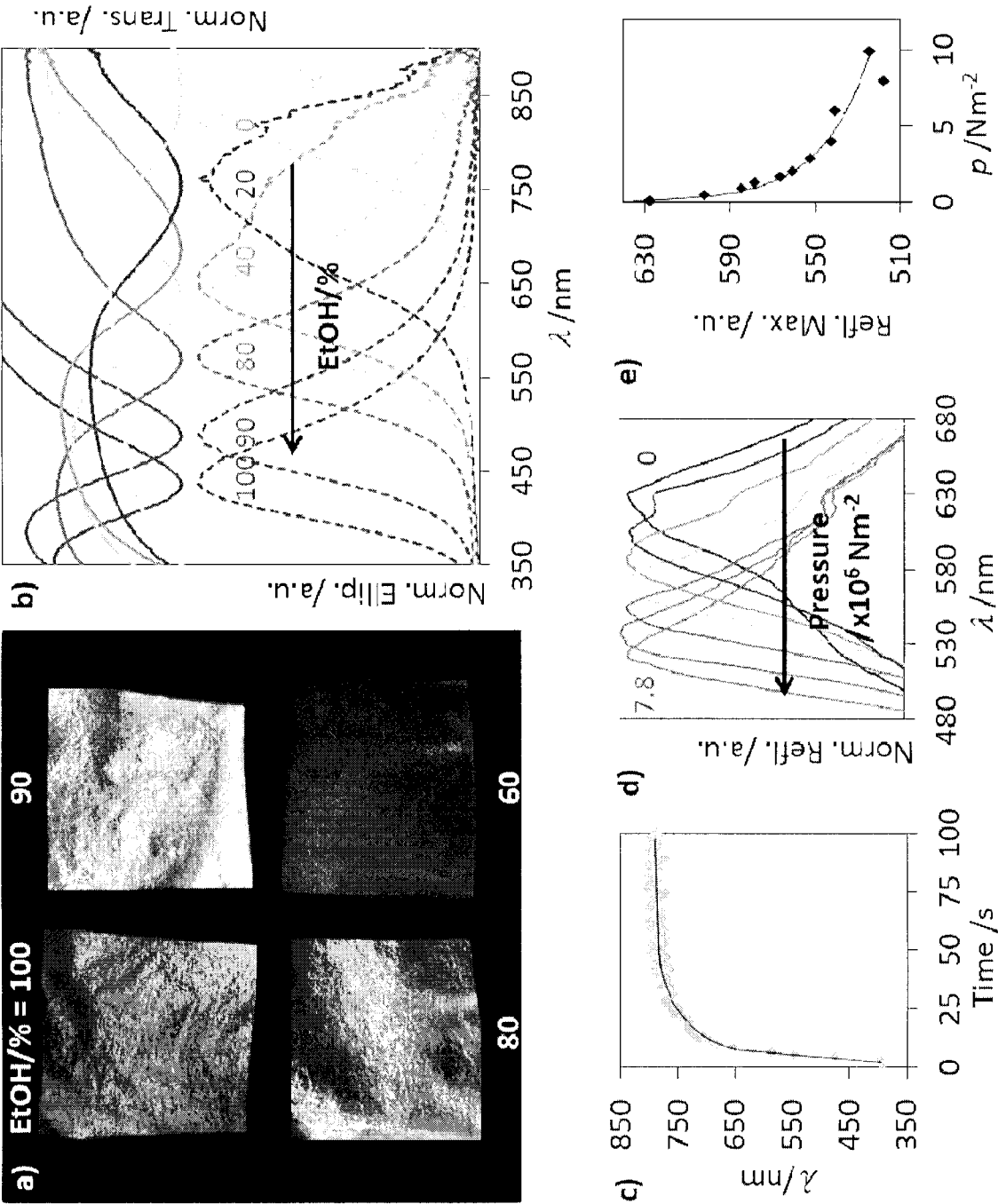


FIG. 42

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2014/000289

A. CLASSIFICATION OF SUBJECT MATTER IPC: C08B 15/00 (2006.01), B01J 20/285 (2006.01), C08J 5/24 (2006.01), C08J 9/28 (2006.01), C08L 1/02 (2006.01), C08L 61/00 (2006.01)		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC: C08B 15/00 (2006.01), B01J 20/285 (2006.01), C08J 5/24 (2006.01), C08J 9/28 (2006.01), C08L 1/02 (2006.01), C08L 61/00 (2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Totalpatent (including US, EP, WIPO, GB, and Canadian Patent databases), Scopus. Terms: nanocrystalline cellulose, microcrystalline cellulose, cellulose microfibrils, cellulose nanowhiskers, thermoset*, acetaldehyde, formaldehyde, plasticizer		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	CA 2 810 627 A1 (SHOSEYEV, O., HEYMAN, A., LAPIDOT, S., NEVO, Y., GUSTAFSSON, T.) 15 March 2012 (15-03-2012). Pg. 19. Examples 1-4. Claims 1, 20.	1-4, 7, 9-14, 17-23, and 25 --- 5, 6, 15, 16, 62, 64 (part), 65
Y	WO 93/10172 A1 (SMITH, B., GOUDSWAARD, I., CHANZY, H., CARTIER, N) 27 May 1993 (27-05-1993). Pg 5 127-39. Claims.	5, 6, 15, 16
Y	WO 2011/123929 A1 (MACHLACHLAN, M., SHOPSOWITZ, K., HAMAD, W., QI, H) 13 October 2011 (13-10-2011). Claims.	62, 64 (part), and 65
Further documents are listed in the continuation of Box C. See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 07 July 2014 (07-07-2014)		Date of mailing of the international search report 07 July 2014 (07-07-2014)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476		Authorized officer ADAM MACKENZIE (819) 994-6514

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2014/000289**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group I. Claims 1-25, 62, 64 (part), and 65 relate to a composite of NCC and a thermosetting polymer wherein the NCC is embedded in a matrix of the polymer.

Group II. Claims 26-52 relate to a porous thermosetting polymer having chiral nematic order.

Group III. Claims 53-61, 64(part), and 66 relate to a desulfated NCC having chiral nematic order.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos.: 1-25, 62, 64(part), and 65

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2014/000289

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
CA2810627A1	15 March 2012 (15-03-2012)	CA2810627A1 AU2011300350A1 CN103370190A EP2613935A1 JP2013536896A KR20130141475A US2013171439A1 WO2012032514A1 WO2012032514A8	15 March 2012 (15-03-2012) 21 March 2013 (21-03-2013) 23 October 2013 (23-10-2013) 17 July 2013 (17-07-2013) 26 September 2013 (26-09-2013) 26 December 2013 (26-12-2013) 04 July 2013 (04-07-2013) 15 March 2012 (15-03-2012) 10 October 2013 (10-10-2013)
WO9310172A1	27 May 1993 (27-05-1993)	WO9310172A1 NL9101920A	27 May 1993 (27-05-1993) 16 June 1993 (16-06-1993)
WO2011123929A1	13 October 2011 (13-10-2011)	WO2011123929A1 AU2011238367A1 CA2795375A1 CN102985365A EP2556019A1 JP2013533836A RU2012147660A US2011248214A1 US8623237B2	13 October 2011 (13-10-2011) 01 November 2012 (01-11-2012) 13 October 2011 (13-10-2011) 20 March 2013 (20-03-2013) 13 February 2013 (13-02-2013) 29 August 2013 (29-08-2013) 20 May 2014 (20-05-2014) 13 October 2011 (13-10-2011) 07 January 2014 (07-01-2014)