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Investigation of the effect of the graft density of cellulose diacetate-modified layered perovskite nanosheets on mechanical properties of the transparent organic-inorganic hybrids bearing covalent bonds at the interface

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Abstract

Transparent organic-inorganic hybrids with a whitish colour were prepared from cellulose diacetate (CDA) nanosheets derived from Dion-Jacobson-type ion-exchangeable layered perovskite $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ (HLaNb) to prepare CDA-based hybrids bearing covalent bonds between HLaNb nanosheets and CDA matrices for improved mechanical properties. An *n*-decoxy derivative of HLaNb (C10_HLaNb) was exfoliated in acetonitrile by ultrasonication. TEM and AFM images revealed that C10_HLaNb was exfoliated into individual nanosheets. In order to explore the local environment around HLaNb nanosheets, a very small amount of CDA was reacted with a C10_HLaNb nanosheet dispersion (molar ratio $\text{COH}:(\text{NbOH}+\text{NbOC}_{10}\text{H}_{21}) = 4:1$) at 80°C, and solid-state ^{13}C NMR with cross polarization and magic angle spinning techniques showed that an alcohol-exchange-type reaction was proceeded to graft the CDA chains to the HLaNb nanosheets *via* new Nb-O-C covalent linkages. The CDA-based hybrids were prepared by dispersing 5 mass% of HLaNb nanosheets in CDA and subsequent heating at 80°C for 1-7 days to cause a grafting reaction, and the product prepared by a 1-day grafting reaction exhibited improved mechanical properties compared to neat CDA; the Young's modulus, tensile strength and toughness increased by 18%, 34% and 78%, respectively. The mechanical properties deteriorated with further extension of the reaction period, however. In addition, a hybrid film prepared by mixing CDA and a C10_HLaNb nanosheet dispersion exhibited only a slight improvement in mechanical properties. These results clearly indicate that formation of an appropriate number of Nb-O-C bonds at the nanosheet/CDA interfaces is effective for improving mechanical properties.

Keywords: cellulose diacetate; layered perovskite; nanosheet; Nb-O-C bond; organic-inorganic hybrid; mechanical properties

38 Introduction

39 Petroleum-based polymeric materials have been extensively developed due to their excellent
40 mechanical properties, lightweight, barrier properties and processability (Marsh and Bugusu 2007;
41 Ojijo and Sinha Ray 2013). In recent decades, however, their impact on the global environment has
42 become a serious problem, because they are prepared from fossil fuels and become undegradable
43 wastes spontaneously after use (Sinharay and Bousmina 2005). Biopolymers are thus attracting
44 increasing attention as alternate polymeric materials because they are biodegradable and made from
45 renewable resources. Since cellulose is the most abundant biopolymer on earth, replacement of
46 conventional petroleum-based polymers with cellulose has been extensively studied (Huber et al.
47 2012). Cellulose has been chemically modified by esterification, and the properties can be controlled
48 by varying the substituted groups and degree of substitution (DS) to overcome the absence of
49 processability due to strong inter- or intra-molecular hydrogen bonds in cellulose (Edgar et al. 2001).
50 Among the various cellulose esters, cellulose diacetate (CDA) has been applied in a diverse range
51 of materials, such as clothing fibers, packaging materials, coatings, and membranes, due to its optical
52 transparency, relatively high mechanical strength and electrical insulation (Morita et al. 2007).
53 Further applications may be possible if its properties are improved (Glasser 2004).

54 It is well known that preparation of polymer-based hybrids incorporating inorganic nanosheets,
55 prepared *via* exfoliation of inorganic layered materials, can lead to dramatic enhancement of the
56 mechanical, thermal and barrier properties relative to neat polymer due to the high 2D anisotropy
57 and specific surface area of the inorganic nanosheets (Hussain 2006). Interfacial interaction between
58 matrix and nanosheets plays a critical role in acquiring excellent final properties (Terrones et al.
59 2011). Interactions can be divided into two categories: covalent interactions (Fang et al. 2010;
60 Podsiadlo et al. 2007; Salavagione and Martínez 2011; Wang et al. 2011; Zaman et al. 2011) and
61 non-covalent interactions such as hydrogen bonds (Morimune et al. 2012), electrostatic interactions
62 (Jin et al. 2013) and π - π interactions (Liu et al. 2010). It is proposed that formation of covalent bonds
63 at their interfaces is effective for enhancing the mechanical properties (Liu et al. 2012). Since
64 grafting reactions of graphene have been developed (Lonkar et al. 2014), various functional groups
65 can be covalently bound to graphene. Thus, polymer chains have been covalently bound to graphene
66 nanosheets *via* “grafting from” and “grafting to” approaches (Rohini et al. 2015). In another
67 approach, reactive groups, such as amine groups and epoxide groups, were bound to graphene
68 covalently *via* grafting reactions, and were involved in formation of matrices. The introduction of
69 graphene nanosheets improved the mechanical properties of polymers, but, at the same time, the
70 resulting hybrids became colored even at very low loading levels. So far, the application of this
71 strategy to attain biopolymer-based hybrids with improved mechanical properties has been
72 extremely limited (Campos et al. 2015; Mittal et al. 2014).

73 Some interlayer surfaces of inorganic layered compounds exhibit reactivities towards organic
74 compounds, and such organic derivatives can be exfoliated to form organically modified nanosheets
75 (Sugahara 2014). It was reported that exfoliated nanosheets exhibited a reactivity for a grafting
76 reaction (Shori et al. 2015). Thus, since some organic derivatives of inorganic layered compounds
77 undergo substitution reactions, it is expected that exfoliated nanosheets will show reactivities

towards substitution reactions with organic compounds. One of the ion-exchangeable layered perovskites, $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ (HLaNb), undergoes grafting reactions with alcohols, and the resulting alkoxy derivatives underwent further alcohol-exchange-type reactions with various molecules possessing hydroxyl groups, including alcohols, organophosphonic acids and one monosaccharide D-glucopyranose (Asai et al. 2014; Shimada et al. 2009; Suzuki et al. 2003; Takeda et al. 2006; Wang et al. 2012b; Yoshioka et al. 2003). Since a decoxy derivative of HLaNb exhibited reactivity with D-glucopyranose *via* an alcohol-exchange-type reaction (Wang et al. 2012b), it is expected that the decoxy derivative of HLaNb can react with CDA, which is an organic derivative of polysaccharide, cellulose, even after exfoliation into individual nanosheets.

Here we report the preparation of cellulose diacetate (CDA)-based hybrids with inorganic nanosheets bearing covalent bonds at the interfaces by utilizing their hydroxyl groups (**Fig. 1**). Nanosheets were obtained *via* ultrasonication of an *n*-decoxy derivative of HLaNb and HLaNb nanosheets are dispersed in CDA without covalent bond formation. By heating the resulting hybrids, the covalent Nb-O-C bonding between CDA and the HLaNb nanosheets were gradually formed at the CDA/HLaNb interfaces *via* an alcohol-exchange-type reaction. The grafting density of covalent Nb-O-C bonds was controlled by changing the heating period. In order to investigate the local environment, the HLaNb nanosheets were reacted with a very small amount of CDA, since the environment of CDA around the HLaNb nanosheets cannot be explored by analyzing hybrids that contain a large number of free CDA. The mechanical properties of the covalent-bonding hybrids and the non-covalent bonding hybrid were evaluated, and the superior mechanical properties were observed for covalent-bonding hybrids.

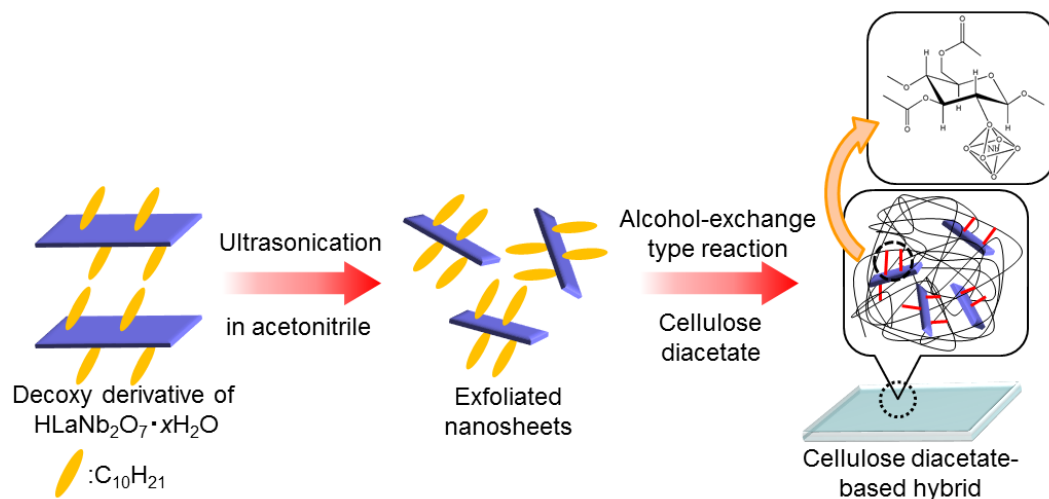


Fig. 1

Experimental

Materials

$\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ (HLaNb) and its *n*-decoxy derivative (C10_HLaNb), which had an interlayer distance of 2.71 nm, were prepared as described elsewhere (Gopalakrishnan et al. 1987; Suzuki et

al. 2003). Acetonitrile was used without further purification. Cellulose diacetate (CDA) was purchased from Sigma-Aldrich (2.45 degree of substitution, molecular mass: 30000 g/mol, $[C_6H_7O_2(OCOCH_3)_{2.45}(OH)_{0.55}, CDA]$).

Instrumentation

Transmission electron microscopic (TEM) observation was performed with a JEOL JEM-1011 microscope operating at 100 kV. TEM samples were prepared by dropping droplets of a nanosheet dispersion on a carbon-supported copper mesh TEM grid and subsequent evaporation of acetonitrile. Atomic force microscopic (AFM) observation was performed on a Digital Instruments Multimode AFM Nanoscope III microscope. An AFM sample was prepared by evaporating a nanosheet dispersion on a silicon wafer with (100) facet. Thermogravimetry (TG) was performed on a Rigaku TG8120 thermobalance in a temperature range from room temperature to 800°C at a heating rate of 10°C/min. CHN analysis was performed with a PERKIN ELMER PE2400 instrument. Solid-state ^{13}C NMR spectra with cross polarization and magic angle spinning techniques (^{13}C CP/MAS NMR) were obtained with a JEOL CMX400 spectrometer at 100.52 MHz (contact time: 5 ms, relaxation delay: 5 s). Scanning electron microscope (SEM) observation was performed with a Hitachi S-3000N microscope operating at 25.0 kV. UV-Vis spectra were measured with a JASCO V-630 UV-Vis spectrometer within the range of 350-720 nm. Tensile tests were performed with a Shimadzu autograph AGS-1kND instrument at a crosshead speed of 1 mm/min. The average values for the mechanical properties were obtained from three repetitions.

Exfoliation of C10_HLaNb

One hundred mg of C10_HLaNb were dispersed in 50 mL acetonitrile and sonicated for 30 min using a homogenizer (Digital Sonifier, BRANSON Ltd.) in an ice bath. After centrifugation (4000 rpm, 15 min) and removal of the precipitate, a nanosheet dispersion (C10_HLaNb_NS) was obtained.

Investigation of local environments

After CDA and C10_HLaNb_NS were mixed at a molar ratio of COH : (NbOH+NbOC₁₀H₂₁) = 4 : 1, the dispersion was degassed, sealed in an autoclave and heated at 80°C for 1, 5 and 7 days [CDA_HLaNb_x_le, x: reaction period (day)]. This molar ratio was selected as a slightly excess amount of COH groups in CDA to NbO groups (NbOH+NbOC₁₀H₂₁) in the nanosheets to highlight the environment of the grafted CDA chains. For ^{13}C CP MAS NMR, the resultant solution was added to a glass petri dish and dried at 50°C to evaporate the volatiles. After evaporation, the resultant films were dried under reduced pressure. For TG analysis, the resultant films were dissolved in acetonitrile, supercentrifuged (14000 rpm, 10 min), and then washed with acetonitrile to remove the unreacted CDA and dried under reduced pressure (CDA_HLaNb_x_w, x: reaction period).

Preparation of CDA-based hybrids

CDA was reacted with 5 mass% of C10_HLaNb_NS in an autoclave using the reaction procedure described above. After the reaction, the resultant dispersions were added to a glass petri dish and dried at 50°C to evaporate the volatiles. The resultant films were dried under reduced pressure. The thicknesses of these films are about 60 μm determined by the cross-section SEM images (see Fig. S1 in the **Electronic Supplementary Material**). CDA-based hybrids were denoted as CDA_HLaNb_x_gf (x: reaction time). For comparison, CDA films mixed with 5 mass% of C10_HLaNb_NS was prepared (CDA_C10HLaNb). The sample codes in this study were summarized in **Table 1**.

Table 1

Sample code	Preparation procedure	Characterization
C10_HLaNb	Layered <i>n</i> -decoxy-modified HLaNb	TEM
C10_HLaNb_NS	<i>n</i> -decoxy-modified HLaNb nanosheets	TEM AFM
CDA_C10HLaNb	CDA hybrid film with C10_HLaNb_NS ²⁾	Tensile test
CDA_HLaNb_x_le ¹⁾	Degassed CDA and C10_HLaNb_NS in an autoclave was heated at 80°C and subsequently dried under reduced pressure.	¹³ C CP MAS NMR
CDA_HLaNb_x_w ¹⁾	After dissolving CDA_HLaNb_x_le in acetonitrile, the supercentrifugation and rinsing with acetonitrile were repeated, and the product was dried under reduced pressure. ³⁾	TG
CDA_HLaNb_x_gf ¹⁾	After reaction of CDA with C10_HLaNb_NS at 80°C, the hybrid films were prepared by drying the resultant dispersion in a glass petri dish. ²⁾	Photograph UV-vis Tensile test

¹⁾ x: reaction period (1, 5, or 7 days)

²⁾ Nanosheet content: 5 wt%

³⁾ Molar ratio of COH : (NbOH+NbOC₁₀H₂₁) = 4 : 1

Results and discussion

Exfoliation of C10_HLaNb

Figure 2 shows TEM images of C10_HLaNb and C10_HLaNb_NS. After ultrasonication (C10_HLaNb_NS), a sheet-like morphology image whose contrast is lighter than that of C10_HLaNb is observed, indicating that exfoliation has proceeded successfully. The electron diffraction (ED) pattern (inset in Fig. 1b) of C10_HLaNb_NS can be indexed as a tetragonal cell with $a = b = 0.39$ nm, which coincides with the lattice parameters of HLaNb ($a = b = 0.3891$ nm) (Gopalakrishnan et al. 1987), demonstrating that the structure of individual nanosheet of HLaNb was retained by ultrasonication.

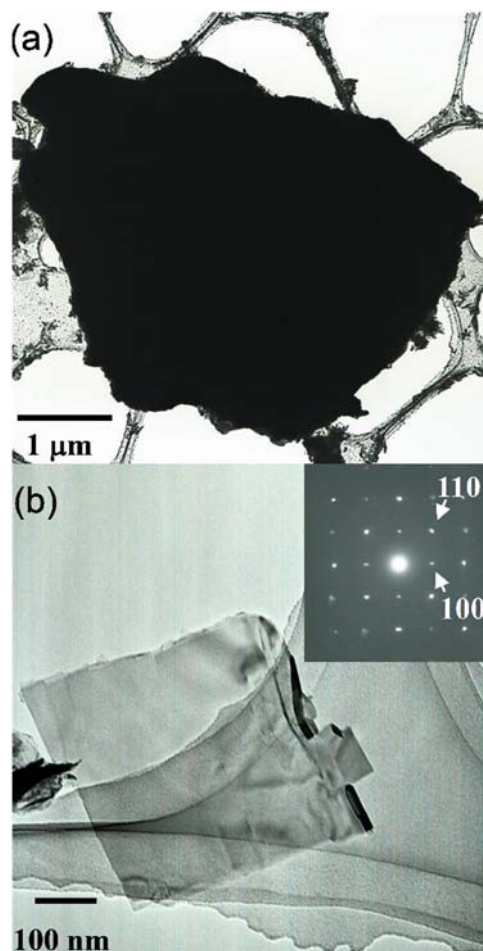


Fig. 2

In an AFM image of C10_HLaNb_NS (Fig. 3), a sheet-like morphology is observed, and its height profile shows that its thickness is $2.7 (\pm 0.01)$ nm. This thickness corresponds to the interlayer distance of C10_HLaNb, 2.71 nm determined by the XRD patterns, indicating that C10_HLaNb was exfoliated into individual nanosheets by ultrasonication in acetonitrile.

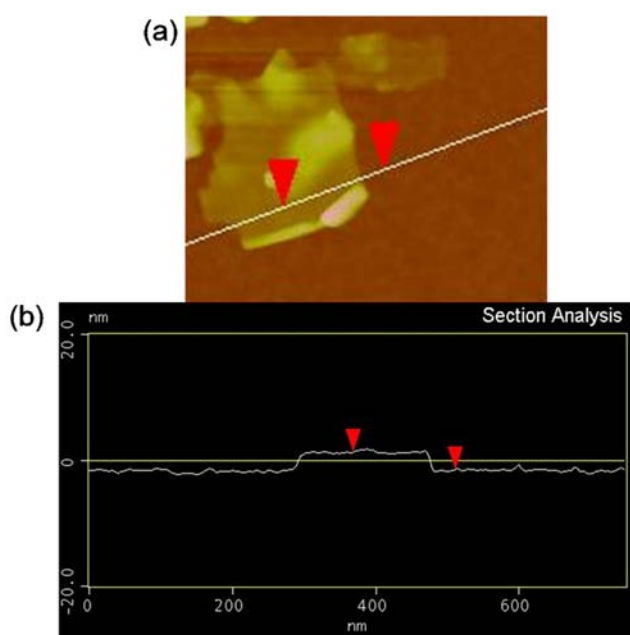


Fig. 3

168

169 Investigation of local environments

170 The HLaNb nanosheets were reacted with CDA with $\text{COH} : (\text{NbOH} + \text{NbOC}_{10}\text{H}_{21}) = 4 : 1$. Since
171 the stoichiometric amount corresponds to $\text{COH} : (\text{NbOH} + \text{NbOC}_{10}\text{H}_{21}) = 1 : 1$, a slight excess amount
172 of CDA was added to allow us to study the local environments of CDA around the HLaNb
173 nanosheets. The solid-state ^{13}C CP MAS NMR spectra of CDA_HLaNb_1, 5, 7_le are demonstrated
174 in **Fig. 4**. In the spectra, signals ascribable to CDA are observed at 168 (OCOCH_3), 100 (C1 carbon),
175 72 (C2-C5 carbons) and 61 (substituted C6 carbon) ppm (Barud et al. 2008). The spectra are different
176 from that of neat CDA, however (**Fig. 4a**): new signals are present at 86-87 ppm, while the signals
177 at 81 (C4 carbon neighboring unsubstituted C3 carbon) and 58 (unsubstituted C6 carbon) ppm, both
178 of which are present in the spectrum of neat CDA, are absent. It was reported that the α carbon signal
179 shifted downfield after formation of an Nb-O-C bond with alcohols (Suzuki et al. 2003) and that
180 reactions with α carbons in the C1 and C4 positions of D-glucopyranose led to downfield shifts of
181 about 7 and 15 ppm, respectively (Wang et al. 2012b). It is thus suggested that the new signal is
182 ascribable to a downfield shifted signal of an α carbon in the C2 or C3 position (originally the 72
183 ppm position) by the formation of an Nb-O-C bond. The disappearance of the signal at 58 ppm after
184 the reactions is also likely to be ascribable to the formation of an Nb-O-C bond with an α carbon in
185 the C6 position, leading to a downfield shift somewhat similar to the disappearance of the signal
186 described above. The corresponding shifted signal cannot be observed in the spectra, however. It is
187 thus assumed that the signal at 58 ppm shifts downfield, but the shifted signals overlap with broad
188 signals at 72 ppm, leading to the absence of the shifted signal. The disappearance of a signal
189 ascribable to the C4 carbon at 81 ppm can be explained as follows. It was reported that when an α
190 carbon in the C3 position in native cellulose was acetylated, the corresponding signal shifted
191 downfield, inducing an upfield shift of the β carbon signal in the C4 position from 79 ppm to 75
192 ppm (the so-called “ β effect”) (Sei et al. 1985). In the present study, downfield shifts of α carbon
193 signals are likely caused by the formation of Nb-O-C bonds *via* alcohol-exchange-type reactions. It
194 is thus assumed that the proceeding of alcohol-exchange-type reactions also causes the β effect in a
195 way similar to that of acetylation of native cellulose: the formation of an Nb-O-C bond at the α
196 carbon in the C3 position induces an upfield shift of the C4 carbon signal. It is also likely that the
197 shifted signals cannot be observed in the spectra due to overlapping with the broad signal at 72 ppm
198 in a fashion similar to the absence of the signal shifted from 58 ppm. These results show formation
199 of covalent bonds at the CDA/HLaNb interfaces *via* an alcohol-exchange-type reaction. IR spectra
200 of CDA hybrids containing with C10_HLaNb_NS also support the formation of Nb-O-C bonds
201 between CDA and HLaNb nanosheets because of disappearing the adsorption bands of $\nu(\text{C-O})$
202 assignable to *n*-decoxy groups in the hybrids (see **Fig. S2** in the **Electronic Supplementary**
203 **Material**).

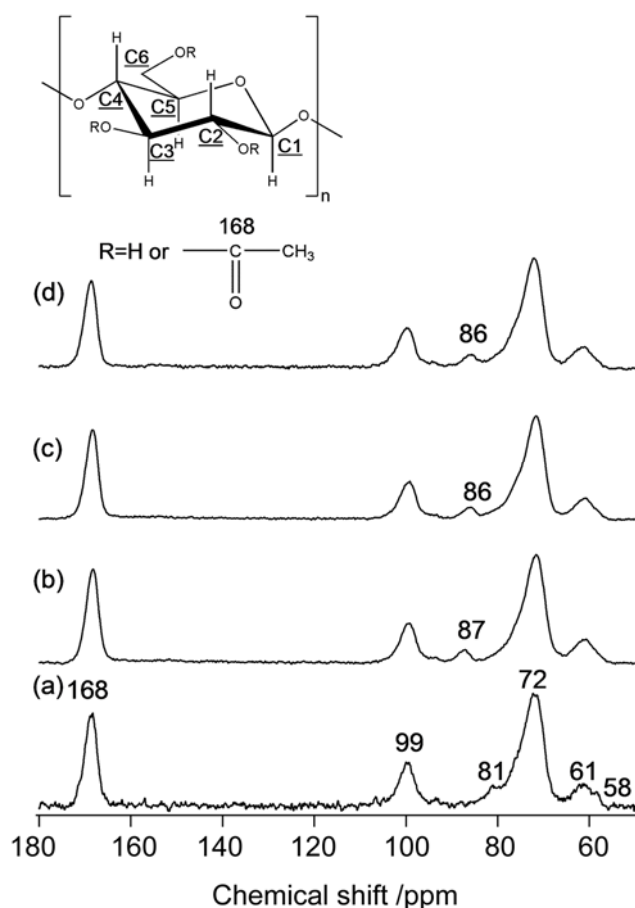


Fig. 4

The amounts of modified CDA are estimated from the TG results (Fig. 5). In order to evaluate grafting densities of CDA on HLaNb nanosheets, the samples were prepared by removing the ungrafted CDA from the hybrid films through washing with acetonitrile. The total mass losses of CDA_HLaNb_1_w, 5_w, and 7_w are 31.9%, 40.4%, and 49.2%, respectively. CHN analysis was also conducted and the carbon contents (in mass%) for CDA_HLaNb_1_w, 5_w, and 7_w were 13.22, 13.89 and 14.83, respectively. These results indicate that a larger amount of CDA is grafted in a longer reaction period. In the TG curves, the initial mass loss at a temperature lower than the temperature for decomposition of organic components (< ca. 250 °C) is assignable to evaporation of adsorbed water from the surfaces due to hydration of the grafted CDA. Because of the larger amount of adsorbed water on higher densely CDA-modified nanosheets, the mass loss assignable to water evaporation depends on the amount of grafted CDA.

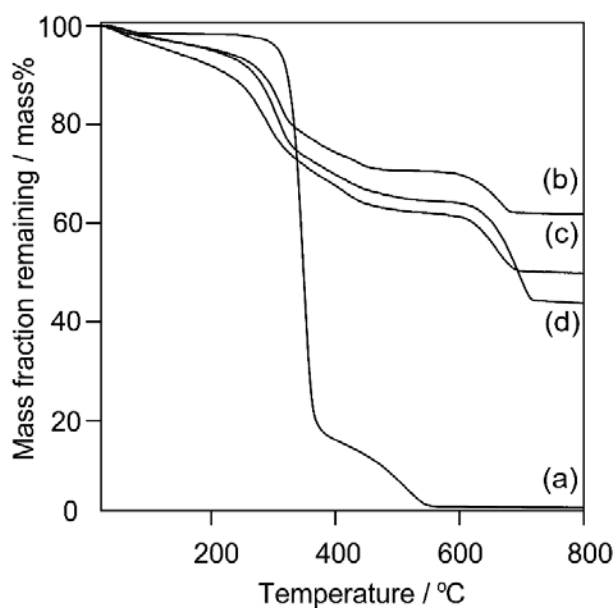


Fig. 5

Preparation of CDA-based hybrids and their mechanical properties

The UV-Vis spectra of hybrid films are demonstrated in Fig. 6, and the photographs of hybrid films are shown in Fig. 7. CDA_HLaNb_1_gf, 5_gf, and 7_gf are all transparent films with a whitish colour. The transmittance value of neat CDA at 633 nm is 89.5%, and those of CDA_HLaNb_1_gf (86.9%), CDA_HLaNb_5_gf (84.9%) and CDA_HLaNb_7_gf (83.1%) are comparable after the addition of nanosheets. The transmittance decreases gradually with extension of the reaction period. The transmittance of the nanosheet/CDA hybrids reflects at the dispersing status of the nanosheets, because Rayleigh scattering occurs on an optical path at above 40 nm through nanosheets to decrease the transmittance of the hybrids (Althues et al. 2007). These results indicate that aggregation of HLaNb nanosheets in CDA matrices was promoted during the grafting reactions.

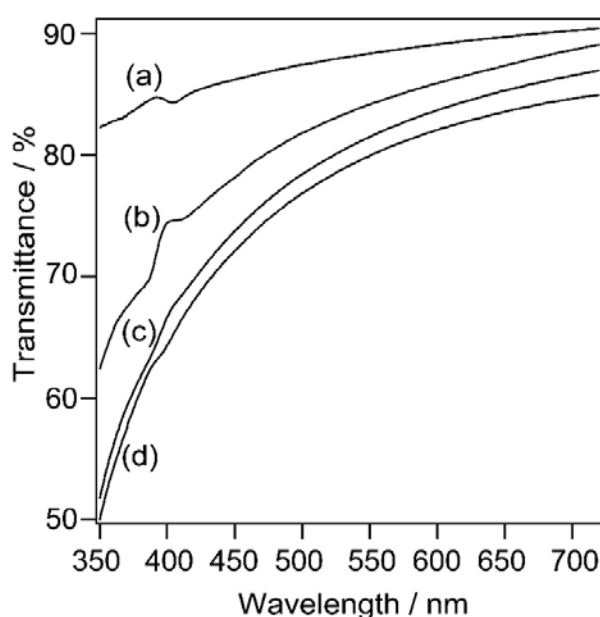


Fig. 6

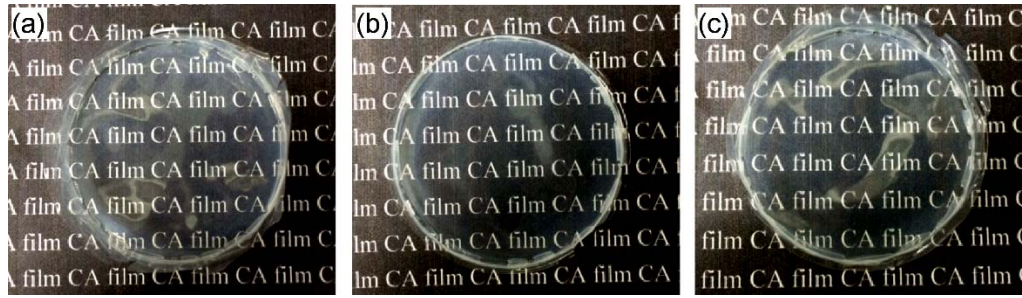


Fig. 7

Figures 8 and 9 show the stress (σ)-strain (ε) curves and relationship between the reaction period and Young's modulus (E), tensile strength ($\sigma_{\max}$), strain at break ($\varepsilon_{\max}$) and toughness (K) (see also **Table 1**). Compared to neat CDA, CDA_C10HLaNb prepared by mixing CDA and C10_HLaNb_NS shows slightly improved mechanical properties: Young's modulus, tensile strength and toughness increase by 10%, 6% and 14% respectively. On the other hand, the mechanical properties of CDA_HLaNb_1_gf are significantly improved: Young's modulus, tensile strength and toughness increase by 18%, 34% and 78% respectively. In Figure S1, the morphology of CDA hybrid films is the same as that of bare CDA at the micrometer level. The optical and mechanical properties of the hybrids thus depend mainly on their microscopic structures on the scale of nanosheets. Although Young's modulus increases with extension of the reaction period, however, tensile strength and toughness decrease upon further reaction (CDA_HLaNb_5_gf and CDA_HLaNb_7_gf). These results indicate that use of the appropriate grafting density of covalent Nb-O-C bonds at the nanosheet/CDA interface was more effective for improving the mechanical properties than use of CDA_C10HLaNb, although a further increase in the grafting density led to deteriorated properties. The strong interfacial interaction through the covalent Nb-O-C bonds induces a restriction of chain mobility and effective load transfer from the CDA matrix to the nanosheets, leading to a high Young's modulus and increased tensile strength (CDA_HLaNb_1_g), although the excess restriction occurring in a much larger grafting density of covalent Nb-O-C bonds also leads to brittleness of the resultant hybrids (Wang et al. 2011). Another possible reason for the deteriorated properties is an aggregation of nanosheets confirmed by the results of UV-Vis spectroscopy, which can be a starting point for cracking under concentrated stress. Thus, CDA_HLaNb_5_g and CDA_HLaNb_7_g are likely to exhibit a higher Young's modulus but lower tensile strength and toughness than CDA_HLaNb_1_g with extension of the reaction period.

Table 2

Sample	E/GPa	$\sigma_{\max}/\text{MPa}$	$\varepsilon_{\max}/\%$	$K/\text{J} \cdot \text{g}^{-1}$
neat CDA	1.43 ± 0.17	32.4 ± 1.8	2.00 ± 0.37	0.073 ± 0.012
CDA_HLaNb_1_gf	1.69 ± 0.09	43.3 ± 5.5	2.82 ± 0.15	0.130 ± 0.036
CDA_HLaNb_5_gf	2.13 ± 0.11	32.3 ± 7.6	1.48 ± 0.27	0.075 ± 0.032
CDA_HLaNb_7_gf	2.26 ± 0.09	23.6 ± 3.2	1.00 ± 0.16	0.038 ± 0.011
CDA_C10HLaNb	1.57 ± 0.17	34.2 ± 4.2	2.33 ± 0.08	0.083 ± 0.014

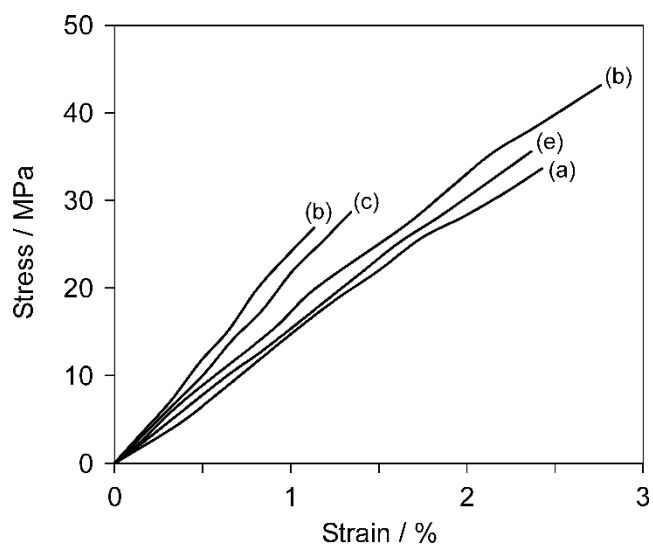


Fig. 8

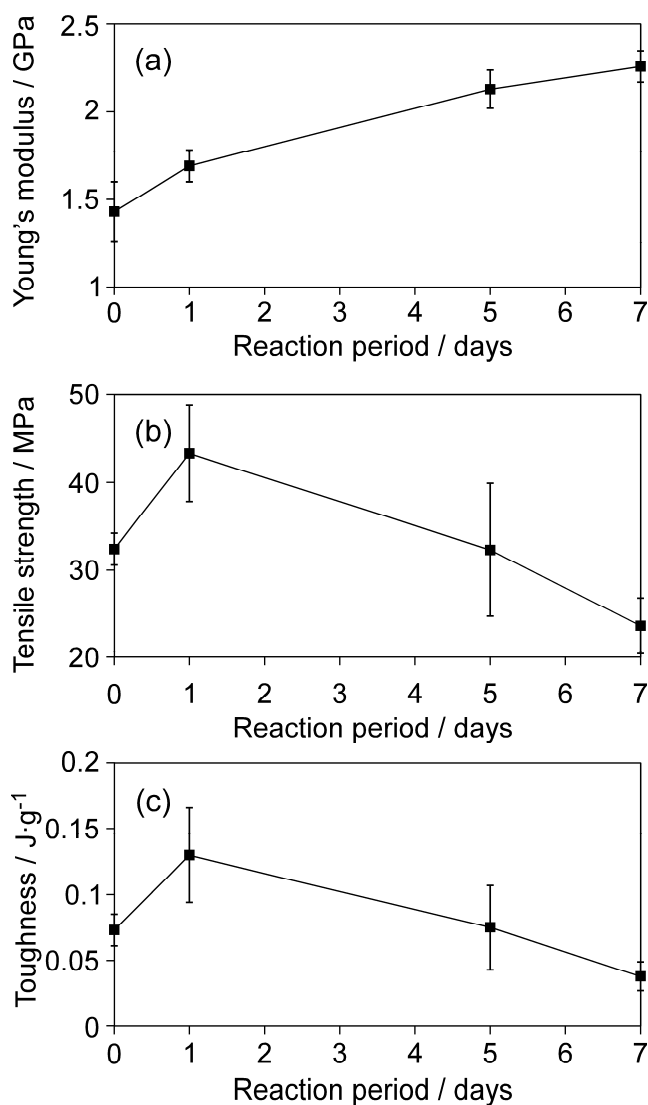


Fig. 9

Polymer-based hybrids possessing covalent bonds at the graphene/polymer interface have so far been reported for various polymers (Campos et al. 2015; Mittal et al. 2014; Rohini et al. 2015), although only graphene nanosheets without organic modification have been employed when it

comes to cellulose and related polymers (Huang et al. 2014; Kabiri and Namazi 2014; Liu et al. 2014; Wang et al. 2012a). With respect to organoclay-loaded cellulose acetate, on the other hand, the tensile strength and modulus were enhanced by using alkylammonium-reacted clay nanosheets with maleic anhydride grafted cellulose acetate butyrate as the compatibilizer (Park et al. 2004). This report suggests that strong interactions occurred between the cellulose acetate matrices and the clay nanosheets *via* a large number of ionic bonds at the interfaces, although covalent bonds were not formed between them. In another study, the tensile strength values for the organoclay/CDA hybrids decreased (Rodríguez et al. 2012). Thus, the present strategy involving covalent bond formation at the interface is highly effective for improving the mechanical properties of nanosheet/cellulose acetate hybrids. The advantage of the present strategy is controlled covalent bond formation: a huge lateral plane of nanosheets can be employed, and the grafting density of covalent Nb-O-C bonds can be tuned by changing the reaction period.

Conclusions

We have demonstrated a new approach to preparation of CDA-based hybrids exhibiting improved mechanical properties and whitish colour. An *n*-decoxy derivative of HLaNb (C10_HLaNb) was exfoliated into individual nanosheets by ultrasonication in acetonitrile. CDA and HLaNb were reacted at a molar ratio of COH : (NbOH+NbOC₁₀H₂₁) = 4 : 1 to investigate the change in the local environment with different reaction conditions. The ¹³C CP MAS NMR spectra clearly showed that an alcohol-exchange-type reaction occurred between CDA and HLaNb. CDA-based hybrids prepared by reaction at 80°C for 1 day with 5 mass% nanosheets exhibited improved Young's modulus, tensile strength and toughness compared to neat CDA. Hybrids prepared by mixing CDA and a C10_HLaNb nanosheet dispersion exhibited only a slight improvement in mechanical properties, indicating that the improvement in mechanical properties was likely caused by formation of Nb-O-C bonds at the CDA/HLaNb interfaces. The present study suggests that various biopolymers possessing hydroxyl groups can be reacted with exfoliated HLaNb to prepare new biopolymer-based hybrid materials.

Acknowledgements

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Table and Figure Captions

Table 1 Sample codes in this study.

Table 2 Yonug's modulus (*E*), tensile strength ($\sigma_{\max}$), strain at break ($\epsilon_{\max}$) and toughness (*K*) of HLaNb/CDA hybrids [CDA_HLaNb_x_gf, x: reaction period (day)].

300 **Fig. 1** Overview of the preparation of CDA/HLaNb hybrids.

301 **Fig. 2** TEM image of (a) C10_HLaNb and (b) C10_HLaNb_NS with corresponding ED
 302 pattern (inset). Acceleration voltage: 100 kV. TEM samples were prepared by dropping of
 303 droplets of a nanosheet dispersion on a carbon-supported copper mesh TEM grid and
 304 subsequent evaporation of acetonitrile.

305 **Fig. 3** (a) AFM image of C10_HLaNb_NS and (b) line profile taken along white line. AFM
 306 samples were prepared by evaporating a nanosheet dispersion on a silicon wafer with a (100)
 307 facet.

308 **Fig. 4** ¹³C CP/MAS NMR spectra of (a) neat CDA, (b) CDA_HLaNb_1_le, (c)
 309 CDA_HLaNb_5_le and (d) CDA_HLaNb_7_le. A degassed mixture of CDA and
 310 C10_HLaNb_NS (molar ratio of COH : (NbOH+NbOC₁₀H₂₁) = 4 : 1) in an autoclave was
 311 heated at 80°C for 1, 5 and 7 days [CDA_HLaNb_x_le, x: reaction period (day)]. NMR
 312 conditions; frequency: 100.52 MHz, contact time: 5 ms, relaxation delay: 5 s.

313 **Fig. 5** TG profile of (a) neat CDA, (b) CDA_HLaNb_1_w, (c) CDA_HLaNb_5_w and (d)
 314 CDA_HLaNb_7_w. After the hybrid films were dissolved in acetonitrile, supercentrifugation
 315 (14000 rpm, 10 min) and rinsing with acetonitrile were repeated to remove the unreacted
 316 CDA, and the product was dried under reduced pressure (CDA_HLaNb_x_w, x: reaction
 317 period). TG condition; heating rate: 10°C/min

318 **Fig. 6** UV-Vis spectra of (a) neat CDA (b) CDA_HLaNb_1_gf, (c) CDA_HLaNb_5_gf, and
 319 (d) CDA_HLaNb_7_gf. HLaNb nanosheet content: 5 wt%, wavelength range: 350-720 nm.

320 **Fig. 7** Photographs of (a) CDA_HLaNb_1_gf and (b) CDA_HLaNb_5_gf and (c)
 321 CDA_HLaNb_7_gf. After reaction of CDA with C10_HLaNb_NS (nanosheet content: 5
 322 wt%) at 80°C for 1, 5 and 7 days, the hybrid films were prepared by drying the resultant
 323 dispersion in a glass petri dish [CDA_HLaNb_x_gf, x: reaction period (day)].

324 **Fig. 8** Stress-strain curves of (a) neat CDA, (b) CDA_HLaNb_1_gf, (c) CDA_HLaNb_5_gf
 325 and (d) CDA_HLaNb_7_gf and (e) CDA_C10HLaNb. HLaNb nanosheet content: 5 wt%,
 326 crosshead speed: 1 mm/min.

327 **Fig. 9** Relationship between reaction period and (a) Young's modulus, (b) tensile strength
 328 and (c) toughness of HLaNb/CDA hybrids [CDA_HLaNb_x_gf, x: reaction period (day)].
 329 HLaNb nanosheet content: 5 wt%.

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