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Structure-regulated tough elastomer of liquid crystalline inorganic
nanosheets/polyurethane nanocomposite

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Liquid crystalline nanosheets/polyurethane composite elastomers with superior mechanical properties were successfully synthesized by newly developed in-situ polymerization technique. A layered clay mineral fluorohectorite was fully exfoliated into single-layer nanosheets and formed nematic liquid crystalline (LC) state in N,N'-dimethylformamide/water mixture added with the prepolymer, isocyanate-terminated low-molecular-weight poly(ethylene oxide). The composite elastomer fibers were obtained by injecting this LC mixture into a solution of four-functional crosslinker molecule, triethylenetetramine, followed by solvent removal. In the composite fibers, the single-layer LC nanosheets were macroscopically aligned along the long axis of the fibers as revealed by polarizing microscope and small angle X-ray scattering. Tensile tests showed that the composite fibers have superior mechanical strength while maintaining large breaking strain compared to the pristine polyurethane fibers without the nanosheets. The outstanding improvements were due to physical crosslinks at multiple points between polymer chains and the single-layer nanosheets that are macroscopically ordered.

Introduction

Nanocomposite formation of polymers with inorganic nanoparticles is quite effective way to achieve extraordinarily functions and properties of materials as exemplified by natural nacre that is CaCO\textsubscript{3}/poly peptide nanocomposite with toughness and light weight. Since the pioneering work on nylon-6/clay nanocomposites,\textsuperscript{4, 6, 8, 9} inorganic nanosheets or stacked nanosheets obtained from layered crystals have been utilized as excellent nanofillers for nanocomposites due to large specific surface area, large aspect ratio, low cost, and availability of variety of materials with desired electric and optical properties.\textsuperscript{5, 11} Mechanical strength,\textsuperscript{7, 9, 12} gas barrier property,\textsuperscript{5, 13, 14} thermal stability,\textsuperscript{6, 7, 15} and thermal conductivity\textsuperscript{16-20} are improved and electrical and optical properties are also tunable when even small amount of a layered crystal is composited with a polymer material.

However, when a layered crystal is not fully exfoliated into single layers and is not dispersed homogeneously in composites, improvements of the materials' properties are limited; maximized properties along a certain direction and other smart properties is expected only when the orientation and spatial distribution of the nanosheets are precisely controlled. Nevertheless, fabrication of such ideal nanocomposites is still very challenging.

In the most conventional synthesis of nanosheets/polymer nanocomposites,\textsuperscript{21} clay mineral powders intercalated with alkyl ammonium ions, organo-clays, are kneaded in molten polymer. Polymerization of monomers added with organo-clay crystals (in-situ intercalative polymerization) is another general method. In these classical methods, however, the layered crystal is usually not fully exfoliated and the control of orientation and spatial distribution of nanosheets is not possible. Layer-by-layer deposition of thin composite films\textsuperscript{22} is a sophisticated technique to fabricate precisely designed heterostructures; however, only ionic polymers can be used and large scale synthesis is not possible. Doctor-blading,\textsuperscript{23} spray coating,\textsuperscript{24} vacuum filtration,\textsuperscript{25, 26} or simply casting\textsuperscript{27} of polymer-coated nanosheets or polymer/nanosheet solution on a substrate and formation of regulated structures upon solvent evaporation have been also recently reported. In these methods, however, structure formation depends on the solvent evaporation process so that precise structural control is not straightforward; kinetic control in the complicated situation is necessary in which intrinsic phase separation of polymer and nanosheet occurs due to depletion effect,\textsuperscript{28} while partial isotropic-nematic transition is driven by excluded volume effect\textsuperscript{29} and viscosity increases.

Considering the above situation, for fabrication of ideal bulk nanocomposite materials with highly regulated structure, separation of the synthesis process into (1) superstructure formation process of the fillers and (2) fixation processes by in-situ polymerization, starting from nanosheets/prepolymer mixture, should be an effective strategy. In line with this
strategy, we have been highlighting the structured liquid crystalline colloidal nanosheets since early 2000's.\textsuperscript{30} Due to the anisotropic shapes of nanosheets, free rotational motion is restricted and LC phase is formed when nanosheet concentration is higher as explained by Onsager's theory.\textsuperscript{29} By tuning this entropic interaction as well as attractive and repulsive interactions between charged nanosheets, orientational\textsuperscript{30} and positional\textsuperscript{31} ordering of nanosheets are precisely controllable on mesoscopic scales in the colloidal state. Further, electric,\textsuperscript{32} magnetic,\textsuperscript{33} and shear\textsuperscript{30} fields are effective to achieve macroscopic alignment of these mesophases, leading to hierarchical structural control. After a regulated hierarchical superstructure of single-layer nanosheets is obtained, a monomer dissolved in the LC colloid is photo-polymerized to finally obtain structured nanocomposite gel.\textsuperscript{34,36} In these gels, not only a great improvement in mechanical strength but also anisotropic optical and molecular transport properties were demonstrated. However, it has been difficult to apply this synthetic technique to industrially important plastic or elastomer materials mainly composed of hydrophobic polymers because inorganic nanosheets are generally hydrophilic.\textsuperscript{7,37}

In this study, we demonstrate a novel synthetic method to obtain LC single layer nanosheets/polyurethane composite elastomer in which exfoliated nanosheets are embedded retaining the regulated superstructure of the original LC colloid. The new synthetic method (Figure 1a) makes use of isocyanate-terminated low-molecular-weight prepolymer (Figure 1b) which is soluble in water/polar organic solvent mixture that is also compatible with the liquid crystalline nanosheets. The composite elastomer fiber was successfully obtained by extruding the nanosheets/prepolymer mixture into a four-functional crosslinker solution (Figure 1c and Figure S1). Although, in general, isocyanate moiety is hydrolyzed easily, it is more reactive with amino groups of the crosslinker triethylenetetramine than water so that the crosslinking reaction predominantly proceeds.\textsuperscript{38} Due to the shear stress in the extrusion process, the macroscopic orientation of the nanosheets was strongly induced, giving rise to mechanical properties. The present process is also characterized as a new-type wet-spinning system where chemically crosslinked network polymer is obtained in-situ in contrast with the conventional system where polymer or nanosheets are physically crosslinked by coaggregation with Ca\textsuperscript{2+}\textsuperscript{39,41} or solidified by precipitation of a polymer in a poor solvent.

Experimental
Preparation of the nanosheet colloid
The aqueous sol of synthetic clay mineral fluorohectorite (NHT-B2 SOL) was supplied by Topy Industries. The as-received aqueous sol was centrifuged at 15,000 rpm for 1 h, followed by removing the supernatant, to finally obtain concentrated NH\textsubscript{4}-fluorohectorite nanosheet/water/DMF colloid. During the exfoliation process, mechanical treatments such as ultrasonication was not necessary. Different from van der Waals type layered crystals like BN and MoS\textsubscript{2,43,44} it is known that ionic-type layered crystal such as Na-fluorohectorite are spontaneously exfoliated into single layers in water under a mild condition without hard mechanical treatment because of osmotic swelling.\textsuperscript{42} This was also the case for the present case: NH\textsubscript{4}-exchanged fluorohectorite in DMF/water mixture.

Preparation of the nanosheets/polyurethane composite fiber
Polyurethane composite fiber was synthesized by the following method. First, 1.90 g (1.90 mmol) of poly(ethylene glycol) (PEG, Mw: 1,000, Sigma-Aldrich) was placed in N\textsubscript{2}-purged flask and dissolved in 4 mL of super dehydrated DMF (Tokyo Chemical Industry [TCI]). Then, 0.784 g (4.00 mmol) of 1,3-bis(isocyanatomethyl)cyclohexane (TCI) and 0.027 g (0.043 mmol) of dibutyltin dilaurate (TCl) were added and stirred at 60 °C for 2 h to obtain the solution of the prepolymer which have isocyanate groups at both terminals of the PEG (Figure 1b). This prepolymer solution (1.00 g) was added with the nanosheet colloid (0.0941, 0.491, or 1.04 g) and extruded into a DMF solution (3.54 M) of the cross-linking agent triethylenetetramine (TCI) by using a syringe pump at the flow rate of 8 mL min\textsuperscript{−1} (Figure S1). At this time, the beaker containing the crosslinking agent solution was rotated by a turntable at 70 rpm. The cross-linking reaction spontaneously proceeded (Figure 1c and Figure S1) upon the extrusion and the swollen cross-linked nanosheets/polyurethane composite fiber was obtained. The fiber was stored in the crosslinker solution for 1 day to allow completion of the crosslinking reaction. After the reaction, the composite fiber was stored in DMF for 1 day to remove unreacted prepolymer and cross-linking agent and was dried it in a vacuum oven at 70 °C for 2 hours to finally obtained nanosheets/polyurethane elastomer composite fiber samples.

Characterizations
For atomic force microscope (AFM; AFM5000II, HITACHI) observation of the nanosheets, nanosheet colloid diluted to 0.001 wt% was dropped and dried on a mica substrate. Polarized optical microscope (POM; OLYMUPS BX51) with crossed polarizers and a wave plate (530 nm) was used to observed the nanosheet colloid and the prepolymer solution enclosed in a cell having a thickness of 1 mm. The composite fibers were also observed with the same device. Small-angle X-ray scattering (SAXS) was performed using Rigaku NANOPIX equipped with CCD-type two-dimensional detector. For the SAXS observation. The nanosheet colloid and the prepolymer solution were enclosed in a glass capillary having a thickness of 0.01 mm and an optical path length of 2 mm, while the composite fiber was measured without a capillary. The field emission scanning electron microscope (SEM) observation and
energy dispersive X-ray analysis (EDS) were performed on JEOL JSM-7100F with acceleration voltage of 1 and 10 kV, respectively. The thermogravimetric-differential thermal analysis (TG-DTA) of the composite fiber was measured with Rigaku TG8120 with the temperature increasing rate of 2 ºC min\(^{-1}\). The tensile test of the composite polymer was measured with Shimadzu EZ-L at a tensile speed of 100 mm/min.

Results and discussion

Nanosheets were completely exfoliated in the DMF/water mixture (8:2) and formed a LC phase even in the presence of the prepolymer. In the AFM image (Figure S2), many nanosheets with the thickness of 1 nm are observed and no stacked nanosheets or aggregates were found, confirming complete exfoliation into single layers. Based on the AFM images, the average particle size of the nanosheets was evaluated as around 2.5 µm. In the POM observation (Figure S3a), aggregated particles were not observed, while the permanent birefringence and optical textures were observed, indicating that the nanosheets form LC phase that occurs only when the degree of
exfoliation is very high. Even after the addition of prepolymer, the good dispersion and the liquid crystal phase of the nanosheets were maintained (Figure S3b). In contrast, no birefringence was observed in the prepolymer solution without nanosheets (Figure S3c).

As shown in Figure 2A, long fibers of the composite gel and composite elastomer were obtained continuously. The synthesized composite gel fiber (left image of Figure 2A) was transparent and tough enough to be held with a tweezer, while it turned white and turbid after evaporation of the solvent (right image of Figure 2A). The change in the sample appearance by solvent evaporation is explained by the formation of macroscopic wrinkles on the fiber surface as well as the formation of sub-micrometer scale heterogeneous domain of polyurethane/fluorohectorite intercalation compounds as described later.

In the POM images of the composite fibers (right images in Figure 2B), blue and yellow interference colors were observed when the long axis direction of the fiber is parallel and perpendicular to the wave plate, respectively. No aggregated particles were observed. This indicates that the nanosheets maintained a well-dispersed state and the superstructures of the original LC phase without aggregation even after embedded in polyurethane and that the nanosheets are oriented along the long axis of the fiber. To further characterize the structure, the cross section of the fibers was observed by POM (left images of Figure 2B). According to this observation, the nanosheets are oriented along the outer surface of the fiber. In the sample with 10 wt% of nanosheets, several domains with different orientational directions were formed inside the fiber.

SEM observations of the composite elastomer fiber further confirm that the nanosheets are well-dispersed in the polymer.
matrix without aggregation with the alignment flat along the fiber surface. In the cross-sectional SEM image (Fig. S4a-c), rough surface with thin streaks of several μm length are observed. The corresponding EDS mapping image (Fig. S4e,f) shows that Si due to nanosheets and C due to polymer are uniformly distributed without any distinct texture, confirming that the nanosheets are well-dispersed in the polymer matrix without aggregation. The side surface of the composite fiber (Fig. S4d) is covered with platy object with the size of several μm. In contrast, in the case of elastomer without the nanosheets (Fig. S5), flatter cross-section and side surface are observed.

SAXS results (Figure 2C) also revealed that the nanosheets maintained ideal dispersion and orientation in the obtained composite fiber, whereas they partly formed intercalation compounds with the polymer chains when nanosheet concentration is high. In the nanosheets/polyurethane composites (Figure 2C, b-d) as well as LC colloid (Figure 2C, e), anisotropic 2D SAXS pattern was observed and the anisotropy increased with increasing nanosheet concentration in contrast with the pristine polyurethane fiber without the nanosheets (Figure 2C, a) that show isotropic scattering. Note that the scattering due to nanosheets are much stronger than the polymers so that the scattering pattern of the composites gives information of the nanosheet superstructure but not of the
polymers. These results suggest that the degree of orientation of the nanosheets increases as the concentration increases. In the $I(q)$ vs $q$ scattering profiles, broad peaks were found in the wide-angle side for the samples with 5 wt% and 10 wt% of nanosheets (Figure 3d and e). From the peak position ($q = 4.6 \text{ nm}^{-1}$), the $d$ value of the nanosheet is calculated to be 1.35 nm according to the relationship of $d = 2n / q$. This value is slightly larger than the reported value (1.23 nm) for Na-fluorohectorite.\(^{45}\) The gallery height between the nanosheet is calculated as 0.37 nm by subtracting the thickness of the nanosheet (0.98 nm). Since the thickness of the polyurethane chain is estimated as 0.2 ~ 0.3 nm, it is considered that the polyurethane chains are intercalated between the nanosheets. Furthermore, the slope of the profiles (Figure 2C, b-e) in the range of $0.1 < q < 1$ was -2, that is ascribed to the form factor of exfoliated nanosheets. Thus, the most of the nanosheets keeps good dispersed state without aggregation even when compounded in polyurethane.

Considering the above results, the schematic structures are deduced. The nanosheets in nematic order with a weak positional order are macroscopically aligned along the long axis of the fiber and maintain fully-exfoliated state. While they are mostly dispersed as single layers at low concentrations (Figure 2D), part of nanosheets form layered compounds intercalating polyurethane chains at higher nanosheet concentrations (Figure 2E).

The composite elastomer showed improved thermal stability as characterized by TG-DTA (Figure 3A-B). The pristine polyurethane without nanosheets showed two-step weight loss characterized by the two DTG peaks at around 300 ºC and 460 ºC accompanied by exothermal DTA peaks. In the present system, that is a network polymer crosslinked with $n$-functional crosslinker, one PEG chain ideally has two terminal groups and $2/n$ crosslinker molecules. Thus, the weight ratio of PEG chain to the total polymer weight, $w_{\text{PEG}}$, is calculated as:

$$w_{\text{PEG}} = \frac{M_{\text{PEG}}}{M_{\text{PEG}} + 2M_{\text{Mr}} + 2/(2n)M_{\text{Mr}_2}},$$

where $M_{\text{PEG}}$, $M_{\text{Mr}}$, and $M_{\text{Mr}_2}$ are the molecular weight of the PEG chain (1000), terminal group (196), and crosslinker (146), respectively. With $n = 4$, $w_{\text{PEG}}$ is calculated as 68% and this value is roughly corresponding to the weight loss at the first DTG peak (82%). Thus, DTG peaks at 300 ºC and 460 ºC are ascribed to combustion of PEG and other part of the polymer network, respectively. In the nanosheets/polyurethane nanocomposites, the new DTG peak appeared at the intermediate temperature (360-390 ºC), replacing the original peak at 300 ºC. This new peak can be ascribed to combustion of PEG moiety interacting with the nanosheets because the DTA peak as well as the DTG peak shifted to higher temperature as the nanosheet concentration increased. Thus, it is probable that the presence of the nanosheets in the polyurethane matrix is effective to increase the combustion temperature due to heat absorption by the nanosheets as well as lowering of polymer chain motion through nanosheet-polymer interactions. Meanwhile, the residue weight at 900 ºC corresponds to the weight of nanosheet in the present composite elastomer. The value increased with the loading amount of nanosheet: 0.0, 0.2, 2.7, and 7.1 wt% for the samples loaded with 0, 1, 5 and 10 wt%. The slight difference between the measured value and the loaded amount is in the range of measurement error (±3 wt%), while it is also possible that a part of loaded nanosheet escaped into the solution phase during the crosslinking process.

Due to the regulated structure and good dispersion of the nanosheets, the present nanocomposite elastomers showed outstanding mechanical property as revealed by tensile tests (Figure 3D). Pristine polyurethane fiber showed the elastic modulus of 0.0053 MPa and the stress-strain (S-S) curve typical to rubber materials,\(^{46}\) while it was broken at the stress of 1.6 MPa and the strain of 542%. With 1 wt% of the nanosheets, the elastic modulus, breaking stress, and breaking strain increased to 0.018 MPa, 4.1 MPa, and 519%, respectively. As the nanosheet concentration increased to 5 wt%, an elastic modulus of increased to 0.14 MPa, while the breaking stress was 9.3 MPa and the breaking strain was almost unchanged (548%). With 10 wt% of the nanosheets, the S-S curve shows yielding point at the strain of 8.4%, followed by stress relaxation. The elastic modulus and breaking stress were largely increased to 0.69 MPa and 5.2 MPa, respectively, while the breaking strain was kept similar to other cases (520%). Thus, it is confirmed that the elastic modulus increases as the nanosheet concentration increases, while the breaking stress showed the maximum at nanosheet concentration of 5 wt%.

Compared with previously reported clay/polymer nanocomposite materials, the above-mentioned mechanical reinforcement in the present system is outstanding. In the present system, increase of the breaking stress and elastic modulus reaches up to 5.9- and 26.8-fold, respectively. In addition, this mechanical improvement was achieved without decrease of breaking strain. In contrast, in usual polymer/clay composites, elastic modulus increases with the increase of clay loading whereas breaking strain and breaking stress significantly decreases. This means that the material becomes harder but more brittle.\(^{41}\) In some good cases of nanocomposite elastomers,\(^{4, 47-49}\) breaking strain only slightly decreases or even increases; however, as shown in Figure 3E, the factor of increase of breaking stress is only around 2 or lower that is much smaller than the present system.

The mechanical reinforcement in the present nanocomposite elastomer is explained by weaker and stronger physical crosslinks between the polyurethane chains and the nanosheets. Due to the lack of chemically modifiable group such as -OH on the surface of the clay mineral nanosheets, the formation of covalent chemical bond is not plausible. Because the reinforcement is by physical crosslinks, not by covalent bonds, the crosslinks can slide and form again and again, avoiding reduction of breaking strain. The weaker crosslink is due to hydrogen bonds between negatively charged -OH on the surface of the clay mineral nanosheets. Due to the lack of chemically modifiable group such as -OH on the surface of the clay mineral nanosheets, the formation of covalent chemical bond is not plausible. Because the reinforcement is by physical crosslinks, between negatively charged nanosheets and polar polyurethane chains.\(^{49}\) (Figure 3F). Although the interaction is weak, very large surface area of the single layer nanosheets and the interactions at multiple points on the polymer chain and nanosheet surface make the physical crosslinks very effective. The mechanical strength improvement at lower nanosheet loading is mainly explained by this model. The stronger one is due to the formation of intercalation compound in which polyurethane chains are sandwiched.
between nanosheets (Figure 3G). It is considered that the steep increase of the tensile stress in the low strain region (Figure 3D) of the sample with 10 wt% nanosheets is due to the breaking of this stronger physical crosslink. After these strong physical crosslinks are mostly broken at the yielding point, the reinforcement by the weaker physical crosslink only works. Further, the reinforcement by these physical crosslinks is maximized by the macroscopic ordering of the nanosheets. If the nanosheets plane were perpendicular to the stretching direction, that is the long axis of the fiber, the polymer chains are disturbed by the nanosheets so that the reinforcement effect should have been reduced.

Conclusions

The single-layer nanosheets that are forming LC phase with highly regulated superstructures were successfully compositized with the polyurethane elastomer by the newly developed in-situ polymerization technique for the first time. The LC nanosheets/polyurethane composite fibers showed superior thermal and mechanical properties due to good exfoliation and the regulated superstructure of the nanosheets originated form the LC phase. Since the present nanocomposite elastomer is synthesized by simple contact of the two solutions, production of thin film or small spherical particles as well as fibers would be possible. For their superior properties as the elastomer, wide range of industrial applications for medical materials, smart fabrics, flexible electronics, and dielectric elastomer-based power generation device are expected.

Conflicts of interest

There are no conflicts to declare.

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