Design of Chemically Recyclable Nanocellulose Chiral Liquid Crystal Photonic Elastomer Vitrimer and its Mechanosensitive Colour-changing Materials

Jinlong Zhang,[a,*] Weiguo Li,[b] and Qinglin Wu [c,*]

The development of nanocellulose (CNCs) chiral liquid crystal photonic elastomeric vitrimer materials is promising for achieving needed reduction in carbon emissions (elastomer material recycling) and developing novel photonic functional materials. The primary questions discussed are about what is the basic principle of chiral liquid crystal and photonic property of CNCs, how to design vitrimer elastomer materials, and what is the general approach to designing CNC chiral liquid crystal photonic elastomer vitrimer and mechanosensitive colour-changing materials.

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Contact information: a: School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287, USA; b: College of Aerospace Engineering, Chongqing University, Chongqing, 400044, China; c: School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, LA, 70803, USA;

Corresponding authors: jzhan620@asu.edu; QWu@agcenter.lsu.edu

What is the basic principle of unique chiral liquid crystal photonic property of nanocellulose?

The liquid crystal property in cellulose crystallites was discovered by Marchessault in 1959 (Marchessault *et al.* 1959), and the chiral nematic liquid crystal phase structure in cellulose nanocrystal (CNC) suspension under a given concentration between 3 and 7 wt% has been further confirmed. Interestingly, the well-preserved chiral helical structure of CNCs can be observed in its dry film *via* the evaporation induced or vacuum assisted self-assembly methods. For the hierarchically helical structure of CNCs, it consists of superimposing planar layers. Within each layer, it consists of rod-like CNCs arranged in a given twisting angle and parallel-alignment. The helical pitch (P) can be defined as the length for a complete rotation of the planar layer in 360^o. The resulted dry films show the miraculous photonic property attributed to the reflective lights from the photonic film surface. As the lights shine on the CNC film surface, the reflective lights follow Bragg diffraction resulted from the refractive index difference between layers, which can be determined *via* the following formula,

$$\lambda = n_{\mathrm{ave}} P \sin\theta \tag{1}$$

where n_{ave}, θ, and λ represent the average of the refractive index of helicoidal structure, the angle of incidence, and the wavelength of reflective light, respectively. Therefore, reflective wavelength can be tailored by helicoidal pitch, thereby achieving colour change in resulted films. However, how to control different parameters in terms of CNC source and extraction method, its concentration, aspect ratio, shape and surface charges to obtain desired helical pitch and structural colour in CNC photonic films still needs to be extensively studied. The helicoidal pitch can also be tuned by different physical and chemical modification of CNCs to achieve selective absorption ability in different wavelengths of the resulting CNC photonic films. Brittleness and susceptibility to redissolution in water is another issue of CNC photonic films. Using cross-linked elastomer materials to lock CNC chiral liquid crystal structure makes it possible to impart resulted photonic film with both enhanced flexibility property, water resistance, and reversible structural colour variation. This is because the pitch variation induced by the mechanical stimuli contributes to the wavelength shift of structural color. However, the structural colour of CNC photonic materials in its long-term service can be unavoidably destroyed by the external force, which possibly results in the reduction or loss of its function. It follows that disposal of these waste elastomer materials are also a challenging issue. Therefore, the design of CNC chiral photonic elastomer materials with chemically recyclable and reprocessible functions is highly needed.

How to design elastomer vitrimer materials?

The development of environmentally friendly, chemically recyclable, and mechanical durable cross-linked elastomer materials is an important and urgent issue. One promising strategy is to introduce dynamic covalent bonds into a cross-linked elastomer network structure to impart its recycling and durable ability, as the dynamic covalent bond enables its reversible construction and destruction. A new concept called "vitrimer," with excellent mechanical durability and repeated recycling property, was put forth from the French professor Lebler in 2011 (Montarnal *et al.* 2011). Thus, the study of elastomer vitrimer materials provides a novel approach for the design of CNC chiral photonic elastomer materials with chemically recyclable, reprocessible, and mechanically durable performance. The design of elastomer vitrimer materials primarily involves two steps. The first step is to confirm conditions in dynamic bond exchange reactions. Namely, the small molecule model compound is usually employed for demonstration of bond exchange reactions. Such reactions are confirmed *via* spectroscopic methods, such as liquid chromatography-mass spectrometry and *in situ* proton nuclear magnetic resonance. The second step is to integrate dynamic bonds into the cross-linked networks of elastomers and then confirm the vitrimer features of cross-linked network *via* swelling tests, stress relaxation, recycling, and reshaping experiments. The features of elastomer vitrimer material mean: 1) integrity of cross-linking points, confirming that elastomer network can be only swelled but cannot be dissolved; 2) reutilization multiple times, which means that the cross-linked network elastomer material can be recycled and reprocessed; 3) glass-like feature, indicating that viscosity of cross-linked network elastomer materials even drops followed by the regulation of viscosity-temperature Arrhenius equation; and 4) malleability and reshaping property. Namely, bond exchange reactions take place in the cross-linked elastomer system under external stimuli (*e.g.*, temperature and light). This releases stress and transforms its original shape into a new shape, which is a typical feature of dynamic covalent network elastomer materials. For instance, a new type of polyurethan-urea elastomer vitrimer with a mild processing temperature and excellent recycling performance has been designed *via* the two step approaches (Zhang *et al.* 2020).

What is the general approach to design CNC chiral photonic elastomeric vitrimer materials and mechanosensitive colour-changing materials?

To improve the service lifetime of CNC photonic elastomer vitrimer materials and reduce its end-life products on the environmental impact, it is highly demanding to design repeatedly recyclable CNC photonic vitrimer materials to replace the conventional covalent cross-linked network elastomers, *e.g.*, silicone rubber, polyurethane, vinyl elastomer, and elastomer-like ethylene-vinyl acetate soft plastics. Thus, one straight-forward question is about how to design the CNC photonic elastomer vitrimer materials. Its direct synthetic approach is by forming homogeneous solution of CNCs, prepolymers (monomers or oligomers), and cross-linkers, followed by the step growth or chain growth polymerization. However, miscibility among hydrophilic CNCs, hydrophobic monomers (oligomers), and cross-linkers needs to be considered. A solvent exchange procedure for CNCs from hydrophilic aqueous solutions to acetone followed by good solvents of prepolymers and cross-linkers makes it possible to tailor its miscibility. The follow-up question is what the general approach should be in design of CNC photonic elastomer vitrimer functional materials. The general strategy in terms of prepolymer design is a priority for development of photonic elastomer vitrimer materials. For one strategy, the prepolymer is directly synthesized from target monomers *via* versatile polymerization methods (*e.g.*, step growth polymerization, controlled radical polymerization, or ring-opening polymerization). For instance, a renewable resource lignin derived prepolymer structure is prepared *via* ring-opening polymerization followed by cross-linking with dynamic covalent crosslinkers; the resulting vitrimer material maintained excellent mechanical property after recycling a few times (Snyder *et al.* 2020). Post-modification as another strategy. This can be done by directly transforming commercial rubber elastomer [*e.g.*, poly(styrene-butadiene-styrene) and ethylene-vinyl acetate] or oligomers into prepolymers, *e.g.*, C-H functionalization. For instance, a well-designed dynamic covalent cross-linker participating in C-H functionalization reaction achieved recycling of almost all commercial plastics or elastomers, such as polyethylene terephthalate, polystyrene, and polypropylene, which open a new door for the design of vitrimer elastomer prepolymers (Clarke *et al.* 2023). In addition to post-modification directly, some elastomer materials have active sites on their side chains, thereby enabling them to be replaced with functional groups for the prepolymer design indirectly, *e.g.*, replacing the polyacrylate side chain with functionally reactive sites.

Inspired from the skin colour variation of chameleons upon shrinking and stretching of their muscles, which can be attributed to helical variation of three-dimensional photonic structure inside of cells, the design of CNC photonic elastomer vitrimer mechanosensitive colour changing material is an emerging field. Given unique optical properties of CNC chiral liquid crystal photonic elastomers, its nematic liquid crystal structure is very sensitive to the external mechanical stimuli. Upon stretching or compressing mechanical response, its space structure of chiral liquid crystals enables it to be reversibly tunable, thereby producing different structural colours. Bioinspired hydroxypropyl cellulose chiral photonic hydrogel soft material has been shown to display diverse structural colors upon external stretching and pressure stimuli, but the structure durability of hydrogel substrates in photonic functional materials is still a big issue, resulted from the water evaporation compared to the elastomer substrates (Zhang *et al.* 2020). The PS@SiO_2 photonic polyurethane elastomer vitrimer with excellent mechanically induced structural colour variation and durability and the disulfide bond also imparted photonic elastomer vitrimer with self-healing performance, while its recycling performance is still unknown (Guan *et al.* 2023). In addition, angle dependence of structural colors of CNC photonic elastomer vitrimers is also an issue. Inspired by butterfly wings, the advanced manufacturing technique is promising, *e.g.*, extrusion based digital light or direct ink writing 3D printing.

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