



# High-performance carrageenan film based on carrageenan intercalated layered double hydroxide with enhanced properties: Fire safety, thermal stability and barrier effect



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## ABSTRACT

Bio-based polysaccharides show potentials to substitute petroleum-based polymers. Herein,  $\kappa$ -carrageenan intercalated layered double hydroxide (LDH-Carra) was prepared to impart  $\kappa$ -carrageenan film with improved thermal stability, fire safety and gas barrier. Results showed that the temperature at 5% mass loss of carrageenan film with 3 wt% LDH-Carra (Carra/LDH-Carra) was increased by 55 °C. Carra/LDH-Carra presented 42.9% and 52.0% reduction of peak heat release rate and total heat release respectively with higher LOI and self-extinguishment in horizontal burning test. In parallel, LDH-Carra endowed Carra film with 18% and 200% increment of tensile strength and tensile modulus. Barrier test revealed approximately 50% reduction of oxygen permeability without deterioration of transparency after addition of LDH-Carra. The property enhancement was relevant to the exfoliated dispersion of LDH nanosheets in Carra film. Prospectively, polysaccharides intercalated LDH serves a feasible approach to multifunctional enhancement of polymers.

## 1. Introduction

The rapid depletion of petroleum pushes the search for respective substitutes. Currently, the natural bio-based polymers offer an alternative to partially replace the traditional polymers in certain fields [1]. Carrageenan, as a galactin extracted from red algae (Rhodophyta), represents an important texturing component in food industry [2]. The carrageenan is utilized as food package due to broad availability and good mechanical property. In order to widen applications of carrageenan film in high-demanding conditions with preferential focus on fire safety, gas barrier and mechanical property, the feasible approaches were adopted including nanocomposites and polymer blending [3,4]. Nanocomposites were given more attentions due to the enhancement of integral properties [5]. In terms of fire safety, nanocomposites with 2-D nanosheets demonstrated better fire safety than 1-D and 0-D nanofillers due to the easier formation of protective carbonaceous layers during combustion [6]. Recent reports showed that the rational functionalization of 2-D nanosheets (e.g., graphene [7,8] and boron nitride [9]) facilitated the formation of higher-quality chars with enhanced barrier

effect. Meanwhile, 2-D nanosheets imparted relatively higher gas barrier due to the longer “walking path” of gas [10]. It was reported that the surface reaction of nanosheets contributed to higher gas barrier due to the better dispersion from strengthened interfacial adhesion [11]. The strengthened interface favored stress transfer between polymer matrix and nanosheets.

Layered double hydroxide (LDH) is comprised of positively charged metal hydroxide nanosheets and negatively charged anions. LDH has been broadly utilized as nanofillers. In terms of LDH-based polymer nanocomposites, the exfoliation of LDH nanosheets played a critical effect in fire safety and gas barrier. In order to attain the target of exfoliation, the intercalation modification of LDH was performed using various intercalators [12]. Herein,  $\kappa$ -carrageenan intercalated LDH was employed in fabricating  $\kappa$ -carrageenan film. The main considerations included: 1)  $\kappa$ -carrageenan intercalated LDH was prone to be swollen in  $\kappa$ -carrageenan aqueous solution, which promoted the exfoliation due to the strong interaction between matrix and LDH sheets 2) Exfoliated LDH nanosheets acted as the excellent barrier of heat and volatiles for fire safety 3) Exfoliated nanosheets in carrageenan film increased the

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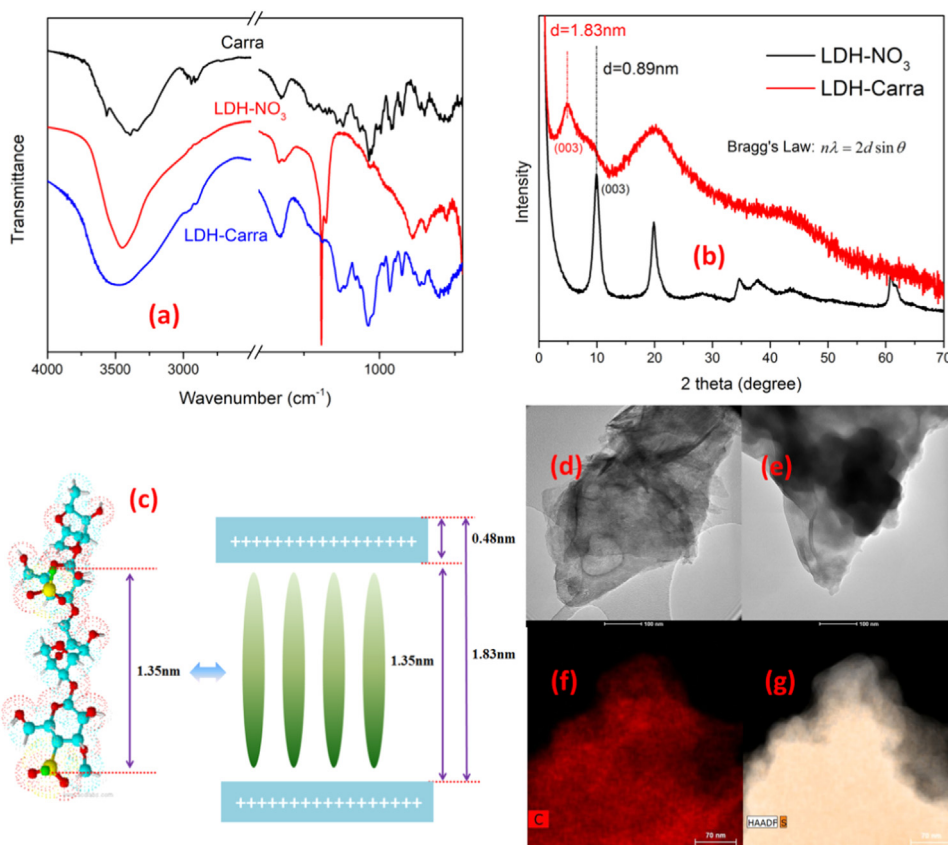


Fig. 1. (a) FTIR spectra of Carra, LDH-NO<sub>3</sub> and LDH-Carra; (b) XRD spectra of LDH-NO<sub>3</sub> and LDH-Carra; (c) intercalated structure of LDH-Carra; (d) TEM images of LDH-NO<sub>3</sub> and (e) LDH-Carra; (f) C mapping image of LDH-Carra; (g) combination of S-mapping and high angle angular dark field (HAADF).

gas diffusion distance for gas barrier 4) Exfoliated nanosheets acted as the physical crosslinking points to favor the mechanical property.

Aiming to impart carrageenan film with enhanced thermal stability, fire safety and gas barrier, the carrageenan intercalated magnesium aluminum layered double hydroxide (LDH-Carra) was prepared with urea-assisted co-precipitation route. Subsequently, LDH-Carra filling carrageenan nanocomposite film (Carra/LDH-Carra) was fabricated using solution casting. The successful exfoliation of LDH nanosheets in Carra film was verified. The multifunctional enhancement including thermal stability, fire safety, oxygen barrier and tensile behavior were analyzed.

## 2. Results and discussion

As was shown in Fig. 1(a), carrageenan (denoted as Carra) showed peaks at 2944 cm<sup>-1</sup>, 1283 cm<sup>-1</sup> (1241 cm<sup>-1</sup>), 1070 cm<sup>-1</sup> (917 cm<sup>-1</sup>) and 844 cm<sup>-1</sup>, which were respectively attributed to C-H, C-C-C backbone, C-O in 3,6-anhydro-L-galactose and C-O-SO<sub>3</sub> [13]. In parallel, NO<sub>3</sub><sup>-</sup> intercalated LDH (LDH-NO<sub>3</sub>) exhibited peak at 776 cm<sup>-1</sup> assigned to metal-oxygen bond. LDH-Carra combined the peaks from Carra (C-H, C-C-C backbone, C-O in 3,6-anhydro-L-galactose and C-O-SO<sub>3</sub>) and metal hydroxide nanosheets of LDH-NO<sub>3</sub> (metal-oxygen bond). Interestingly, the peaks of C-C-C backbones and C-O in 3,6-anhydro-L-galactose revealed wavenumber shifts compared with Carra, which was due to the configuration alternation of Carra after confinement in LDH gallery.

XRD patterns (Fig. 1(b)) of LDH-NO<sub>3</sub> and LDH-Carra illustrated notable peaks, which evidenced the presence of ordered structure. In detail, LDH-NO<sub>3</sub> showed peaks at 9.9° (003) and 19.8° (006) with respective basal spacings of 0.89 nm and 0.45 nm. In terms of LDH-Carra, the (003) and (006) crystal faces shifted to the lower reflection angles of 4.9° and 8.1° with basal spacing of 1.83 nm and 1.09 nm. The enlargement of the gallery spacing illuminated the successful intercalation

of carrageenan molecules into LDH gallery. In order to clarify the arrangement of carrageenan in LDH gallery, the distance of the oxygen atoms in neighboring sulfonate groups was calculated as 1.35 nm according to ChemSketch Software (Fig. 1(c)). The calculated value was properly attributed to the distance of neighboring nanosheets (ca.1.35 nm) from XRD measurement. In combination of the above analysis, it was inferred that carrageenan molecules possibly aligned in the vertical position.

Aiming to visualize LDH-Carra structure, TEM and EDS were carried out in Fig. 1. Compared with LDH-NO<sub>3</sub> (Fig. S1(a) and Fig. 1(d)), LDH-Carra demonstrated the similar lamellar structure with micrometer-scale lateral size (Fig. S1(b) and Fig. 1(e)). EDS analysis (Fig. 1(f) and (g)) disclosed the homogeneously distributed C and S elements on LDH nanosheets, which further evidenced the successful intercalation of carrageenan molecules in LDH gallery.

ATR-FTIR (Fig. 2(a)) of Carra, Carra/LDH-NO<sub>3</sub> and Carra/LDH-Carra did not show obvious difference with the exception of peak at 1109 cm<sup>-1</sup> (C-OH in -CH<sub>2</sub>OH in the inset structure). Visibly, the peak (1109 cm<sup>-1</sup>) of C-OH in neat carrageenan was shifted to 1122 cm<sup>-1</sup> in Carra/LDH-Carra, which indicated the intensive interaction of matrix and LDH nanosheets. In contrast, the shift was absent in Carra/LDH-NO<sub>3</sub>. It indirectly manifested the electrostatic interaction between carrageenan matrix molecules and LDH-Carra nanosheets due to the alteration of bond motion.

The exfoliation of LDH nanosheets in Carra film was studied using XRD and TEM. In Fig. 2(b), Carra/LDH-NO<sub>3</sub> remained (003) peak of pristine LDH-NO<sub>3</sub> without shift of reflection angle. Comparatively, (003) peak of LDH-Carra did not persist in Carra/LDH-Carra. In Fig. 2(c) and Fig. S2(a), LDH-Carra nanosheets exhibited more uniform dispersion in carrageenan matrix with smaller LDH area (black part) compared with that of LDH-NO<sub>3</sub>. The further TEM images in Fig. 2(d) and Fig. S2(b, c) presented a significantly enlarged spacing (about

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