

Supplementary Materials:

Structural Nanocomposite Fabrication from Self-Assembled Choline Chloride Modified Kaolinite into Poly(methylmethacrylate)

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Purification of Kaolinite

The raw clay was first mixed with distilled water and the suspension was passed through 325 mesh (micron) screen to make it free from larger size sand and silica. The overflow was discarded and underflow was filtered. The filtrate was discarded and the cake was dried in the oven at 100°C for 8 h. The dried cake was ground with a mortar and pestle.

Modification of Kaolinite by Choline Chloride

In the present study, choline chloride modified kaolinite was prepared by adsorption onto the negatively charged kaolinite with protonated choline chloride. 0.95 gm pure kaolinite was suspended in 25 mL distilled water in a beaker and it was stirred at room temperature. Then 2.5 mL choline chloride was gradually dropped into the kaolinite suspension where the ratio (w/w) of kaolinite and choline chloride solution was maintained at 1:1. The resulting suspension was stirred with a hot plate with magnetic stirrer for 4 h. After 4 h, the resulting suspension was agitated by a sonicator for 50 min. Then the suspension was sprayed drop wise through a dropper at a constant rate into the 20 mL co-solvent of aqueous sodium hydroxide (15%) and ethanol (95%) (4:1) to maintain a pH of about 10. Then the composite was separated by filtration. The formed composite bead was washed with deionized water until the solution became neutral. The composite bead was dried in the oven at 60°C for 10 h. This way the modification of kaolinite by choline chloride was done.

Fabrication of PMMA/ CCMK Nanocomposite Films

A schematic illustration for the fabrication of composite film from choline chloride modified kaolinite (CCMK) and PMMA is shown in Figure S1 and before and after drying of the films from different ratios of CCMK/kaolinite is also given in Figure S2.

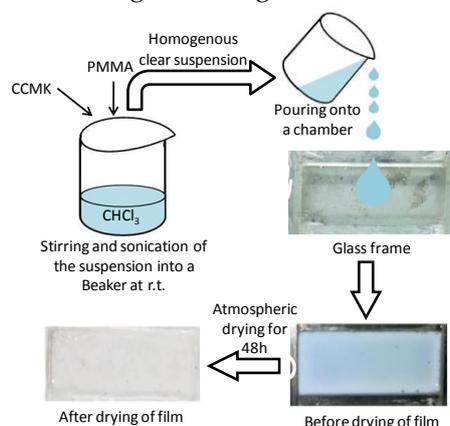


Figure S1. Illustration of fabrication technique of nanocomposite films.

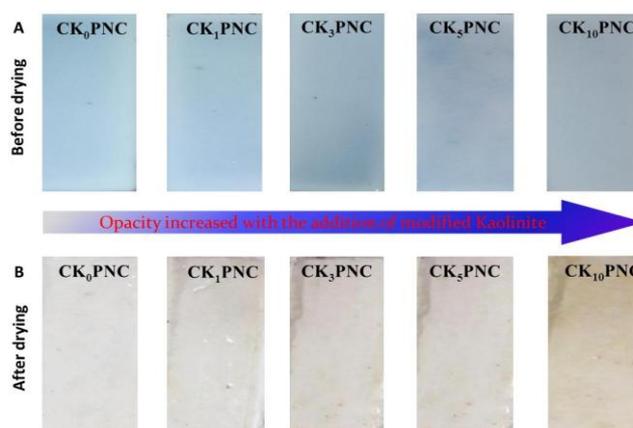


Figure S2. Camera images of nanocomposite films before (A) and after drying (B).

Characterization of Choline Chloride Coated Kaolinite

ATR-IR spectral analysis: The choline chloride coated kaolinite particles were characterized using ATR-IR spectroscopy and XRD spectral analysis. The Figure S3 shows ATR-IR traces of kaolinite, choline chloride and choline chloride coated kaolinite core-shell nanoparticles. In Figure S3a, it is evident that kaolinite showed characteristic absorption bands at 3689.83 and 3620.39 cm^{-1} . The peak 3689.83 cm^{-1} was assigned to the stretching vibration of inner-surface hydroxyl group positioned above the aluminum layer. The peak at 3620.39 cm^{-1} was assigned to the stretching vibration of the inner hydroxyl group which was positioned below the aluminum layer and extended towards the vacant octahedral hole of kaolinite [1–3].

The peaks at 2924.04 and 1620 cm^{-1} were assigned to the H–O–H stretching and bending vibrations, due to adsorbed water [4]. The band at 1114.86 cm^{-1} was assigned to Si–O symmetric stretching; 1029.99 and 1006.84 cm^{-1} for in plane Si–O–Si anti-symmetric stretching vibrations; 912.33 cm^{-1} for Al–OH bending vibrations; and 786.96 cm^{-1} for Si–O (quartz) [5,6].

The spectrum in the Figure S3c showed the absorption band at 3305.99 cm^{-1} which was assigned to the O–H stretching overlapped with C–N stretching of choline chloride. The absorption bands at 2931 cm^{-1} and 2862.30 cm^{-1} were assigned to asymmetric and symmetric stretching modes of CH_2 in the methylene chain respectively. The absorption bands at 1379.10 cm^{-1} , 1311.59 cm^{-1} , 1255.66 cm^{-1} were assigned to asymmetric and symmetric vibrations for CH_3 –N deformation modes in choline chloride. The absorption bands at 1132.21 cm^{-1} were assigned to stretching vibration C–O for the alcoholic group of choline chloride. The absorption band at 1637.55 cm^{-1} was assigned to the H–O–H stretching vibration due to adsorbed water. The peak at 1525.69 cm^{-1} was assigned to scissoring vibration to the C–H in choline chloride [7]. The spectrum of nanocomposite showed the combination of characteristic absorption bands due to kaolinite and choline chloride.

From the Figure S3b, it is obviously seen that the absorption peaks of kaolinite and choline chloride were present in the nanocomposites. The identical peaks of kaolinite at around 3690 and the broad peak for –OH of choline chloride at around 3300 cm^{-1} were recorded for the composites.

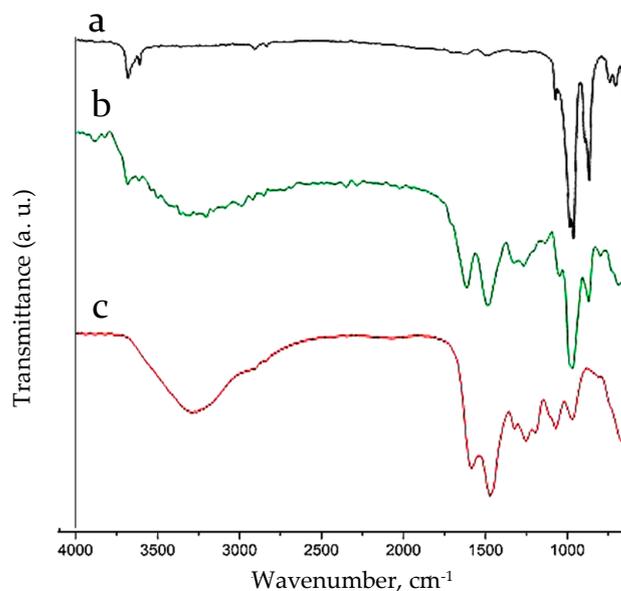


Figure S3. spectra of kaolinite (a), choline chloride modified kaolinite nanocomposites (b), and choline chloride (c).

The peaks at 1369 cm^{-1} , 1303 cm^{-1} and 1176 cm^{-1} were assigned to symmetric vibrations for $\text{CH}_3\text{-N}$ deformation modes in choline chloride. It was clear that absorption bands at 1379 cm^{-1} , 1311 cm^{-1} , 1255 cm^{-1} for symmetric vibrations for $\text{CH}_3\text{-N}$ deformation modes in choline chloride were shifted to 1369 cm^{-1} , 1303.88 cm^{-1} , and 1176 cm^{-1} respectively in composite. This shifted occurred due to the electrostatic interaction between protonated amine groups of choline chloride and negatively charged sites of kaolinite. Therefore, it confirmed the formation of a kaolinite–choline chloride composite or choline chloride modified kaolinite (CCMK).

XRD Analysis

One of the most important methods for studying the interlayer spacing is X-ray diffraction (XRD). The clay mineral peak displacement at 2θ is a suitable criterion to evaluate the interlayer spacing; specifically a decrease in the 2θ angle indicates an increase in interlayer spacing. The XRD pattern of pure kaolinite is shown in Figure S4. The kaolinite showed well defined reflections at 2θ around 12.356° ($d = 7.1565\text{ \AA}$), 24.916° ($d = 3.5707\text{ \AA}$) and 26.682° ($d = 3.3382\text{ \AA}$). These peaks correspond to the reflections from (001), which are typical characteristic peaks of kaolinite.

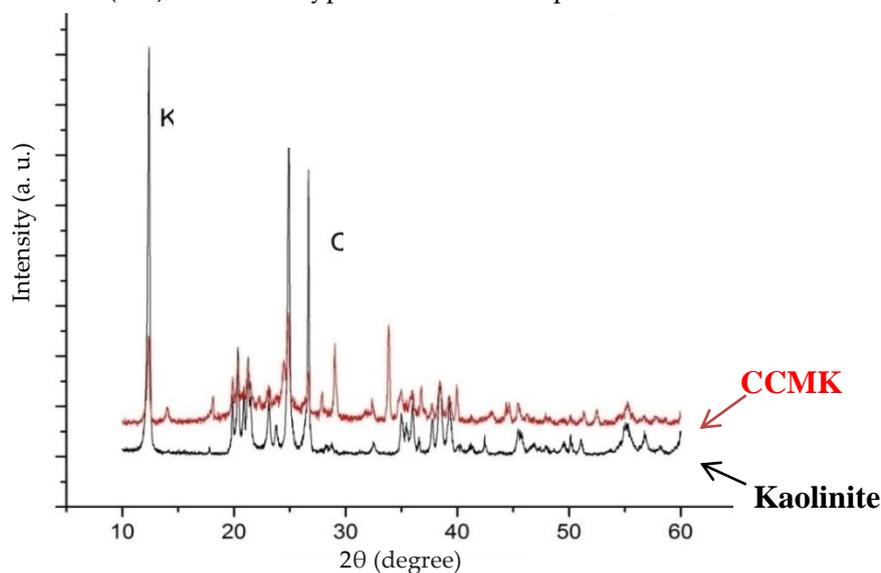


Figure S4. Patterns of kaolinite and choline chloride modified kaolinite.

The d-spacing of pure kaolinite and choline chloride modified kaolinite (CCMK) samples, as shown in Figure S4, were almost unchanged at the corresponding angle (2θ), but the intensity of coated kaolinite was dramatically reduced due to its soft behavior. This indicates that there was no intercalation of choline chloride into kaolinite, but that the electrostatic interaction played key role for modification only. There were some new peaks observed in the modified kaolinite; those could be due to the interfacial opening of kaolinite crystallites.

Stress–Strain Relationship

This Figure S5, reveals the relationship between engineering stress and strain of the pure PMMA film and the films fabricated from composites. Here we found the elasticity and plasticity for each of the curves. The vertical lines from the tangents of each curve indicate the elastic behavior of the film where the films deform reversibly. The tangent line from the origin for the CK₅PNC film is longer than that of CK₀PNC, confirming its elasticity enhancement.

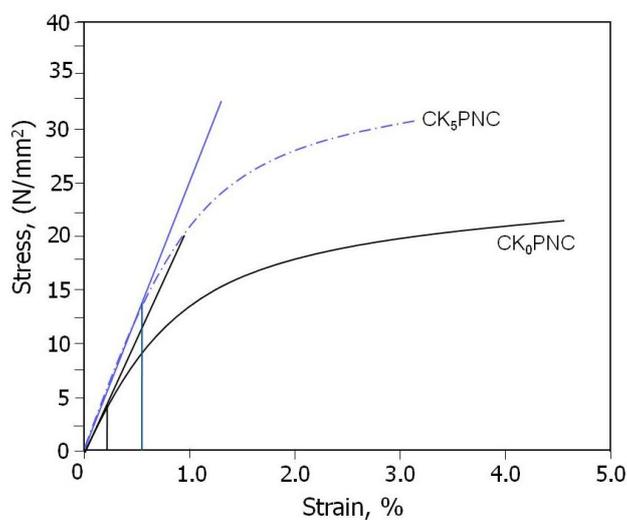


Figure S5. Stress–strain relationship.

SEM Morphological Studies of Kaolinite and Choline Chloride Modified Kaolinite

Figure S6A,B show images of kaolinite and choline chloride modified kaolinite respectively. It is quite clear from the image of kaolinite that there were sharp edges and grains, denoted by arrows, due to its crystalline structures. When the kaolinite was modified with choline chloride, it lost sharpness and was covered by the soft, polymeric thin film, and displayed swollen wool like structures.

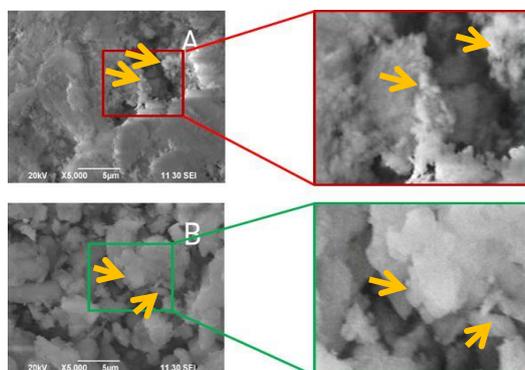


Figure S6. Electron microscope (SEM) images of kaolinite (A), modified kaolinite (B), respectively.

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