층상무기물과 나노에멀젼을 이용한 층상자기조합

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Layer-by-layer using layered inorganic material and nano-emulsion

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Clay minerals have attracted great interest in the field of organic/inorganic hybrid materials because of small particle size and intercalation properties, which exhibit unexpected synergistic effect from two components [1-2]. The study of organic/inorganic hybrid colloids has provided important fundamental insights into some new functional materials [3]. Currently, the microstructure of colloidal particles and their aggregation under various fields are attracting more and more attention [4]. These promising hybrids have presented remarkable properties due to their unique combination of the good process ability of organic compounds with the stability of the inorganic component. Montmorillonite (MMT) clay is an important class of lamellar inorganic compounds, which has lower density and better antisedimentation properties, whose interlayer spacing can be modified by cation exchange. Therefore, MMT has been widely used for preparing the organic-inorganic hybrid materials.

It was reported that drug incorporation into clays takes place by adsorption, both by intercalation into the clay structure within the interlayer spacing (by replacing thewatermolecules), and on the surface. The most important interactions taking place between the two components of the hybrid system are ionic [5]. The ionic exchange process may take place by mixing ion exchangers with ionic drugs in a solution. In biological fluids, “counterions” can displace the drug from the substrate and deliver it into the body, while the exchanger is being eliminated [6]. It was confirmed that basic molecules bonded strongly to montmorillonite, while complexes with anionic and non-ionic drugs exhibited much weaker interaction bonds and more rapid desorption kinetics. Bonding via adsorption and ion-dipole interactions of acidic and non-ionized molecules with MMT were previously reported [7]. The crucial effect of the ionization degree of drug molecules on their interaction with smectites was then corroborated using dioctahedral smectite as the adsorbent substrate.

Tyrosinase is an enzyme with a copper center that is widely expressed in many life forms and is mainly involved in the formation of pigments, such as melanin and other polyphenolic compounds. The biosynthesis of melanin in melanocytes might be affected by cellular tyrosinase activity [8]. In addition, increased production and accumulation of melanin leads to many

hyperpigmentation diseases such as melasma, solar lentigines, and post-inflammatory hyperpigmentation. Therefore, investigation into depigmentation mechanisms and the clinical aspects of skin whitening agents is very important [9]. Various compounds have demonstrated inhibitory effects on melanogenesis through inhibition of the enzymatic activity of tyrosinase [10]. For example, arbutina has potent skin-whitening agents that are capable of suppressing the function of tyrosinase. Arbutin was first shown to exhibit greater inhibition of tyrosinase activity and to be safer than hydroquinone. Moreover, arbutin demonstrated fast and persistent skin lightening effects both in an animal model and in a human trial [11].

Within this framework, the present article describes the preparation and characterization of a new type of emulsion−MMT hybrids.

Experimental

Arbutin was first pre-dissolved in propylene glycol, and all formulations were prepared by premixing the hydrophilic and hydrophobic phases. After premixing, the hydrophilic and hydrophobic components were emulsified via a high-shear mixer using an agitation.

Emulsion intercalated into MMT(EM-MMT) prepared with 5-30%wt EM-MMT ratios under an optimum condition such as soaking time, temperature and pH value.

Results and Discussion

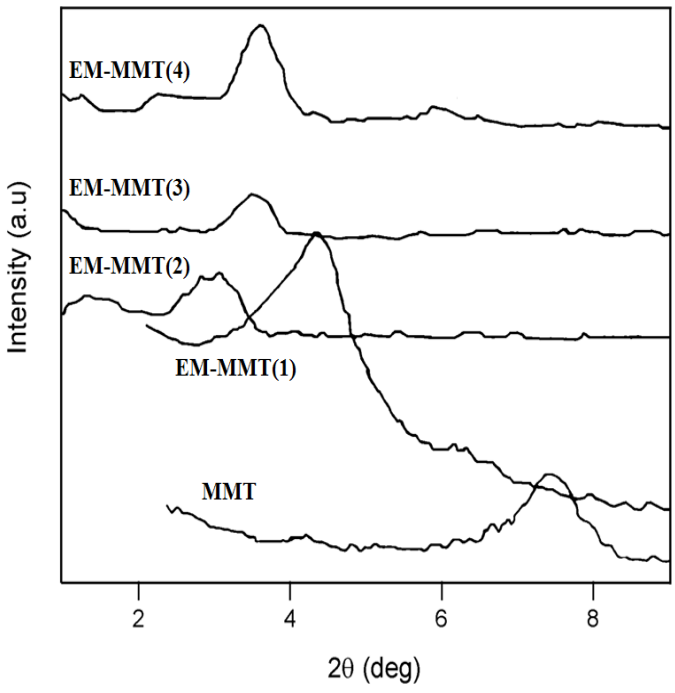
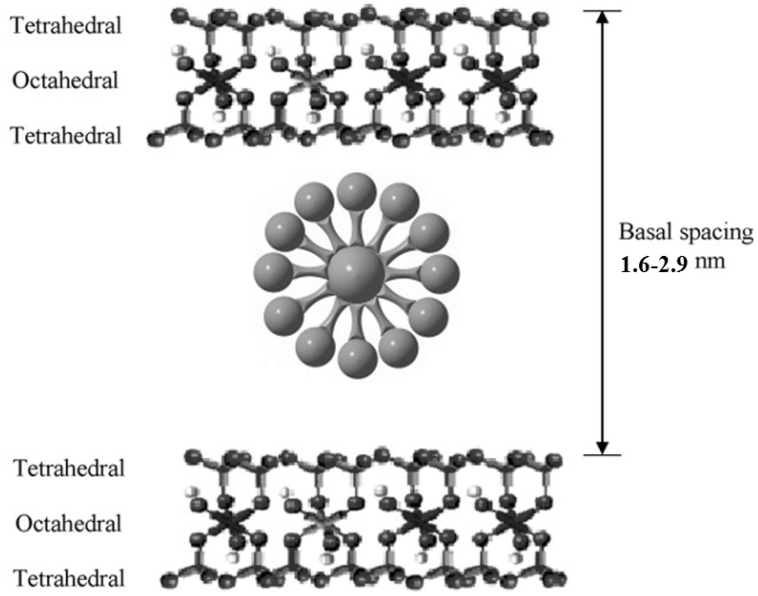


Fig. 1. XRD patterns of MMT and EM-MMT hybrid materials.

Fig. 1 (scheme 1) shows a series of XRD patterns for emulsions intercalated into MMT from 5 to 30wt%. Pristine Na-MMT shows a characteristic diffraction peak at 7.94^{o} corresponding to the d-spacing of 1.15nm on Bragg equation. For EM-MMT(1), the diffraction peak is observed at 4.46^{o} corresponding to the d-spacing of 1.94nm. The results show that organic emulsion has been intercalated between MMT layers. Besides, the diffraction peak of EM-MMT(2), EM-MMT(3) and EM-MMT(4) were around 3~3.4^{o} corresponding to the d-spacing of 2.94 to 2.60nm indicating further enlarged interlayer space. This increase could probably originate from the intercalation of emulsion molecules within the galleries of the hydrophilic silicate.



Scheme 1. Possible structural arrangement of EM-MMT.

The montmorillonite spectrum shows characteristic peaks at 3620cm^{-1} for O-H stretching, at 3439cm^{-1} for H-O-H hydrogen-bonded water, and at 1647cm^{-1} for H-O-H deformation. The 1647cm^{-1} vibration weakens upon the formation of EM-MMT hybrid, indicating the release of water from the MMT surface upon emulsion adsorption. The three characteristic bands of emulsion between 2800 and 3000cm^{-1} and the ones around 1480cm^{-1} correspond to CH_2 or CH_3 stretching and bending vibrations, respectively. These vibrations were not altered upon emulsion adsorption, validating that these group are not involved in the interactions with MMT.

In FT-IR spectrum, specific bands of C=O group can be found at 1748, 1706 and 1657cm^{-1} from lactone, carbamate and piridone, respectively. The stretching vibration of aromatic C–C and the bending vibration of C=N appear both at 1515cm^{-1}. The bands at ~1620cm^{-1} and 1234cm^{-1} correspond to aromatic C=C and to C–CH_3 stretching vibrations. Esther C–O has a stretching vibration peak at 1150cm^{-1} and the broad band found at 3431cm^{-1} is due to associated OH groups.

The TGA curves of MMT showed two distinct steps at <150^{o}C due to free water evaporation and at 550-700^{o}C due to the release of structural water. In case of EM-MMT, the mass loss at 300-500^{o}C is due to decomposition of intercalated emulsion and at 550−700^{o}C due to structural hydroxyl groups. Decomposition at around 300^{o}C in EM-MMT confirmed the adsorption of emulsion on MMT.

Conclusion

In summary, we have shown the intercalation of EM into MMT and in vitro release of EM from EM-MMT hybrid. The intercalation of EM into MMT was rapid process and equilibrium was attained within 1h. The maximum amount of EM intercalated into MMT is 30wt% MMT within 1h at pH 6.7 and 30^{o}C. Intercalation of EM into MMT depends on the pH of the interaction medium. XRD patterns of hybrid material shows an increase in the d-spacing, conforming the intercalation of EM into the interlayer of MMT. TG-DTA of EM-MMT shows a sharp weight loss at about 200^{o}C due to decomposition of exchanged EM.

These results indicate that MMT can be used as the sustained release carrier of EM in cosmetic administration.

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