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SHORT COMMUNICATION

Synthesis and electrorheological response of nano-sized laponite stabilized poly(methyl methacrylate) spheres

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Abstract Poly(methyl methacrylate) (PMMA) nanospheres were fabricated via surfactant-free Pickering emulsion polymerization, in which hydrophilic laponite clay was used to stabilize the emulsions of methyl methacrylate dispersed in distilled water. These synthesized PMMA nanoparticles, of which the surface is compactly wrapped by laponite clay, are observed, as confirmed by scanning electron microscopy and transmission electron microscope images. Fourier-transform infrared spectra and thermogravimetry analysis confirm the chemical composition, thermal property, and mass percent of the laponite located on the surface of PMMA particles. Finally, laponite-wrapped nano-sized PMMA spheres were adopted as an electrorheological material. By using an optical microscope, the chain-like structure was observed when an external electric field was applied. In addition, the ER performance was also examined via a rotational rheometer equipped with a high voltage generator.

Keywords Poly(methyl methacrylate) · Laponite · Emulsion · Electrorheological fluid · Nanocomposite

Introduction

Polymer/inorganic nanocomposites have gained great attention due to their outstanding synergetic properties in optical, mechanical, electrical, catalytic, and rheological aspects [1]. Specifically, polymer/clay nanocomposite particles exhibit superior electrical property due to intrinsic electrical property of the clay, thus they have been adopted as electrorheological (ER) materials [2–8]. Here, the ER fluids are a kind of smart materials, whose rheological properties are accurately controllable through the applied electric field [9–11]. This ER behavior is said to stem from the polarization of the particles, resulting in the structural change. The most common type of ER fluids is a colloidal suspension of solid dielectric or conducting particles dispersed in an insulating fluid, showing a Newtonian fluid behavior without an applied electric field [12, 13]. However, when an electric field is applied to the ER fluid, the particles are polarized and aligned along the direction of an electric field resulting in an increased shear viscosity and its rheological behavior can be expressed by a Bingham fluid equation with a yield stress [14, 15] along with their magnetically analogous magnetorheological suspensions under external magnetic fields [16–18].

Recently, employing emulsion polymerization technique to obtain homogeneous and uniform polymer/clay nanocomposite particles has become prevailing [19, 20]. Various polymeric systems, such as polystyrene encapsulated by laponite via miniemulsion polymerization, polyacrylamide latex particles stabilized by organically modified clay via inverse emulsion, and Poly(methyl methacrylate) (PMMA)/SiO_2 particles via surfactant-free emulsion have been introduced [21, 22]. Especially, when particles instead of surfactant are used to stabilize an emulsion system, it is named as 'Pickering emulsion', in which the solid particles (<100 nm) are in general strongly adsorbed at the interface of aqueous and organic liquids and then produce both oil/water (O/W) and W/O emulsions with significant stability [23, 24].

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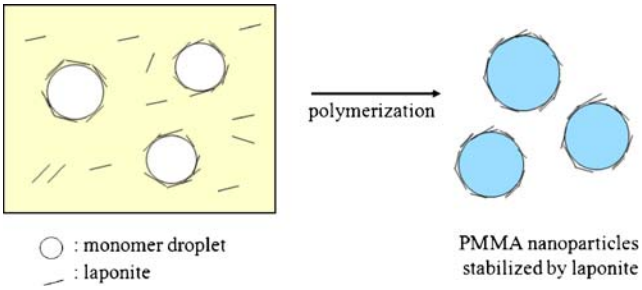

Fig. 1 Scheme of mechanism of Pickering emulsion polymerization

Therefore, in this study, based on the above Pickering emulsion approach, we adopted disc-shaped laponite clay as a stabilizer to synthesize nano-scaled PMMA nanospheres. The laponite particles are synthetic clay with a lateral diameter of ~20 and 1 nm in thickness [23] composed of two tetrahedral silica sheets and a central octahedral magnesia sheet. The silicon and magnesium atoms are balanced by 20 oxygen atoms and four hydroxyl groups, with empirical formula of $0.7Na^+[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$ and cationic exchange capacity about 50~55 mmol/100 g. A negative surface charge density is about 0.014 e^-/Å. Due to the more uniform and smaller dimension of laponite than those of other clay species, such as montmorillonite and bentonite, laponite has attracted more and more attention in stabilizing emulsion systems.

Experimental

Sample preparation

PMMA nanoparticles were synthesized via Pickering emulsion polymerization by using laponite plates as a stabilizer. Methylmethacrylate (MMA) (Daejung, Korea), *n*-heptane (Daejung, Korea), and 2, 2′-azobis(2-methylpropionamidine) dihydrochloride (AIBA) (Aldrich, USA) were used as monomer, organic phase, and cationic water-soluble initiator, respectively. Small amount of laponite (Laporte Industries, UK) was dispersed in distilled water under sonication until a clear aqueous solution was obtained. At the same time, the MMA was added in *n*-heptane. Pickering emulsion system was prepared by mixing the MMA solution in *n*-heptane into the laponite dispersion under sonication for 3 min and then AIBA was added. Once the monomer was initiated by AIBA, the color of the reacting mixture changed from turbid to milky white. After polymerization at 60ºC for 12 h, the final product was centrifuged with both distilled water and methanol to remove excess initiator, monomer, and free laponite plates, and then dried in vacuum oven at 65ºC for 2 days. Finally, the product was dispersed in silicone oil and sonicated for 1 h to obtain a uniform ER fluid at 10 vol.%.

Characterization

Morphology of the synthesized PMMA nanoparticles stabilized by laponite was observed by both SEM (S-4300, Hitachi, Japan) and transmission electron microscope (TEM) (Philips CM200). Thermal property and mass composition were also checked via TGA (TA instrument Q50, USA) under nitrogen environment with a heating rate of 20°C/min. In order to apply for an ER fluid, electrical conductivity of the synthesized composite nanoparticles was measured though a ring-probe method by using a resistivity meter (Hiresta UP, Mitsubishi Petrochemical) at room temperature. In order to observe the formed chain-like structure of ER fluid, an optical microscope (OM) (Olympus BX51, USA) equipped with a DC high voltage generator was used. The ER behavior was measured by a rotational rheometer (Physica, MC-120, Germany) equipped with a Couette type cylinder geometry (Z4-DIN) and a high voltage generator.

Results and discussion

The mechanism of Pickering emulsion polymerization has been reported and the scheme of Pickering emulsion polymerization in presence of laponite is illustrated in Fig. 1. Laponite dispersed in di-water is adsorbed onto the surface of the MMA monomer droplet to stable the O/W system. After adding initiator (AIBN), the color of reaction mixture immediately changes from turbid to milky white. Thus, polymerization takes place via the stabilization of laponite at the interface.

Figure 2 is a SEM image of the surface morphology for PMMA nanoparticles stabilized by laponite plate, in which the spherical nano-scaled PMMA/laponite particles possess irregular rough surface with a diameter ranging from 200 to 400 nm. These PMMA nanoparticles are considered to possess

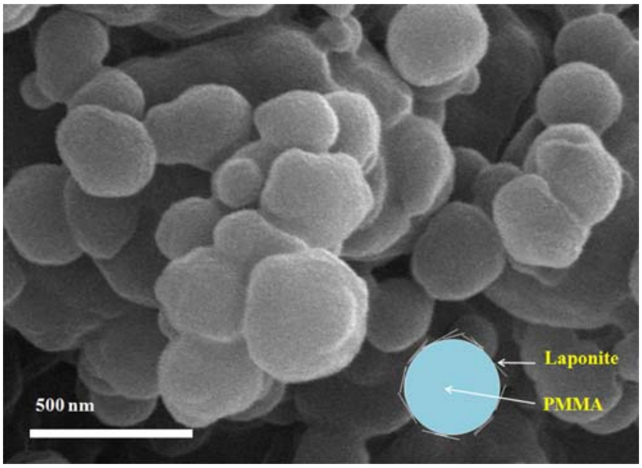

Fig. 2 SEM image of PMMA nanoparticle stabilized by laponite

core-shell structure as shown in the inset of the proposed scheme. The irregular rough surface of PMMA nanoparticles is attributed to the loading of laponite platelets which act as a stabilizer in this Pickering emulsion polymerization.

Cross-sectional view of the core-shell structure for synthesized PMMA nanoparticles was characterized via TEM view as given in Fig. 3. The grey spherical regions and dark strips are considered as PMMA cores and laponite plates, respectively. It is observed that the grey cores are surrounded by numerous densely stacked laponite plates, consequently proving the role of laponite plates as a stabilizer. Finally, the particle size observed via the TEM image is found to be similar with that from the SEM image.

In order to confirm chemical structures of the synthesized PMMA/laponite, Fourier-transform infrared spectra (FT-IR) spectra of synthesized PMMA, laponite, and PMMA/laponite nanoparticles are presented in Fig. 4. Characteristic peaks of the PMMA appeared at about 2,997 cm^{-1} and 2,955 cm^{-1} are attributed to C–H stretching vibration. A sharp peak at 1,730 cm^{-1} represents to C=O stretching vibration, while the peaks located at 1,448 cm^{-1} and 1,147 cm^{-1} are attributed to the C–H bending and C–C bond. These peaks indicate that the PMMA nanoparticles are successfully synthesized. From the FT-IR spectrum of laponite, the peaks detected at about 1,015 cm^{-1} and 470 cm^{-1} are classified to Si–O band and Si–O bending vibrations, and the peak found at 660 cm^{-1} indicates Mg–O bond. Furthermore, FT-IR spectra of the PMMA/laponite nanoparticles exhibit typical chemical characteristics of both PMMA and laponite.

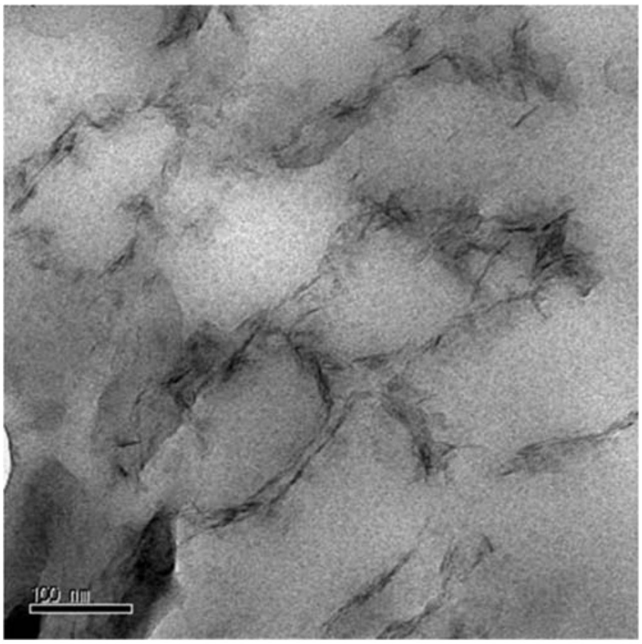

Fig. 3 TEM image of PMMA nanoparticle stabilized by laponite

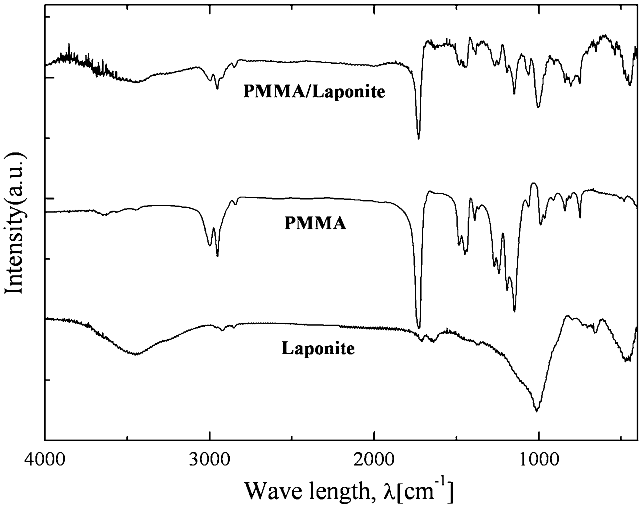

Fig. 4 FT-IR spectra of laponite, PMMA, and laponite stabilized PMMA nanoparticle

Figure 5 represents thermal property as well as thermal decomposition of the samples studied. The weight loss of laponite is found to be about 7% when the temperature increases from 100 and 700ºC which is in agreement with the amount of sodium salt ion or impurities, in which pure PMMA particles are found to decompose step by step as a function of temperature. The weight loss of PMMA particles at around 150ºC is attributed to the oligomer or the short chains with low molecular weight, while thermal decomposition of long chain of PMMA starts at 300ºC. When the temperature exceeds 450ºC, PMMA is considered to be completely thermally degraded. On the other hand, the PMMA stabilized by laponite plates shows about 90 wt.% weight loss at the temperature range of 150 to 450ºC, corresponding to the degradation of organic

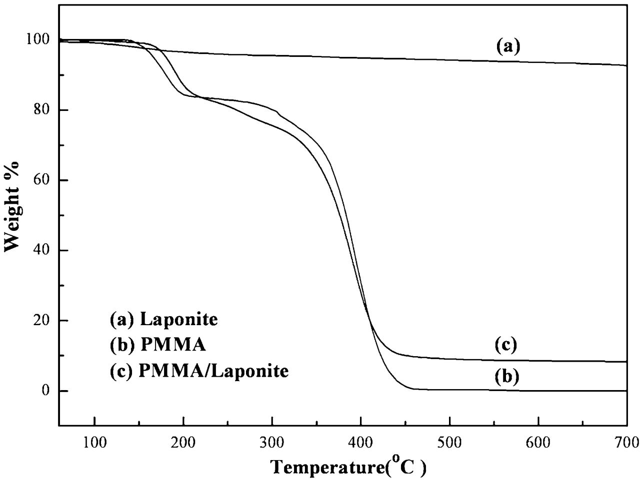

Fig. 5 TGA spectrum of (*a*) laponite, (*b*) PMMA, and (*c*) laponite stabilized PMMA nanoparticle

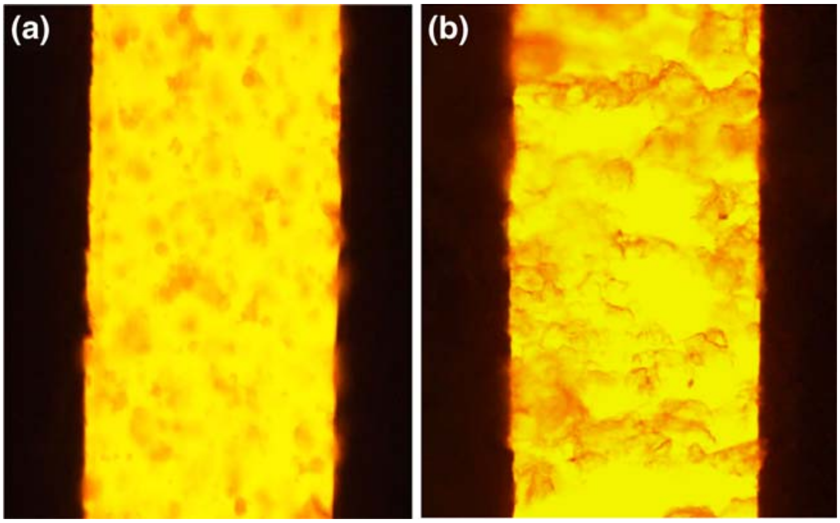

Fig. 6 OM images of the ER fluid based on PMMA nanoparticles stabilized by laponite without an electric field (*left*) and with an electric field (*right*)

PMMA; however, considering the 7% weight of pure at high temperature, the total organic laponite content of PMMA/laponite is regarded as about 3%. Without regarding the weight loss caused by washing or drying, we consider that this result well coincided with the initial reactant loading.

Finally, before taking ER characterization, the DC conductivity of PMMA and PMMA nanoparticle stabilized by laponite are 1.31×10^{-13} and 4.34×10^{-10}S/cm, respectively. This increase in the electrical conductivity is attributed to the successful loading of the charged laponite plates.

The ER fluid was prepared by dispersing laponite stabilized PMMA nanoparticles in silicone oil and the changes in microstructure for this ER fluid were then observed by using an optical microscope under a DC applied electric field using a DC high voltage source [25]. The gap between two parallel electrodes was fixed at ca. 400 μm. A DC electric field was maintained for 3 min at 25°C to obtain an equilibrium columnar structure. Figure 6 represents that the laponite stabilized PMMA nanoparticles-based ER fluid shows a typical ER fibril structure. When the electric field is absent, the particles were found randomly dispersed in silicone oil, thus leading to a liquid-like state. Nevertheless, when the electric field is present, particles start to move and form chains or columns with the adjacent particles. At last, particles align along the direction of the applied electric field forming strong fibrillated structure. Normally, this phenomenon for the ER fluids forming the fibril chains under external applied electric field takes place within milliseconds and the structure remain as long as the field is applied [26].

Furthermore, ER behavior of shear stress vs. shear rate was investigated using a rotational rheometer equipped with a high voltage generator. Figure 7 represents the flow curve obtained from the controlled shear rate test for synthesized PMMA/laponite nanoparticles under different electric field strengths. Without applying electric field, the PMMA/laponite nanoparticles suspended ER fluid behaves similarly to a Newtonian fluid, in which the shear stress increases linearly proportional to the shear rate. However, when exposed to the applied electric fields, the shear stress curves initially exhibit wide plateau region at low shear rate which can be interpreted in the term of polarizability of the suspending particles [25, 27, 28]. The dispersed particles are being polarized and form chain-like structures similar as shown in OM photo, and thus span the electrodes due to the attractive forces generated between dipoles. This fibril structure will resist and reformed, finally the flow starts till the shear rate approaches a critical value, in which the fibril structure was destroyed and experienced a yield point consequently [29, 30].

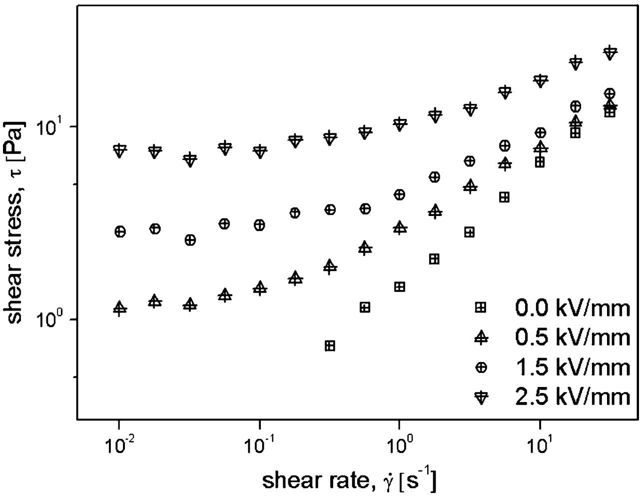

Fig. 7 Shear stress curves for fabricated PMMA/laponite nanoparticles-based ER fluid

Conclusions

Nano-sized PMMA particles were synthesized in the presence of laponite instead of surfactant via an emulsion polymerization, in which nano-sized laponite were located at the interface of aqueous phase and monomer phase, enabling the formation of Pickering emulsion. About 3 wt.% of laponite plates were confirmed via SEM/TEM image and TGA data in the PMMA nanocomposite. It was found that the ER fluid based on PMMA nanoparticle stabilized by laponite exhibits typical ER behaviors.

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References

1. Bandyopadhyay J, Ray SS, Bousmina M (2007) J Ind Eng Chem 13:614
2. Kim DH, Kim YD (2007) J Ind Eng Chem 13:879
3. Fang FF, Choi HJ, Joo J (2008) J Nanosci Nanotech 8:1559
4. Choi HJ, Jhon MS (2009) Soft Matter. doi:10.1039:B818368F
5. Cheng YC, Guo JJ, Xu GJ, Cui P, Liu XH, Liu FH, Wu JH (2008) Colloid Polym Sci 286:1493
6. Stenicka M, Pavlinek V, Saha P, Blinova NV, Stejskal J, Quadrat O (2008) Colloid Polym Sci 286:1403
7. Kim YD, Kim JH (2008) Colloid Polym Sci 286:631
8. Yuan L, Liang QZ, Xie JQ, He SB (2007) Colloid Polym Sci 285:781
9. Yin J, Zhao XP, Xia X, Xiang L, Qiao Y (2008) Polymer 49:4413
10. Choi HJ, Hong CH, Jhon MS (2007) Int J Mod Phys B 21:4974
11. Lim JY, Kim ST, Park BJ, Choi HJ (2007) Int J Mod Phys B 21:5003
12. Trlica J, Saha P, Quadrat O, Stejskal J (2000) J Phys D Appl Phys 33:1773
13. Choi HJ, Kim JW, Joo J, Kim BH (2001) Synth Met 121:1325
14. Zhao XP, Yin JB (2002) Chem Mater 14:2258
15. Hiamtup P, Sirivat A, Jamieson AM (2006) J Colloid Interface Sci 295:270
16. Cho MS, Lim ST, Jang IB, Choi HJ, Jhon MS (2004) IEEE Trans Magn 40:3036
17. Bica I, Choi HJ (2008) Int J Mod Phys B 22:5041
18. Park BJ, Hong MK, Choi HJ (2009) Colloid Polym Sci 287:501
19. Kim JW, Kim SG, Choi HJ, Jhon MS (1999) Macromol Rapid Commun 20:450
20. Kim TH, Jang LW, Lee DC, Choi HJ, Jhon MS (2002) Macromol Rapid Commun 23:191
21. Sun Q, Deng Y, Wang ZL (2004) Macromol Mater Eng 289:288
22. Voorn DJ, Ming W, Vanherk AM (2006) Macromolecules 39:2137
23. Balnois E, Durand-Vidal S, Levitz P (2003) Langmuir 19:6633
24. Wheeler P, Wang J, Mathias L (2006) Chem Mater 18:3937
25. Kim SG, Kim JW, Jang WH, Choi HJ, Jhon MS (2001) Polymer 42:5005
26. Jin HJ, Choi HJ, Yoon SH, Myung SJ, Shim SE (2005) Chem Mater 17:4034
27. Kim SG, Lim JY, Sung JH, Choi HJ, Seo Y (2007) Polymer 48:6622
28. Hong CH, Choi HJ (2007) J Macromol Sci B-Phys 46:683
29. Cho MS, Cho YH, Choi HJ, Jhon MS (2003) Langmuir 19:5875
30. Sim IS, Kim JW, Choi HJ, Kim CA, Jhon MS (2001) Chem Mater 13:1243