

공단량체 종류 및 외부전단응력이 스티렌계 공중합체와 유기화
실리케이트 나노복합재료의 용융 충전삽입에 미치는 영향

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**Effects of comonomers and shear on the melt intercalation of
styrenics/clay nanocomposites**

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Introduction

Organic-inorganic hybrids with the intercalated or exfoliated structure form a class of nanocomposites that has recently received considerable attention as an effective way to overcome the shortcomings of conventional mineral filled composites [1]. They can be classified into three categories according to the degree of dispersion and/or exfoliation of silicates: conventional, intercalated, and exfoliated composites. In exfoliated structure, individual silicate sheets lose their layered geometry and are dispersed in the polymers, resulting in excellent physical properties.

The polymer-layered silicate hybrids have been synthesized in many ways. For commercial production, direct melt intercalation method [2] has received lots of attention due to its commercial potential. To exfoliate the layers on a nano scale using a melt process we must consider the factors such as the interaction between polymers and organosilicates and shear force during melt mixing. In this study, we investigate the effect of comonomers and applied external shear force on the intercalation behavior of the hybrids made of styrenic copolymers and organosilicates.

Experimental

Materials The silicate used in this study was MMT from Southern Clay Products Inc. and was modified with dimethyl benzyl hydrogenated tallow ammonium. Inorganic content of the organosilicate (C10) was 61 wt % and powder XRD analysis gives d_{001} of 1.91 nm. Polystyrene (PS) and styrenic copolymers were used as guest polymers. Acrylonitrile (AN), methylvinylloxazoline (OZ) and acrylic acid (AA) were introduced as polar comonomers. The details of the polymers used are listed in Table 1.

Melt Intercalation Melt intercalation was performed in two ways: without shear and under shear. Shear mixing was performed by a Haake batch mixer with a roller blade at 50 rpm of roller speed. After predetermined mixing time, the resultant hybrid melts were sampled and quenched in liquid nitrogen.

Characterization A MAC Science MXP 18A-HF X-ray diffractometer was used to monitor the change in d spacing of the organosilicates before and after intercalation. $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) was used as X-ray source at a generator voltage of 40kV and current of 100mA. Diffraction angle of 2θ was scanned from 1.5° at a rate of $2^\circ/\text{min}$. FTIR spectroscopy was also used to get information on the interlayer environment from the silicates, which were separated from hybrids by the Soxhlet extraction. It was performed using methylethylketone (MEK) as solvent at 100°C for 12 days. Extracted silicates were dried at 65°C in vacuum for 3 days. C10 was annealed at two temperatures (210°C and 220°C) in a convection oven to investigate the effect of thermal treatment on the interlayer structure. Thermal stability of

C10 and annealed C10 was investigated using a thermogravimetric analyzer (TGA), heating from RT to 600 °C at 10 °C/min under N₂ purge.

Results and Discussion

Effect of applied shear Fig 1 shows XRD patterns for the styrenics/C10 hybrids after melt mixing at 210 °C under the shear of 65 sec⁻¹, which corresponds to the rotor speed of 50 rpm. Irrespective of the type of styrenics new basal reflections, which correspond to the increased gallery height of MMT in the intercalated hybrid, are observed, indicating that all polymers used in this study are successfully intercalated into the interlayer of C10.

However, it is noteworthy that the PS/C10 hybrids show quite different XRD patterns from the others with increasing mixing time. At the early stage of intercalation, two distinct scattering peaks are observed, similar to the other systems. As the mixing time increases, the intensity of the peak at $2\theta = 2.5^\circ$ (*intercalated peak*) decreases and eventually, disappears after 20 min mixing. On the other hand, the second peak observed at higher 2θ (*collapsed peak*) shifts to higher angle, finally to 6° with increasing mixing time. Even longer mixing does not change the position and shape of the peak. Since the shift of peak position to higher angle implies the reduction of the gallery height, the shift is explained by the collapse of interlayer alkyl chains. From the fact that the calculated basal spacings with mono- and bilayers of alkyl chains are 1.40 (corresponding to $2\theta \sim 6.2^\circ$) and 1.88 nm ($2\theta \sim 4.7^\circ$), respectively, the shift to higher angle, shown in Figures 1(a), is due to the collapse of the interlayer alkyl chains from bilayer to monolayer. As shown in Fig 1, within 1 min mixing intercalation of polymer chains into organosilicates layer occurs and the structure formed is very stable even for 30 min mixing. It is expected that the comonomers incorporated impart the specific interaction between silicate surface and polymer chains and thus contributes to enhance the stability of the hybrids through anchoring the chains to the silicate surfaces [3]. However, it is revealed that long mixing time up to 30 min is not effective in preparing exfoliated composites within experimental range.

Analysis of extracted silicates Fig 2 shows the FTIR spectra of silicates extracted from styrenics/C10 hybrids mixed for 30 min. For PS/C10 and SAN/C10, any trace of the polymers is not detected, whereas the characteristic bands of C-H stretching in aromatic rings are observed at 3100 ~ 3000 cm⁻¹ in the spectra from RPS/C10 and RAS/C10. This implies that intercalated PS and SAN chains are solved out of gallery but RPS and RAS chains still reside within interlayer after Soxhlet extraction. Fig 3 shows the XRD patterns of silicates extracted from the hybrids. Silicates from the PS and SAN hybrids show reduced basal spacings compared to C10, while those from RPS and RAS do not show any change in d spacings. The results from XRD and FTIR experiments provide a clear evidence that polymer chains of RPS and RAS be strongly entrapped within the interlayer during intercalation.

Effect of comonomer content The interaction between polymer and organosilicate was controlled by changing the content of acrylic acid unit in SAA. Fig 4 shows the change in XRD patterns with increasing the AA unit under shear. In earlier stage of mixing, only intercalation peaks were observed regardless of AA content. Longer mixing induces different behaviors depending on the content of AA units. For SAA with lower AA content, only collapsed peaks were observed. However, intercalated peaks are also observed in SAA's with higher AA content. From these results, it is suggested that intercalated polymer chains come out of interlayer on annealing when SAA with lower AA content is used as guest polymer, because of its weak interaction with silicate surface, while the higher AA content affords more chance to interact with silicate surface resulting the survival of intercalated polymer chains. The stronger interaction seems to act as gluing force which binds together the neighboring silicate layers [4].

Conclusions

It is investigated how comonomers incorporated into PS chains affect the intercalation of organosilicates during melt mixing. Irrespective of the type of comonomers, the hybrids with intercalated structure are prepared through the a melt mixing, but those with exfoliated structure are not prepared even though long mixing time up to 30 min. The polar comonomers incorporated contribute to impart the interaction between polymer chains and silicate surfaces and thus stabilize the intercalated structure formed. When the interaction between polymers and silicates is not strong (PS hybrids), the interlayer alkyl chains between silicates collapse into from bilayer to monolayer during melt annealing. Although SAN also forms intercalated hybrids with C10, its interaction with silicate was not strong enough to overcome the solvating power of MEK.

References

1. P. C. LeBaron, Z. Wang, T. J. Pinnavaia *Applied Clay Sci* **15**, 11 (1999)
2. M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, A. Okada *Macromolecules* **30**, 6333 (1997)
3. N. Hasekawa, H. Okamoto, M. Kawasumi, A. Usuki *ACS Polym. Mater. Sci. Eng.* **80**, 353 (1999)
4. Y. Lyatskaya, A.C. Balazs *Macromolecules* **31**, 6676 (1998)

Table 1. Physical properties of polymers

code	Source	Composition (wt %)				T_g (°C)	M_w (g/mol)
		ST	AN	OZ	AA		
PS	Cheil Industries	100	-	-	-	108	220 K
SAN	Cheil Industries	75	25	-	-	111	107 K
RPS	Nippon Shokubai	95	-	5	-	105	188 K
RAS	Nippon Shokubai	72	23	5	-	106	49 K
SAA1	Synthesized	98.4	-	-	1.6	103	36 K
SAA6	Synthesized	94.1	-	-	5.9	105	48 K
SAA10	Synthesized	89.8	-	-	11.2	112	42 K
SAA20	Synthesized	80.7	-	-	19.3	119	66 K
SAA30	Synthesized	71.3	-	-	28.7	129	54 K

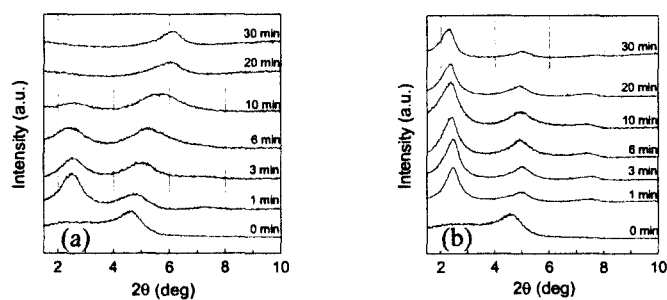


Fig 1. XRD patterns for styrenics/C10 hybrids, prepared at 210 °C using a batch mixer: (a) PS/C10; (b) SAN/C10; (c) RPS/C10; (d) RAS/C10.

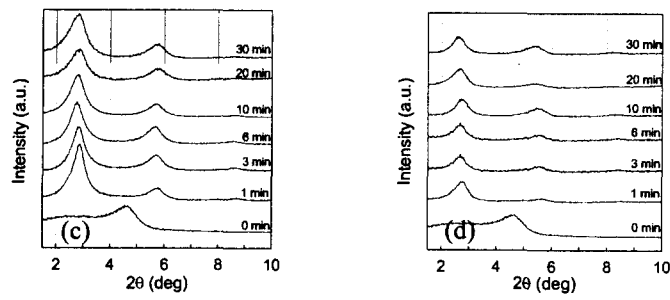


Fig 1. Continued

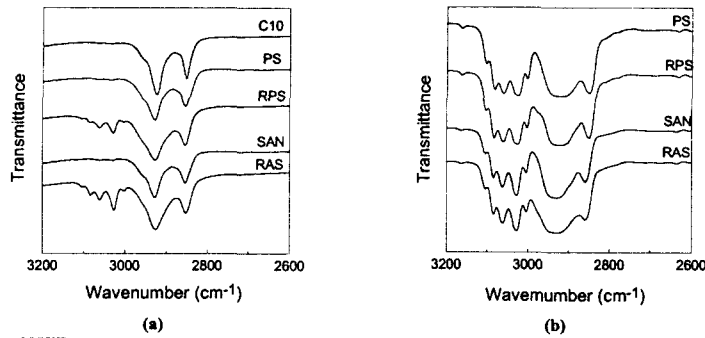


Fig 2. FTIR spectra of (a) extracted silicates and (b) neat polymers.

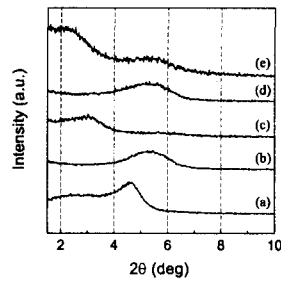


Fig 3. XRD patterns for extracted silicates from (a) C10; (b) PS/C10; (c) SAN/C10; (d) RPS/C10; (e) RAS/C10, respectively.

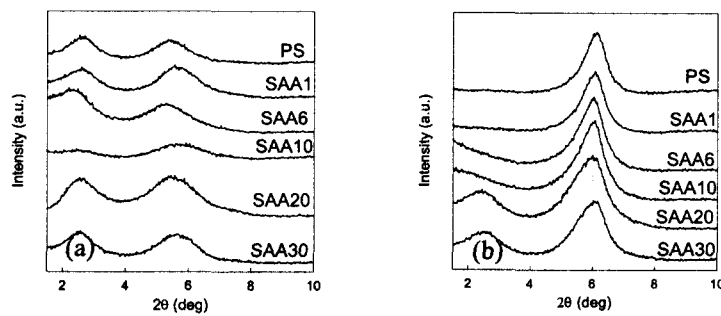


Fig 4. XRD patterns for SAA/C10 hybrids, prepared at 220 °C using a batch mixer (a) 50 rpm/3 min; (b) 50 rpm/3 min + 150 rpm/7 min, respectively.