

충진제의 표면 특성이 고분자의 기계적 성질에 미치는 영향

조 동련, 이 경철
전남대학교 정밀화학과

Effect of Surface Characteristics of Fillers on the Mechanical Properties of Polymers

Dong Lyun Cho, Kyung Cheol Lee
Department of Fine Chemicals and Process Engineering,
Chonnam National University

INTRODUCTION

It is common for polymers to contain foreign material as a filler. The filler may be added for specific purpose or just to reduce the material cost. In this case, however, sacrifice in mechanical properties of the host polymer is often accompanied, especially when the filler is an inorganic material.[1]

The problem is mostly related to the interfacial phenomena such as wetting, dispersion and adhesion. Fillers, especially inorganic fillers, are quite different from host polymers in chemical compositions and structure. Because of this dissimilarity, they have poor compatibility when they are mixed together. Poor compatibility results in poor wetting, poor dispersion and poor adhesion. Poor wetting and poor dispersion cause the agglomeration and nonuniform distribution of the filler particles in the polymer. Poor adhesion causes the formation of weak points along the interfaces between the filler particles and the polymer matrix.

Typical approach to this kind of problem may be the surface modification of fillers to make them compatible with host polymers. The surface modification can be done using a coupling agent such as silane or a surfactant.[2-4] Modification by deposition of an ultrathin film has also been tried using a low temperature plasma process, plasma polymerization.[5-8]

In this study, CaCO_3 powder, which is a common inorganic filler for various polymers, was surface-modified by plasma polymerization. The effects of surface characteristics of CaCO_3 powder on the mechanical properties of polypropylene(PP) were investigated.

EXPERIMENTAL

PP was obtained from Ho-nam petroleum chemicals and Neste Polyeten AB. It has a high melt viscosity ($MI=4.0$) and contains stabilizers. CaCO_3 powders were obtained from Tae Hwa Calcium Co. and Cementa Mineral AB.

The powders were surface-modified by plasma polymerization of propylene in a rotation-type R.F. plasma reactor. The powders were mixed with PP in a Collin twin screw extruder at 220 °C in the final heat zone. 1 mm thick plates were injection molded for the tensile test.

Surface characteristics of CaCO₃ powders before and after plasma polymerization were determined based on ESCA spectra, oil adsorption, and viscosity in water and n-hexane. Mechanical properties of CaCO₃-filled PP were determined by tensile test using Instron.

RESULTS AND DISCUSSION

CaCO₃ powder used in this study was not clean but contaminated with dispersing agents. Figure 1 shows ESCA C_{1s} spectra of CaCO₃ powder surface before and after plasma polymerization. As shown in the figure, there are only 24.8% of CO₃-type carbons(peak at 292 eV) on the surface even before plasma polymerization.

Plasma polymerization of propylene altered the surface characteristics of CaCO₃ powder further to those of hydrocarbons by depositing an ultrathin hydrocarbon film. After plasma polymerization, CO₃-type carbons(at 292 eV) decreased from 24.8% to 11.9%. The reason why CO₃-type carbon peak still appears may be because the powder surface(appeared at 292 eV) is partially covered or film thickness is thinner than the escape depth of photoelectrons(approximately 5-10 nm).

CaCO₃ is a hydrophilic material. However, CaCO₃ powder used in this study showed a little bit lipophilic characteristic, maybe due to the contamination, in the oil adsorption test. When 4 g of the powder was dropped into 6 g of paraffinic oil(n-hexadecane) which is on the top of 6 g of water in a graduated tube, the powder took up 0.48 g of oil while passing through the oil phase to the water phase. If it is highly hydrophilic, not much of oil is expected to be adsorbed on the surface and even the adsorbed oil will be released again after it reaches the water phase. After the modification, the CaCO₃ powder showed highly lipophilic characteristic. 4 g of powder took up 2.12 g of paraffinic oil and some tiny particles failed to pass through the oil phase.

CaCO₃ powder was dispersed in water(30% by volume) and paraffinic oil(8% by volume), respectively, and viscosity was measured in a Bohlin VOR Rheometer at a shear rate from 0.015 to 15/s. Viscosity of paraffinic oil was lower with modified powder than with unmodified powder while viscosity of water was higher with modified powder, as shown in Figure 2. This may be explained by good dispersion in paraffinic oil but agglomeration in water due to lipophilic characteristic of the modified powder.

When CaCO₃ powder(particles larger than 70 μm was sieved) added to PP, large agglomerates were formed with uneven distribution, as shown in Figure 3. This resulted in the embrittlement of PP with a little bit increased modulus but highly decreased strain at break. However, modified powder

showed the good mixing property without formation of large agglomerates. As a result, strain at break could be increased by 15 times with almost the same modulus and yield stress by surface modification when the drawing rate was 5 mm/min. This effect was less pronounced for the powder containing large particles(unsieved). Even in this case, however, stain at break sharply increased as the drawing rate decreased if PP-compound contained modified powder, as shown in Figure 4.

ACKNOWLEDGEMENT

이 연구는 1993년도 전남대학교 학술 연구비에 의해 지원되었으며, 이에 감사드립니다.

REFERENCE

1. D. L. Cho and K. C. Lee, Polymer(Korea), Vol 19, No.5, 578-586(1995).
2. E. P. Plueddmann, "Silane Coupling Agents," Plenum Press, New York, (1982).
3. B. D. Favis, L. P. Blanchard, J. Leonard, and R. E. Prudhomme, J. Appl. Polym. Sci., Vol. 28, 1235-1244(1983).
4. S. H. Morrell, Plastics and Rubber Processing and Applications, Vol. 1 No. 2, 179-186(1981).
5. T. Kobayashi, T. Terada, and S. Ikeda, a paper presented at OCCA Conf.(1989).
6. J. Derce, A. Lodes, L.Lapeik, and J. Blecha, Chem. Zvesti, 38(4), 463(1984).
7. S. Cai, G. Ji, J.Frang, and G. Xue, Die Angewandte Makromolkulare Chemie, 179, 77(1990).
8. H. P. Schreiber and Y. B. Tewari, J. Appl. Polym. Sci., 20, 2663(1976).

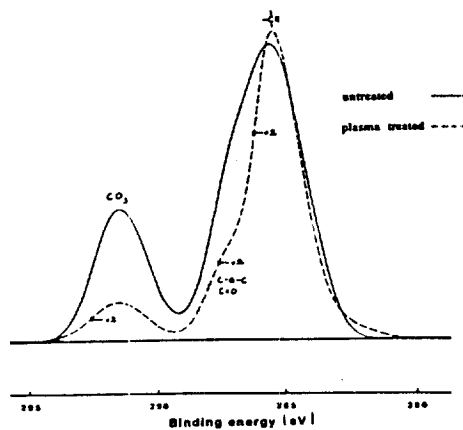


Fig. 1. ESCA C_{1s} spectra of $CaCO_3$ powder surface before and after plasma polymerization of propylene.

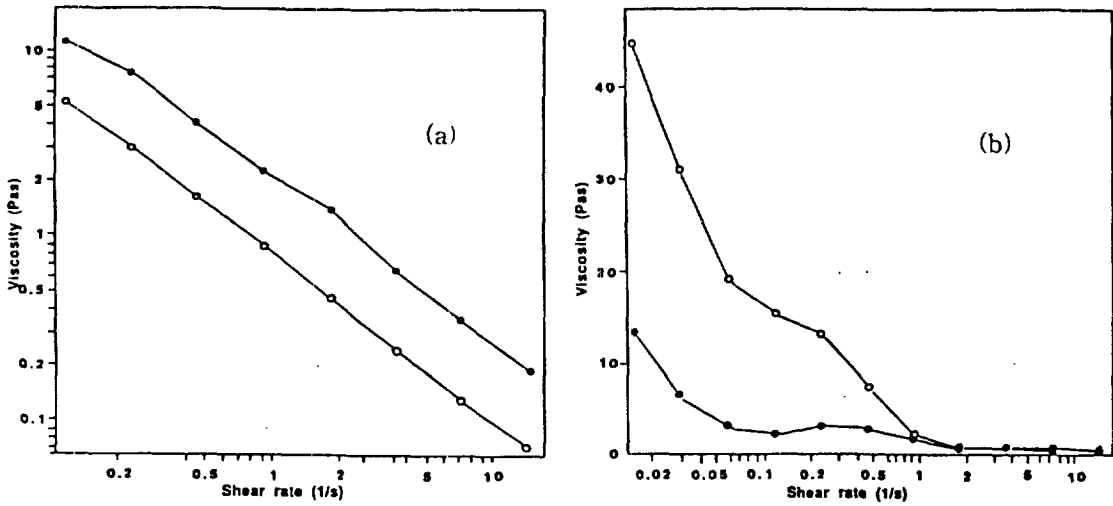


Fig. 2. Viscosity of water(a) and n-hexadecane(b) containing unmodified(○) and modified(●) CaCO₃ powder.

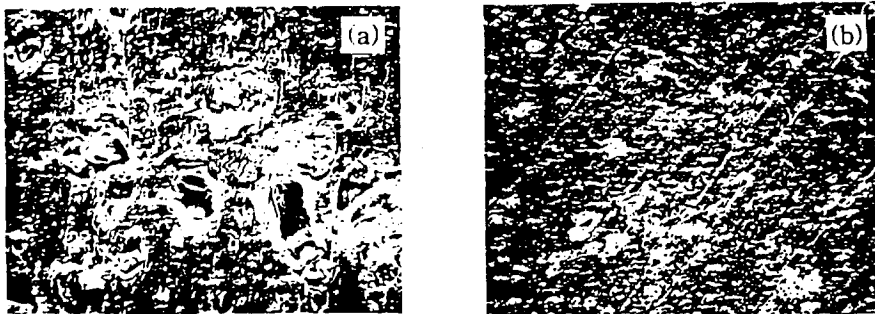


Fig. 3. SEM pictures of CaCO₃ powder in PP-compound (a) unmodified (b) modified.

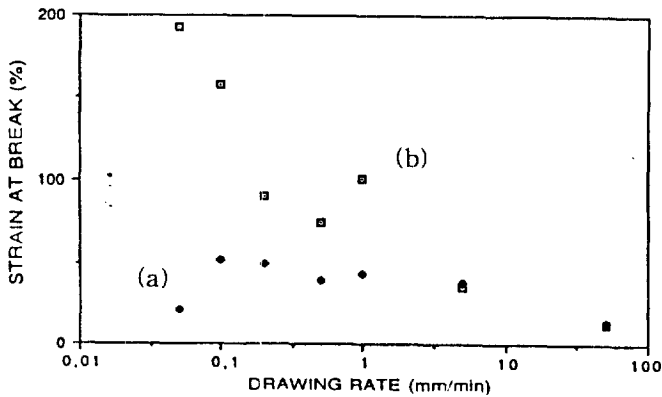


Fig. 4. Strain at break of PP-compound as a function of drawing rate; (a) unmodified CaCO₃(◆) (b) modified CaCO₃(◻).