

Fumed silica가 충전된 Polyethylene terephthalate(PET) Nano복합재의 연구

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Polyethylene terephthalate(PET) Nanocomposites filled with Fumed Silicas by Melt Compounding

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1. Introduction

The polymer nanocomposites are attracting considerable attention on account of the characteristic properties of nanoparticles have extremely large surface area per a unit mass. Recently, mica-type silicates like montmorillonite have received a good deal of attention as effective nano-reinforcement(1), but actually some critical problems such as the difficulties of exfoliation and surface modification, the weak heat-resistance of modifier, and inferior processability due to the increase in melt viscosity have restricted the mass production and various applications of the nanocomposite

Fumed silica, manufactured by high temperature hydrolysis process of silicon tetrachloride in a flame, has extremely small primary particle size of approximately 7~40nm and smooth non-microporous surfaces can be easily modified to the hydrophobic silica(2). If dispersed well in matrix polymer and have good miscibility with polymer, although no opportunity for keying adhesion of the polymer, they are more effectively wetted and it has the potential to improve heat deflection temperature(HDT) and barrier to diffusion of solvent apart from increasing the modulus. The commercial PET used for fiber and film were chosen as the matrix, because has large field to apply and there are very few researches on various mechanical and rheological properties of nanocomposite filled with fumed silica by conventional direct melt compounding.

Therefore, In this paper, On the assumption that fumed silica can have good wettability with non-polar polymer even by simple hydrophobic surface treatment,

the various characteristics such as thermal properties, rheological behaviors under unsteady shear, mechanical performance, and possible morphological changes of nanocomposites induced by the addition of the hydrophilic/hydrophobic fumed silicas are discussed.

2. Experimental

2.1. Materials

Polyethylene terephthalate(PET), IV 0.655 and SBR(Super Bright TiO₂ 0%), a commercially available material for fiber and film, was supplied by Sanhan Co. Ltd. The hydrophilic neat fumed silica, primary particle size average 7nm, was purchased from Sigma and the surface modifiers, methyltrichlorosilane and octadecyltrichlorosilane, were purchased from Aldrich.

2.2. Surface modification of fumed silicas and their characterization

In this study, three types of fumed silica nanoparticles were prepared as filler: neat hydrophilic fumed silica(FS); surface modified hydrophobic fumed silica (M-FS) by methyltrichlorosilane which has a methylated surface; surface modified hydrophobic fumed silica(O-FS) by octadecyltrichlorosilane which has octadecyl chains attached to the surface.

In order to verify the success of surface modification of fumed silica, Fourier transform infrared(FT-IR) spectra obtained using Nicol 760 MAGNA-IR spectrometer and thermogravimetric analysis(TGA) by Perkin-Elmer 7 were performed. Besides the methanol wettability and the measurement of contact angles using G- I type ERMA Inc. were carried out.

FT-IR spectra of each fumed silicas in Fig. 1 show the decrease of hydrogen bonds peak at 3700~3200cm⁻¹ of modified fumed silicas, and the more weight loss of M-FS and O-FS against FS in TGA tests can also be presented as pyrolysis of modifiers on silica surface. The data of methanol wettability and contact angles indirectly prove that O-FS and M-FS have more hydrophobic property than FS. In addition, the reason O-FS has more strong hydrophobic property than M-FS is assumed that the chemical reactivity of octadecyltrichlorosilane is more high or because O-FS has long octadecyl chains which can interrupt the hydrophilic properties of some remaining silanol groups on the surface of silica.

2.3. Preparation of PET nanocomposites and their characterization

PET nanocomposites were prepared via direct melt compounding using Haake twin roll counter-rotating mixer with various mixing conditions such as filler type(FS and M-FS, O-FS) and filler contents rate(0.5~8.0wt%).

Thermal properties of nanocomposites were analyzed by DSC and TGA using a Perkin-Elmer DSC 7 in a nitrogen atmosphere. The dynamic rheological measurements for PET and nanocomposites were conducted on the dynamic oscillatory viscometer(ARES, Rheometric Scientific Inc.) using a parallel-plate geometry. Mechanical properties were evaluated at room temperature following ASTM D882 method using an tensile testing machine(Instron-4465, Instron Corp.).

All materials and test specimens had been kept in vacuum dryer at 90°C over 18 h before used.

3. Results and discussion

The thermal properties of TGA in Fig. 2 show PET/O-FS nanocomposite have weak heat-resistance due to the pyrolysis of long octadecyl chain on the surface of silica as expected, but PET/M-FS is similar in curve to PET/FS. In case of DSC, although glass transition temperature(T_g) and melting temperature (T_m) does not shift, super cooling temperature($\Delta T=T_m-T_c$) at the second cooling decrease definitely in proportion to the increase of filler content rate in all nanocomposites, and that means nano fumed silicas act as nuclear agent beside reinforcement in composites. The results of dynamic rheological measurements in Fig. 3 present very interesting behaviors. The storage modulus(G') of FS increase gradually at low frequency field by the increase of content rate, and finally the cross over phenomenon, G' is higher than G'' and the inherent property of elastomer, occur at 10 rad/s in Fig. 3(b). These can be considered because the three dimensional network due to the interaction among hydrophillic fumed silicas(FS) in matrix dominate the rhological behaviors. M-FS have also similar behaviors to FS since have substantial silanol group not modified. On the contrary, O-FS have strong hydrophobic property don't show. In addition, the loss modulus(G'') of nanocomposites in Fig. 3(a) is lower than neat PET and that is assumed because the fumed silicas act as lubricant while melting state. The mechanical properties of Fig. 4 indirectly present the degree of wettability according to various miscibility. That is, though strain decrease, the stress and modulus of M-FS increase at a lower filler content than conventional polymer composites.

4. References

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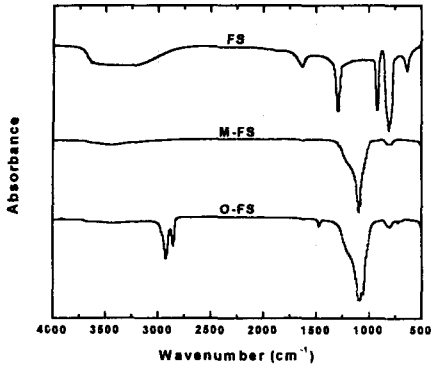


Fig. 1. FT-IR spectra of different fumed silicas: FS, M-FS, and O-FS

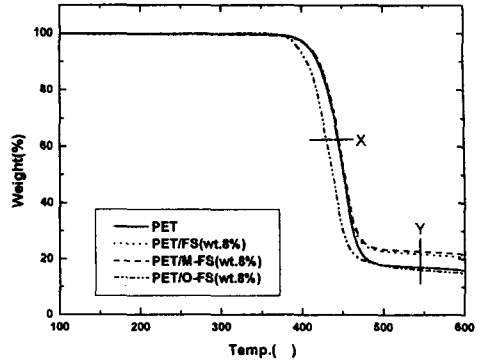
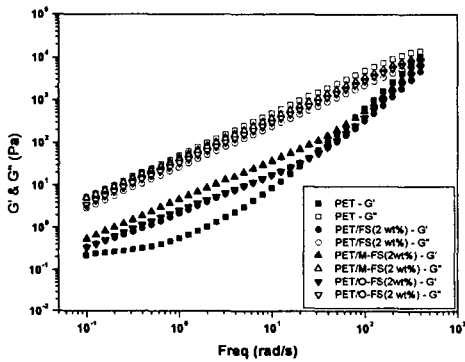
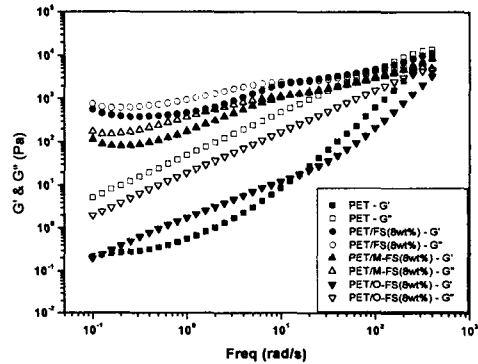


Fig. 2. TGA Variation of different fumed silicas nano-composites

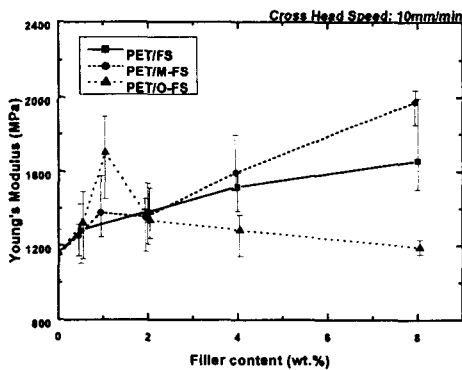


(a)

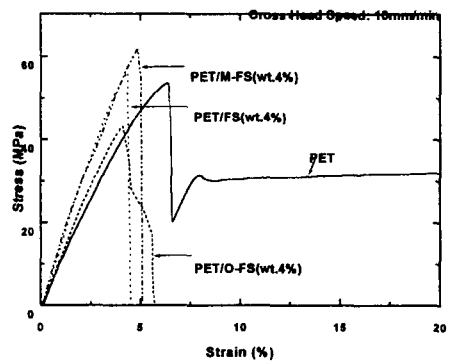


(b)

Fig. 3. Variation of the storage modulus(G') and loss modulus(G'') as function of frequency for nano-composites containing different fillers. Temperature: 270°C; Filler content rate: (a) 2.0wt%, (b) 8.0%



(a)



(b)

Fig. 4. Variation of (a) young's modulus as function of filler content, and (b) strain-stress curve for nano-composites containing different fillers.