

탄산칼슘 충전 고밀도 폴리에틸렌계에 있어서 표면결합제의 효과

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Effect of Coupling Agents on CaCO₃-Filled HDPE Systems

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Abstract: To evaluate the effect of coupling agents on the calcium carbonate (CaCO₃) filled high density polyethylene (HDPE) systems, three types of calcium carbonates- untreated, stearic acid coated, and isopropyl triisostearoyl titanate coated-were blended with HDPE by a twin screw extruder. Three compounded systems were investigated in terms of rheological properties, microstructure, and mechanical properties. At low frequencies, isopropyl triisostearoyl titanate reduced viscosity of the dispersed systems, while stearic acid increased the viscosity. Above the frequency of 20 rad/sec, however, the type of coupling agent had little effect on the viscosity. In general, two coupling agent treated systems increased impact strength and elongation at break but had a slight adverse effect on tensile strength. Examination of the fractured structure by SEM photomicrographs revealed that the two coupling agents might give an ability to form fibrils to the particulated system due probably to the enhanced compatibility between inorganic CaCO₃ and organic HDPE matrix.

1. INTRODUCTION

Fillers have been used in polymer compounding largely for the economic aspects. Addition of fillers, however, increases the viscosity of a dispersed system, which results in poor processability. Further, it often gives poor mechanical properties of the compounded system because

of weak interfacial bond between inorganic filler and organic polymer matrix (i.e., compatibility). Recently, chemical additives capable of enhancing the compatibility, so called, "coupling agent", have been developed to improve both flow properties and mechanical properties¹⁻⁵.

Up to now, the exact mechanism of "coupling" is controversial because a "true" coupling will increase the melt viscosity by its binding effect. One

may postulate that the hydrophobic organic portion of a bifunctional coupling agent physically bonds with the polymer matrix by van der Waals force while the other portion adheres to the filler. Thus, the coupling agent will enhance compatibility of polymer to filler giving better mechanical properties⁶⁻⁹.

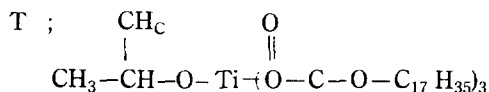
Nowadays, stearic acid and isopropyl triisostearoyl titanate are most widely used as coupling agent in domestic industries. Although it is crucial for the filler supplier and the processor to evaluate the effect of coupling agent, few studies have been carried out. In this study, the effect of stearic acid and isopropyl triisostearoyl titanate as coupling agent on the calcium carbonate filled high density polyethylene was evaluated in terms of rheological properties, microstructure, and mechanical properties.

2. EXPERIMENT

A domestic high density polyethylene (HDPE; Korea Petrochemical Ind. Co., Ltd., Korea) was the base matrix resin having the following properties; melt index = 5, density = 0.963 g/cm³, and melting point = 130°C.

Two coupling agents tested were stearic acid (SA) and isopropyl triisostearoyl titanate (T). Their chemical structures are;

SA; C₁₇H₃₅COOH



The CaCO₃ was treated by the two coupling agents in a Henschel mixer by Korea Filler Chemical Co., Ltd. The detailed coating procedure was proprietary to the company, but the usage levels informed were 2 wt% for SA and 1 wt% for T (on the base of CaCO₃ weight).

Components were compounded with a twin screw extruder (Werner and Pfleiderer, West Germany) at 190°C to 210°C, and the compounded chips were injection molded at 230°C to 240°C to give any desired specimen for testing.

The rheological properties were measured with a Rheometrics Dynamic Spectrometer (RDS) under nitrogen environment. Mechanical properties such as impact strength, tensile strength and elongation at break were measured in accordance with ASTM D 256-73 "Impact Resistance of Plastics and Electrical Insulating Materials" and ASTM D 638-77a "Tensile Properties of Plastics".

The microstructure of the fillers was characterized by TEM photomicrograph, and the fractured surface of the tensile specimens was investigated by SEM photomicrographs.

3. RESULTS & DISCUSSION

3-1. Microstructure of Filler

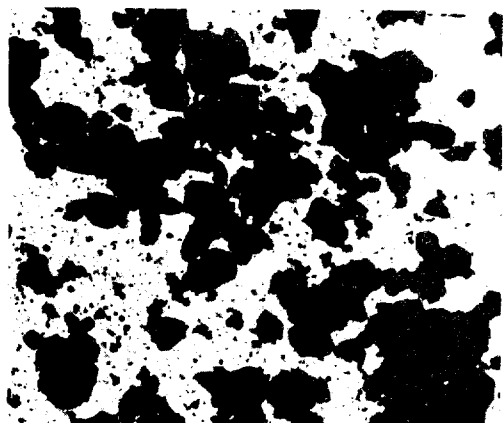
TEM photomicrographs of untreated (UT-CaCO₃) and T-coated CaCO₃ tested (Korea Filler Chemical Co., Ltd., Korea) are shown in Figure 1.

The particle size observed from the photomicrographs was in the range of 0.1μm to 3μm for both cases. In case of T-coated CaCO₃, an organic phase was detected as a faint shadow but the untreated CaCO₃ did not exhibit such an organic phase.

3-2. Rheological Properties of Filled HDPE Melts

Figures 2 and 3 represent variations of complex viscosity (η^*) and storage modulus (G') with frequency for three formulations (UT-CaCO₃, SA-coated CaCO₃ and T-coated CaCO₃) at 200°C and 240°C, respectively. All three systems contained 30 wt% CaCO₃ and 15% strain was applied. As can be seen from the figures, comparison of the dynamic properties of two treated systems with those of untreated system reveals two important facts. First, of the two coupling agents, T reduced the viscosity and storage modulus of the system while SA increased them. Second, there were shear sensitive drops in storage modulus and viscosity in the vicinity of 20 rad/sec with UT and SA systems. But, above this frequency, the type of coupling agents had little effect on the viscosity and storage modulus.

It is a well known fact that a polymer may have



(a) Untreated CaCO₃



(b) T-coated CaCO₃

Fig. 1. TEM photomicrographs showing the microstructures of UT-CaCO₃ and T-coated CaCO₃ ($\times 10,000$).

a tendency to wet the filler but not adhere to it. However, wetting and adhesion of the filler will be improved by use of a coupling agent because the surface modifier may displace air and water from the particle surface and improve the compatibility. So a surface modification of fillers with a coupling agent may give a lower tendency of particle agglomeration due to the diminished particle interaction¹⁰. In addition, it may also impart a lubrication effect onto the system since it can act as an external plasticizer by being diffused into polymer matrix¹⁶. Therefore, a coupling agent is believed to reduce the viscosity on account of deagglomera-

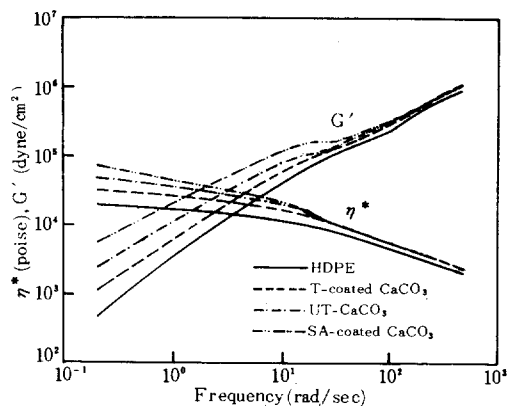


Fig. 2. Dynamic properties of virgin HDPE and 20 wt% CaCO₃ filled HDPE melts at 200°C.

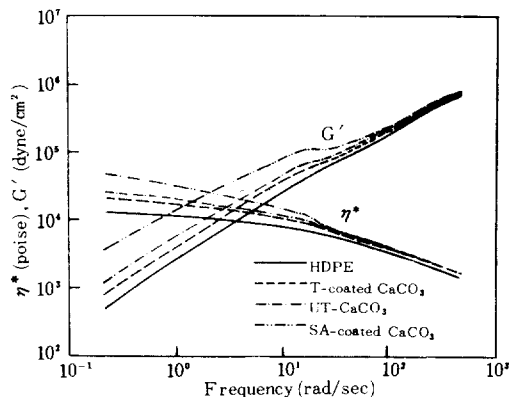


Fig. 3. Dynamic properties of virgin HDPE and 20 wt% CaCO₃ filled HDPE melts at 240°C.

tion and lubrication.

Making allowances for the deagglomeration and the lubrication, it is natural that T should reduce the viscosity. However, the increase of viscosity by use of SA seems to be extraordinary. The opposite effect on the viscosity of the two coupling agents may be explained from their inherent properties. That is, as T contains three long hydrocarbon chains per molecule which are compatible with organic polymer matrix, it may possess a greater cover factor. Further, T has no strong hydrophilic groups, which results in the reduced composite viscosity by improving the dispersion state. On the other hand, SA has only

one hydrocarbon chain in a molecule, and it contains hydroscopic acid groups. So it may easily capture moisture from the air, or it may bring about a secondary agglomeration in processing or during storage on account of strong electrostatic force causing poor dispersion.

Figure 4 shows a schematic diagram of three agglomerated spheres.

As illustrated in the figure, the "apparent" volume is increased by the particle agglomeration because an effective volume will be increased by the formation of immobile layers¹¹. Since the viscosity of a suspension is a function of apparent volume of the particles rather than "true" volume, the particle agglomeration will considerably increase the system viscosity.

In addition, since the storage modulus is a measure of resistance to deformation and the viscosity is the resistance to flow, the existence of such drops in a specific frequency range implies that an interparticle network is broken down in that frequency range due to shearing forces. On the other hand, such drops were not found when T was used. This may imply that T is compatible with HDPE. In other words, T provides larger covering area and it can form a chemical bonds with CaCO₃ through hydrolysis¹². So it may lead to the better dispersion by decreasing surface energy, and hence reduce the hydrodynamic size. Therefore, no structural alteration of the interparticle network would take place over the range of frequencies tested.

The type of coupling agents had little effect on the viscosity above 20 rad/sec since the interparticle networks for three systems would be similar by the high shearing forces. From an engineering viewpoint, however, it may be advisable to

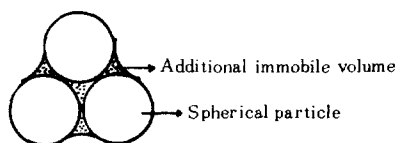


Fig. 4. Increase of apparent volume by agglomeration of three spherical particles.

eliminate hydrophilic groups in a coupling agent to avoid the secondary agglomeration and to improve the compatibility with non-polar polymers.

Figures 5 and 6 give plots of complex viscosity and storage modulus against filler content at 1 rad/sec and 100 rad/sec, respectively.

Since the melt state of the filled systems can be looked upon as a suspension state, the Mooney equation can be employed¹³.

$$\ln (\eta / \eta_1) = \frac{K_E \phi_2}{1 - \phi_2 / \phi_m}$$

in which, η is the suspension viscosity, ϕ_m is the maximum packing fraction representing the highest filler loading possible while still retaining a continuous matrix phase, ϕ_2 is the volume fraction of filler, η_1 is the viscosity of medium and K_E is Einstein coefficient. Value of K_E is very close to 2.5, the number Einstein first derived¹⁴.

In general, the degree of particle interactions increases with the increase of filler concentration, weak at low concentrations and strong at high concentrations. In fact, the filled systems generally exhibited a Mooney type viscosity behavior as

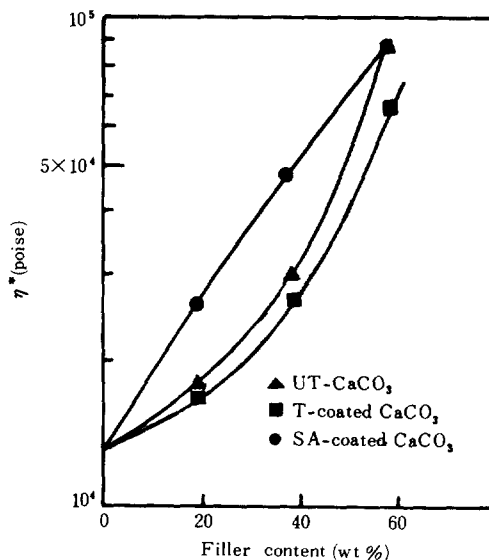


Fig. 5. Complex viscosity versus filler content for three filled systems at 240°C (frequency = 1 rad/sec, and strain = 15%).

shown in the figures.

However, at 1 rad/sec, SA-coated CaCO₃ filled system showed somewhat odd viscosity variations with filler content. In reference to the Mooney equation, the suspension viscosity is increased by the particle agglomeration¹⁵. Therefore, the unusual viscosity behavior by use of SA may also be ascribed to the poor dispersion. Moreover, a careful observation of Figure 5 reveals that the particle interaction via SA is most prominent around the filler content range between 20 to 40 wt% under the given conditions. At 100 rad/sec, however, the coupling agents had little effect on the viscosity.

3-3. Mechanical Properties of Filled HDPE Systems

Figure 7 shows the effect of coupling agent on the izod notched impact strength of the filled systems.

As can be seen from the figure, two coupling agents increased the impact strength due probably to the improved adhesion between filler and polymer. It can be also seen that T gave higher im-

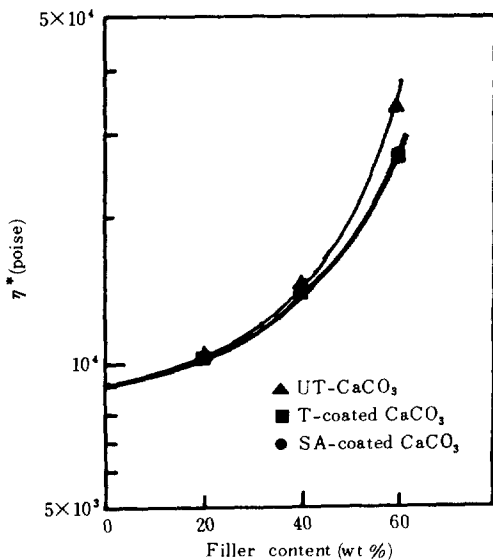


Fig. 6. Complex viscosity versus filler content for three filled systems at 240°C (frequency = 100 rad/sec, and strain = 15%).

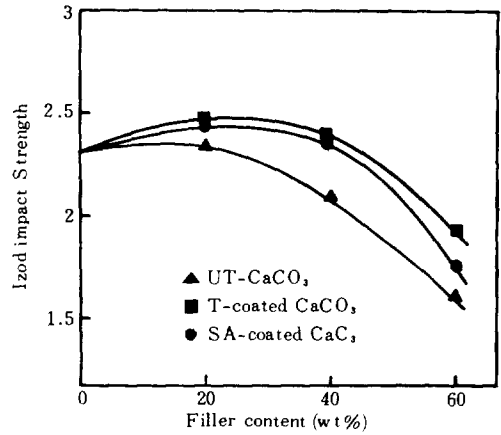


Fig. 7. Effect of coupling agents on the izod notched impact strength of CaCO₃ filled HDPE systems.

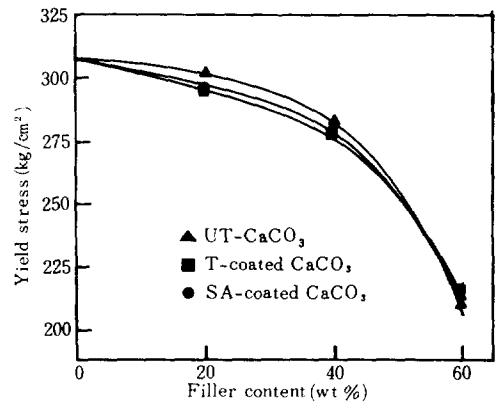


Fig. 8. Effect of coupling agents on the yield stress of CaCO₃ filled HDPE systems.

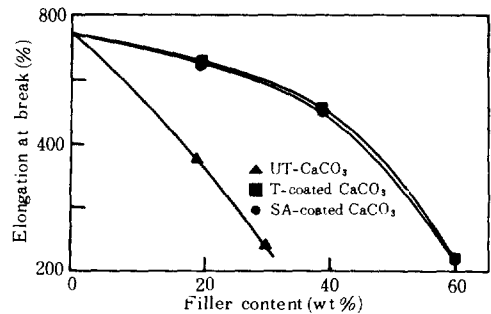


Fig. 9. Effect of coupling agents on the elongation at break of CaCO₃ filled systems.

duct strength than SA. This may be explained by the facts that T possesses better compatibility with HDPE and higher adhesion efficiency resulting from larger covering area than SA.

Plots of tensile strength versus filler content are given in Figure 8.

Two coupling agents exhibited a little adverse effect on the tensile strength. It may be obliged to the facts that both two coupling agents can only be bonded physically to HDPE matrix. But, the hydrocarbon chain might be too short to form a molecular entanglement with the polymer. Therefore, the coupling agents without chemical bonding (i.e., covalent bond) reduces the tensile strength. In fact, the low molecular weight coupling agents may act as a plasticizer in the filled system. A decrease in tensile modulus and tensile strength by use of a titanate coupling agent was also reported by others¹⁶.

Figure 9 represents the effect of coupling agent on the elongation at break.

The extent of elongation was greatly increased by use of a coupling agent. To investigate the cause of this high elongation, SEM photomicrographs were taken for the fractured surfaces of injection molded tensile specimens in Figure 10.

In Figure 10, (b) and (c) show clearly that the HDPE phase exhibits a morphology of long fibrils, whereas such a morphology is not seen in (a). Moreover, the incorporation of CaCO₃ without surface modification brought about a serious cracks even at low elongations, and the filler appeared to be simply "floated" in the HDPE matrix as an isolated state. On the other hand, the incorporation of CaCO₃ treated with T or SA did not show such cracks, and it seemed to be "embedded" between fibril structures as a coupled state.

4. CONCLUSIONS

The effect of coupling agents was investigated on the CaCO₃ filled HDPE systems. From the results, the following conclusions were obtained.

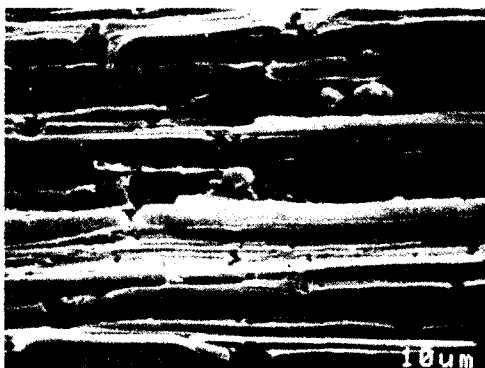
1. At low frequencies, isopropyl triisostearoyl



(a) UT-CaCO₃ Elongation at break = 80%



(b) SA-coated CaCO₃ Elongation at break = 560%



(c) T-coated CaCO₃ Elongation at break = 580%

Fig. 10. SEM photomicrographs of tensile fractured surfaces of three partrculated systems (filler content = 30 wt%).

titanate reduced the melt viscosity of CaCO₃ filled HDPE systems, while stearic acid increased the viscosity.

Above 20 rad/sec, however, the type of coupling agents had little effect on the melt viscosity.

2. The coupling agent treated systems gave higher impact strength in the CaCO₃ filled HDPE systems than the untreated systems.

3. The two coupling agents increased elongation at break by 3 to 5 times through the formation of fibrils but they had a little adverse effect on the yield stress on the stress strain curve.

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