Polymer(*Korea*) Published by The Polymer Society of Korea
Vol. 2, No. 1, 1978
Printed in Republic of Korea

電氣放電法을 利用한 폴리올레핀 複合材料에 關한 硏究

Polyethylene에 對한 Corona 放電이 Polyethylene/Alumina 複合材料의 機械的性質에 미치는 影響

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(1977년 11월 2일 접수)

Polyolefin Composites by Electric Discharge

Effect of Corona Treatment of Polyethylene on Mechanical Properties of Its Composite with Alumina

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(Received November 2, 1977)

要 約: 充塡劑를 넣은 폴리에틸렌 複合材料의 引張强度는 充塡劑를 많이 加할수록 減少되며 부피로 10%以下의 알루미나를 넣은 폴리에틸렌複合材料는 引張强度의 減少率이 훨씬 적어지고 充塡劑容積分率의 Power strength도 0.5以下였다.

폴리에틸렌에 코로나 放電을 하면 폴리에틸렌의 引張强度가 低下되나 알루미나와의 複合材料의 경우는 오히려 增加되며 充塡劑粒子가 적을수록 增加率이 커진다. 또 코로나放電處理를 한 폴리에틸렌과 充塡劑混合物의 熔融粘度는 코로나 放電時間에 의해 別로 영향을 받지 않는다. 따라서 適當한 時間 코로나 放電을 한 폴리에틸렌에 充塡劑를 添加하면 폴리에틸렌만의 强度보다 큰 複合材料를 얻을 수 가 있다.

Abstract: A composite of polyethylene with less than 10% of alumina in volume shows a decrease in the tensile strength to much smaller extent and the power strength of the filler volume fraction is less than 0.5. Treatment by corona discharge definitely lowers the tensile strength of a polyethylene sheet. Corona treatment of polyethylene, however, increases the tensile strength of the composite and the effect of treatment on the strength becomes more significant if a finer powder is used as a filler. The melt viscosity of a mixture of corona-treated polyethylene and a filler changes very littele with the time of corona treatment.

INTRODUCTION

The influence of fillers on mechanical properties of a polymer is of great scientific interest and has important industrial applications. Mechanical strength of a particulate-filled composite has been interpreted as a function of the filler concentration for the cases of perfect adhesion as well as no adhesion between the filler and polymer phases[1]. The diameter of filler particles is also one of the factors controlling the ultimate strength of a filled polymer[2,3].

There have been some discussions on the dependence of tensile strength of a filled polymer on the volume fraction and it is generally accepted that the strength is a function of the volume of a spherical filler to the two-third power[1,4,5]. However, Piggott and Leidner[6] claimed that the neglect of stress concentration effects can result in spurious agreement with the two-third power law and the strength should rather depend on volume fraction to the first power when spherical inclusions are used. This work was, then, criticized by Nicolais and Mashelker[7] who demonstrated that the above authors introduced doubtful assumptions in deriving the theoretical aspect of the strength of polymeric composites containing spherical fillers.

Present work examines the effect of fillers on the tensile strength and derives the power strength of a volume fraction when a filler with irregular shape is used. The effect of corona treatment of polyethylene powder on the mechanical strength of the composites is also investigated. The melt viscosity of the composites with and without corona treatment on polyethylene were measured and compared.

PREDICTION OF TENSILE STRENGTH OF FILLED POLYMERS

Case I. No adhesion

The tensile strength of unfilled and filled polymers, σ and σ', respectively, are defined by equations (1) and (2)

$$\sigma=\frac{F}{A} \tag{1}$$

$$\sigma'=\frac{F'}{A} \tag{2}$$

where F and F' are the breaking load of unfilled and filled polymers, respectively, and A is the cross-sectional area of a specimen. If it is assumed that the load is applied only on the polymer matrix and there is no adhesion between the matrix and filler, tensile strength of a filled polymer, σ', can be given by

$$\sigma'=\sigma\frac{Am}{A} \tag{3}$$

and

$$\sigma'=\sigma(1-R_f) \tag{4}$$

where Am is the cross-sectional area occupied by polymer matrix and R_f is the area fraction occupied by the filler. The area fraction of a filler, R_f, is generally expressed[1,6,7] as

$$R_f=k(V_f)^n \tag{5}$$

where k is a constant, V_f is the volume fraction of a filler and $n\leqq 1$. By combining equations (4) and (5), equation (6) or (7) is then obtained

$$\sigma'=\sigma[1-k(V_f)^n] \tag{6}$$

$$ln(\sigma-\sigma')=lnK+nlnV_f \tag{7}$$

where K is $k\sigma$.

Case II. Adhesion between polymer matrix and filler

The assumption made here is that adhesive strength of the interface between polymer matrix and a filler increases only if a reactive site of polyethylene becomes a polar group by a corona treatment.

The effective surface area of a filler at the interface, Ac, which makes a bonding to corona-treated polyethylene is given by

$$Ac = A_f \cdot y \tag{8}$$

and $$Ac = A_f(1-e^{-st}) \tag{9}$$

where y is the degree of formation of adhesive bonding strong enough to show strength of the matrix, s the rate constant and t the time of corona treatment.

The tensile strength of polymer matrix with some degree of adhesive bonding to a filler is defined by

$$\sigma = \frac{F''}{Am + Ac} \tag{10}$$

where F'' is the tensile load of a composite. One assumes that the filler surface at the interface in a composite makes either complete bonding to polymer or no adhesion at all.

The tensile strength of a composite, σ'', is expressed as

$$\sigma'' = \frac{F''}{A} \tag{11}$$

By combining equations (10) and (11), equation (12) is obtained.

$$\sigma'' = \sigma\left(\frac{Am + Ac}{A}\right) \tag{12}$$

Since we have expressed A as

$$A = Am + A_f \tag{13}$$

equation (14) can be obtained by combining equations (12) and (13) with equation (8).

$$\sigma'' = \sigma\left[1 - \frac{A_f}{A}(1-y)\right] \tag{14}$$

Upon introducing equation (9) into (14), we have equation (15)

$$\sigma'' = \sigma - KV_f{}^n e^{-st} \tag{15}$$

when $V_f{}^n$ is constant, equation (15) becomes equation (16)

$$\log(\sigma - \sigma'') = K' - st \tag{16}$$

where K' is $\log KV_f{}^n$.

EXPERIMENTAL

Polyethylene used was high density polyethylene grade M850 supplied by Korea Petrochemical Ind. Co. Melt index and density of the polyethylene were 5.0 and 0.96g/cm^3. The polymer was in the form of powder dried right after polymerization and contained no additives. Table 1 specifies the alumina used as a filler.

Table 1. Particle Sizes of Fillers

Code	U.S. Sieve No.	Size of the Eye(μ)
F	325	40
M	140	105
C	120	125

Composites were prepared by mixing alumina with the polymer, with or without corona treatment[8]. The alumina was dried in an oven at temperature 150°C prior to use. The mixture was then extruded through a melt indexer with a capillary, L/D ratio of 3.8. The extrudate was cut into a granular form and a sheet was made by using a hot press at temperature of 160°C. Sheets were cut into a dumbbell shape with the width of 5 mm at the center and length of 5 cm for the tensile tests.

Tensile stress-strain curves were obtained on an Instron TMS with a head speed of 5 cm/min. Infrared spectra of polyethylene sheets were obtained on a Perkin Elmer 521 IR spectrophotometer. Concentration of carbonyl groups after the corona treatment was measured with help of the correlation curve made by measurement of carbonyl groups of stearic acid in carbon tetrachloride.

RESULTS AND DISCUSSION

Figure 1 shows the effect of filler content of a composite on the tensile strength. As is predicted[1,2,7,12,13], the tensile strength decreases with an increase in the filler content of the composite. Although shape and size of the fillers

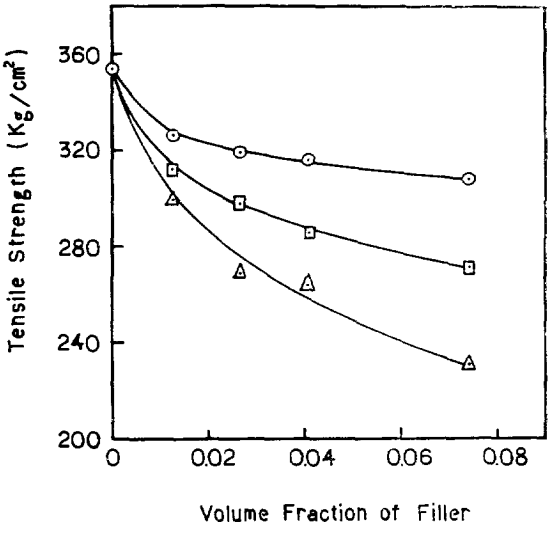

Figure 1. Tensile strength of a composite as a function of the volume fraction of the filler
⊙ : Filler F ⊡ : Filler M
△ : Filler C

used in this work are not examined vigorously, the mechanical strength of the composite seems to depend significantly upon them. When spherical fillers are used in a composite, the mechanical strength of the composite is dependent

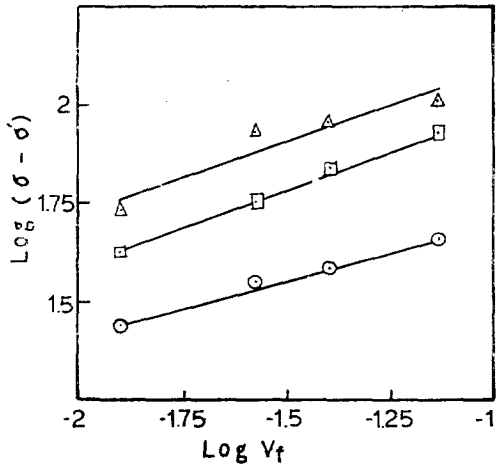

Figure 2. The plot of $\log(\sigma-\sigma')$ *vs* $\log V_f$ of a filler in a composite
⊙ : Filler F ⊡ : Filler M
△ : Filler C

on $d^{-\frac{1}{2}}$, where d is diameter of the spherical filler[6].

In the case of using crashed alumina with irregular shapes, average size of the filler still gives marked effect on the tensile strength of the composite. It is apparent that smaller particles weaken the matrix to a lesser extent than larger particles. Power strength of volume fraction of fillers in the composites are obtained from the slopes of straight lines as shown in Figure 2. When fine powder of alumina with maximum particle size of 40μ is used as a filler, power strength, n is only 0.28, which is much less than that of spherical fillers; $2/3$[1,7] or 1[6]. When the fillers of larger sizes, 105μ and 125μ, are used, the power strengths become 0.41 and 0.45, respectively; much greater than that of the composite with the finer powder, but much less than that of a composite with spherical inclusions[1,6,7]. It is noted that the strength of a composite with less than 10% of filler in volume shows less decrease than with more than 10% of filler in volume reported elsewhere[1,6,7].

Tensile strength of unfilled polyethylene de-

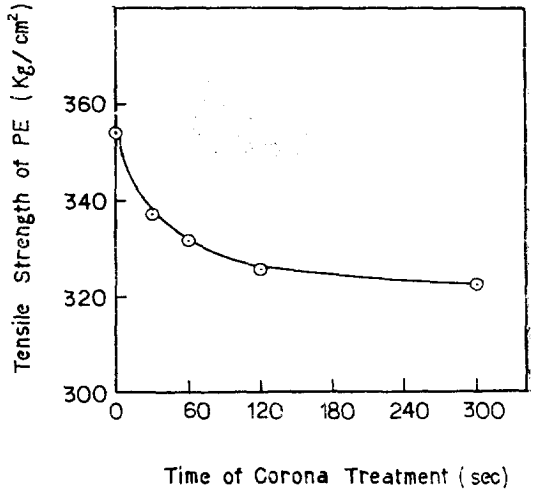

Figure 3. Tensile strength of polyethylene as a function of the corona treatment time

creases with time of corona treatment as shown in Figure 3. It was observed that the carbonyl group measured from absorption peak at 1720cm^{-1} was increased with the time of corona discharge in air. It is obvious that bulk polyethylene, melted and recrystallized after the corona treatment, is a blend of oxidized and unoxidized polyethylene and the crystallinity should drop to show lower tensile strength (Figure 3).

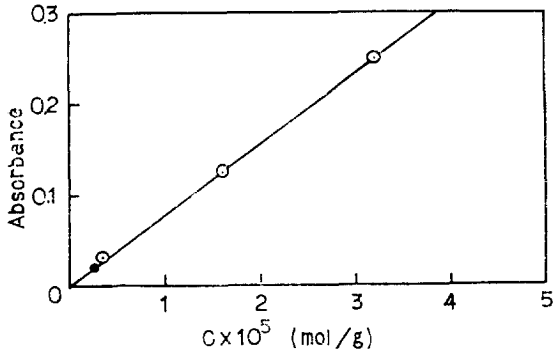

Figure 4. Calibration curve for concentration of carbonyl group measured by an IR spectrophotometer at 1720cm^{-1}
Round dot(●) indicate the concentration of carbonyl in corona-treated polyethylene for 30 min.

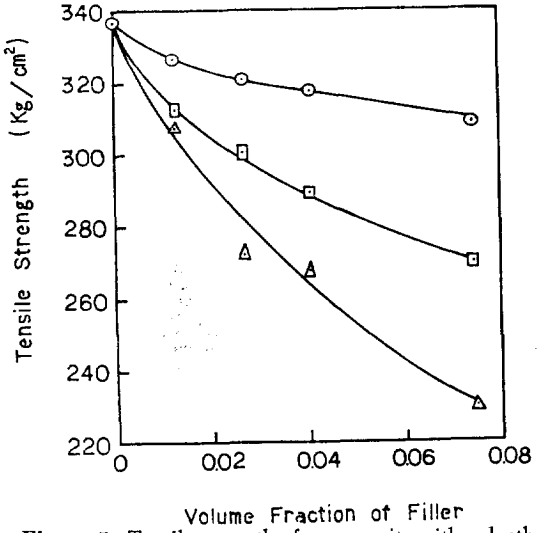

Figure 5. Tensile strength of a composite with polyethylene treated in a corona discharge for 30 sec as a function of the volume fraction of a filler
⊙ : Filler F ⊡ : Filler M
△ : Filler C

Figure 5~8 show the effect of corona treatment on tensile strength of composites as a function of the volume fraction of the fillers.

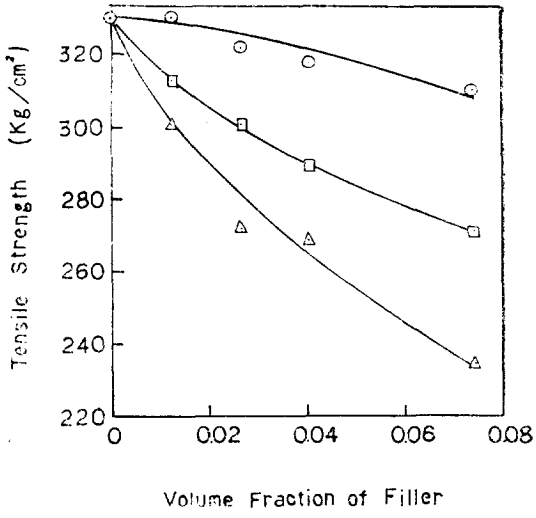

Figure 6. Tensile strength of a composite with polyethylene treated in a corona discharge for 60 sec as a function of the volume fraction of a filler
⊙ : Filler F ⊡ : Filler M
△ : Filler C

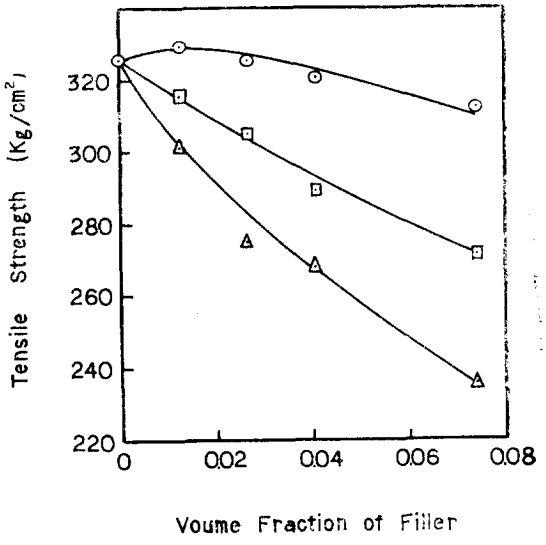

Figure 7. Tensile strength of a composite with polyethylene treated in a corona discharge for 2 min as a function of the volume fraction of a filler
⊙ : Filler F ⊡ : Filler M
△ : Filler C

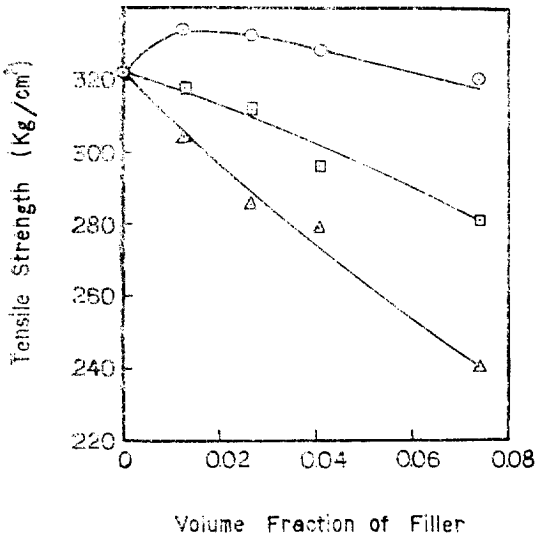

Figure 8. Tensile strength of a composite with polyethylene treated in a corona discharge for 5 min as a function of the volume fraction of a filler
⊙ : Filler F ⊡ : Filler M
△ : Filler C

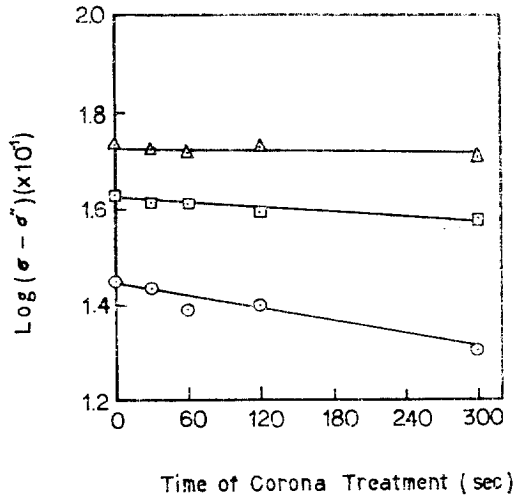

Figure 9. The plot of log $(\sigma-\sigma')$ *vs* time of corona treatment
Volume fraction of a filler; 0.013
⊙ : Filler F ⊡ : Filler M
△ : Filler C

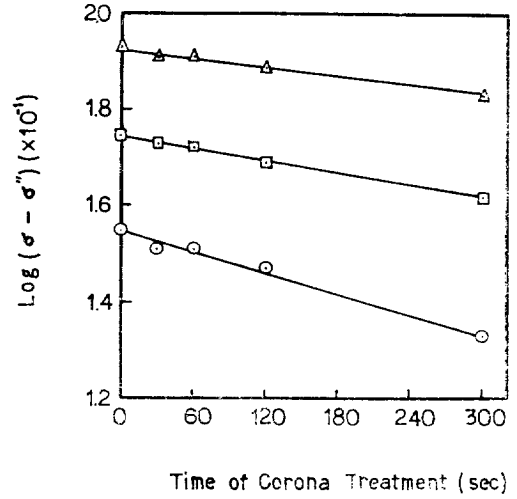

Figure 10. The plot of $\log(\sigma-\sigma')$ *vs* time of corona treatment
Volume fraction of a filler; 0.027
⊙ : Filler F ⊡ : Filler M
△ : Filler C

The strength of the composites formed from corona-treated polyethylene and alumina decreases with an increase of filler contents as does the composite with untreated polyethylene. However, with longer time of corona treatment, the composites tend to show higher strength than those with untreated polyethylene. If polyethylene is treated for 5 minutes in a corona discharge, the composite with the finest filler shows higher strength than that with the untreated. Extent of oxidation on polyethylene by corona treatment for 30 minutes is equivalent to mere 1.3×10^{-6} mole/g of carbonyl when compare with stearic acid as the standard material. It is envisaged that the extent of oxidation on polyethylene by corona treatment for less than one minute is too small to give effective contact between oxidized polyethylene molecules and the filler and, only after two minute treatment, the effect became significant when the fine powder is used as seen in Figure 7. Figure 8 shows the pronounced effect of corona treatment of polyethylene on the strength. It is compared to the result shown in Figure 1.

Changes in tensile strength of the composites

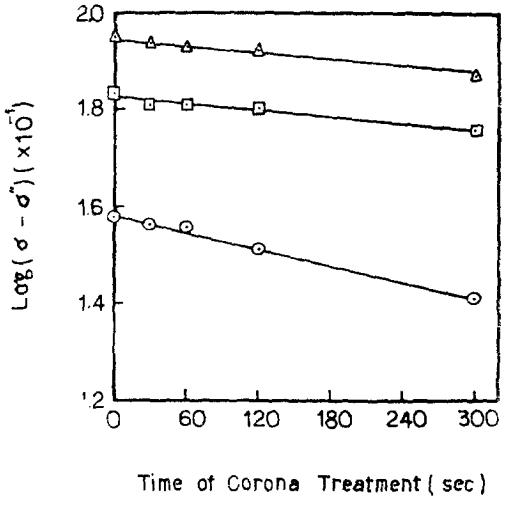

Figure 11. The plot of $\log(\sigma-\sigma'')$ *vs* time of corona treatment
Volume fraction of a filler; 0.041
⊙ : Filler F ⊡ : Filler M
△ : Filler C

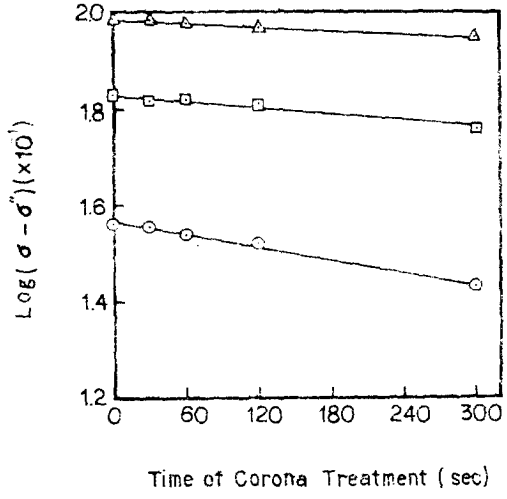

Figure 12. The plot of $\log(\sigma-\sigma'')$ *vs* time of corona treatment
Volume fraction of a filler; 0.074
⊙ : Filler F ⊡ : Filler M
△ : Filler C

with time of corna treatment are plotted according to equation (16), as shown in Figure 9~12. It is noted that, if coarse powder is used as a filler, corona treatment gives little effect on the tensile strength of the composite although the effect is positive. Corona treatment shows distinct effect on tensile strength of a composite if finer powder is used as a filler. The negative slopes illustrate the decrease in difference between tensile strength of the untreated and unfilled polyethylene, and those of corona-treated and filled polyethylene.

Ratio of melt flow rate between the filled and unfilled polyethylene a a function of time of corona treatment is shown in Figure 13. The corona treatment, although increasing the tensile strength of the composites, changes little viscosity.

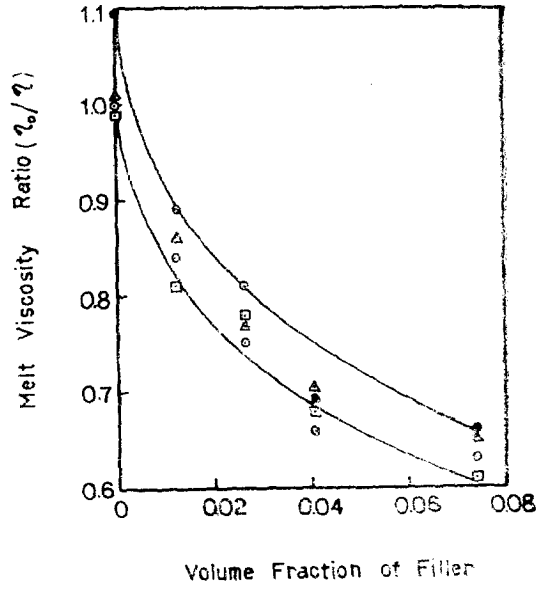

Figure 13. Effect of corona treatment on relative viscosity of composite melts.
Temperature of capillary; 160°C
η_0 and η are viscosities of polyethylene untreated and unfilled, and polyethylene treated and filled, respectively.
Time of corona. treatment; ⊙ 0 sec, ⊡ 10sec, △ 30sec and ● 50 sec.

CONCLUDING REMARKS

The ultimate tensile strength of a particulate-

filled composite decreased with an increase of the filler fraction but the rate of the decrease was much smaller with less than 10% of filler in volume; the power strength of volume fraction was less than 0.5 compared to 0.67~1.0 for a composite with spherical fillers. It was also found that a composite with a finer filler showed higher tensile strength if volume fraction of the filler was less than 10 %.

At both constant volume fraction and filler size, the tensile strength of the composite was a function of time of corona treatment. The composite with a fine filler of which volume fraction is less than 10 % showed higher tensile strength, than the controlled composite if polyethylene was treated in a corona discharge The treatment, however, showed little effect on the melt viscosity of the composites.

Further experiment would be necessary to determine whether the corona treatment on polyethylene powder of different sizes and shapes gives different results on mechanical properties of the composites. The effect of corona treatment on mechanical properties of a composite with higher volume fraction of a filler is to be studied.

ACKNOWLEDGEMENT

This paper is based on the results of research supported in part by a grant from Korean Traders Scholarship Foundation.

The authors wish to thank Messers Chong Kun Shin, Kuk Joong Kim and Sang Dae Kim of Korea Petrochemical Ind. Co., for supplying polyethylene sample. Thanks to Mr. Chie Hoon Yoon for running the IR spectrophotometer.

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