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高分子 複合材料의 接着强度에 關한 硏究(VI)
接觸角 効果

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Studies on Adhesive Strength of Polymer Composites(VI)
Contact Angle Effect

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요약 : Composites의 强度를 左右하는 여러 要因 가운데 matrix와 强化材를 複合시킬때 表面의 擧動을 살펴보기위해, 우선 폴리에틸렌, 폴리프로필렌등의 matrix 및, glass와 coupling agent와의 接觸角을 측정하고 그 關係를 考察하였다. 이것을 실제 强度와 比較한 結果 glass로 强化시킨 matrix의 경우 그 composites의 强度를 支配하는 coupling agent의 效果는 glass에 많이 의존하고 있음을 추정할 수 있었다.

Abstract: To examine the surface behavior on the process of adhesion between matrix and reinforcement among many factors which influence on the strength of composites, the contaet angle, first of all, is measured by using matrix of polyethylene, polypropylene, glass and coupling agent, then, the relations are discussed.

As a result of comparative study with the strength of composite treated by some coupling agents, it is presumed that, in case of the matrix reinforced by glass, the effect of coupling agent influencing the strength of composite depends largely on the glass.

Introduction

Obtaining good strength of polymer composite, a perfect adhesion between polymer matrix and reinforcement is very important. If thermoplastic material, however, is used as polymer matrix, it is not easy to get a perfect adhesion. Basic expression necessary for an understanding of polymer surface phenomena is the contact angle equation.

We may consider a drop of liquid on a solid substrate and the tangent to the drop surface at the region of S, V, L, in equilibrium where the interfacial energies are represented by γ_{SV} (solid-vapor), γ_{SL} (solid-liquid), and γ_{LV} (liquid-vapor). Then $(dG)_{P,T}=\gamma_{SV}dx-\gamma_{SL}dx-\gamma_{LV}dx\cos\theta$, at equilibrium $dG=0$, or $\gamma_{SV}=\gamma_{SL}+\gamma_{LV}\cos\theta$

This is contact angle equation[1,2].

For an adhesion between two factors which has different surface action respectively, a coupling agent having hydrophilic, lipophilic groups in its structure is treated under appropriate condition. By using several coupling agents the surface action between thermoplastic materials and reinforcements is measured from the contact angle and their adhesiveness for improvement of composite strength is studied by this researcher.

Experimental

Materials. Low density polyethylene (LDPE) used in this study is made by Showa Yuka (Grade 2250, Melt Index 5.0), high density polyethylene (HDPE) by Ashahi Kasei (136 F 5, Melt Index 1), polypropylene (PP) by Chisso (Grade K1014, density 0.9) in Japan and the used glass is the sample B as reported previously[3].

The coupling agents (superpure grade) used in this study are the follow three kinds of commercial product of Dow Corning Company.

N-β-aminoethyl-γ-aminopropyl trimethoxy silane (AOFS)

$$(CH_3O)_3Si(CH_2)_3NHCH_2CH_2NH_2$$

Hexamethyl disilazane (SEFS)

$$(CH_3)_3SiNHSi(CH_3)_3$$

Methacrylate functional silane (MEFS)

$$(CH_3O)_3Si(CH_2)_3\overset{\overset{\displaystyle Cl}{+}}{\underset{(CH_3)_2}{N}}(CH_2)_2O\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

Apparatus. Contact angle meter (G-1 type) manufactured by Erma Optical Company.

4-ton press (Shimadzu seisakusho, heating-plate attached) and CM-10 type thickness tester manufacured by the same. company are used.

Measurement of Contact Angle. Films used in this study are prepared as follows. The LDPE is pressed at 135°C to film, approximately 80μ in thickness, HDPE is pressed at 143°C to film with same thickess and PP is also pressed at 175°C to film in same thickess. And the glassplate of 100μ in thickness is used.

The coupling agent in the form of 1% solution prepared as previous reports[4~7] is used.

The contact angle exhibited by a drop on a surface is defined by the interior angle made by a line tangent to the curve of the image of the drop at the surface of the solid and a line defining the base of the drop.

The contact angle measurements were made at room temperature in all cases. Measurements of contact angle made within 3 min. Of the time the drop is placed on the surface were not appreciably affected by the evaporation of the liquid.

The average time required to measure the contact angle was about 1 min., well within the period in which the greatest precision could be obtained for advancing contact angles, Measurements of the contact angle of water drop on the surfaces of the LDPE, HDPE, PP, and glass were made with twice-distilled water.

The apparatus for measuring the contact angle exhibited by a drop is shown in Fig. 1. The contact angle meter is used in measuring contact angle through vertical and lateral adjustments on a status in which a high-intensity tungsten light source was focused on the surface of solid where the liquid drop was placed. At this stage the value is obtained by averaging the eight measurements. The standard deviation of the mean of eight measurements was between ±0. 8′ and ±0. 1′.

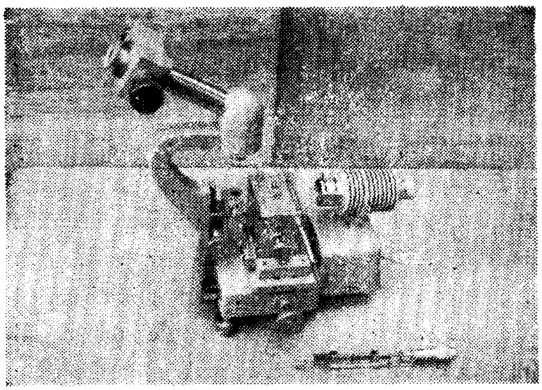

Figure 1. Apparatus for measurements of contact angle.

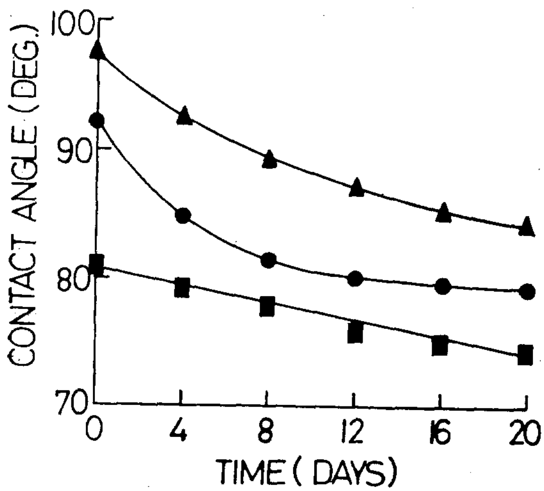

Figure 2. Contact angle measurements on several polymers removed from a steel mold and aged at 20°C.
▲ ; HDPE ● ; LDPE ■ ; PP

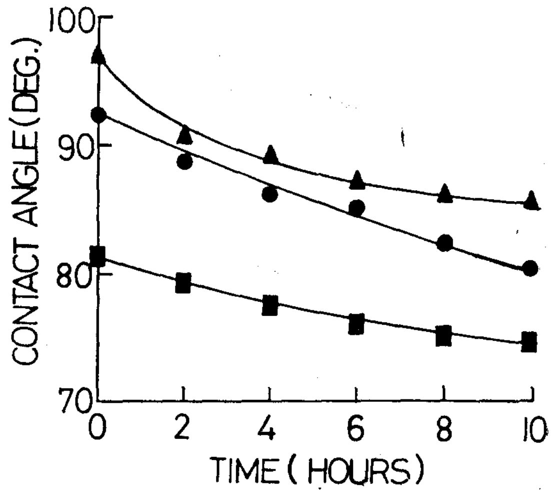

Figure 3. Contact angle measurements on several polymers removed from a steel mold and aged at 65°C.
▲ ; HDPE ● ; LDPE ■ ; PP

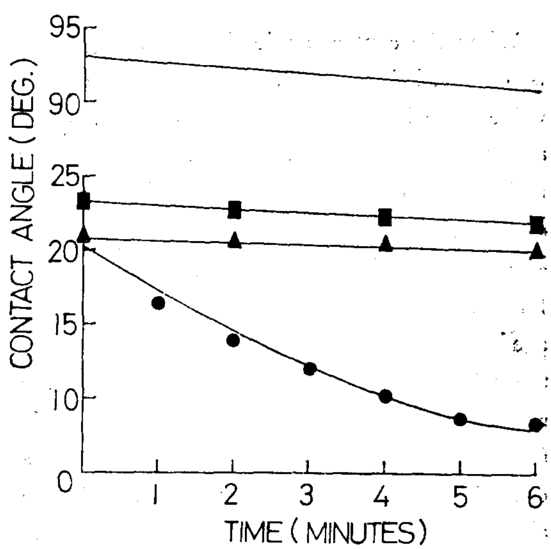

Figure 4. Contact angle measure of several coupling agents on the low density polyethylene.
— ; water ■ ; AOFS
▲ ; MEFS ● ; SEFS

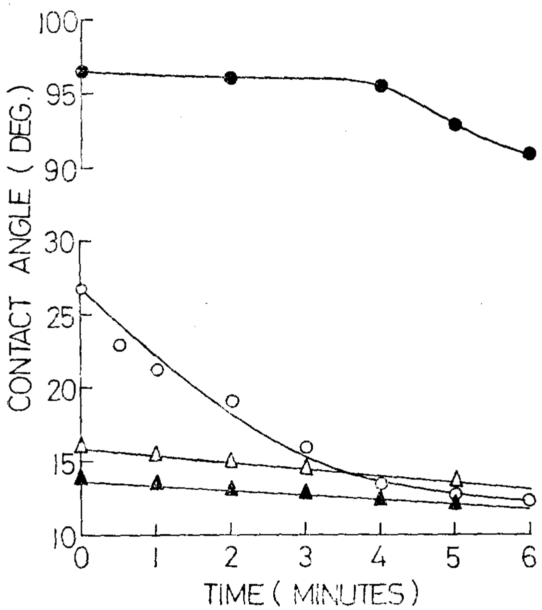

Figure 5. Contact angle measurements of several coupling agents on the high density polyethylene.
● ; water ○ ; SEFS
△ ; AOFS ▲ ; MEFS

Results & Discussion

When the contact angle through aging stage is observed both PE and PP decrease their value little by little by elapse of time. Upon aging the polymers after seperation from the mold, the contact angle changed as a function of time (Fig. 2, 3). Fig. 2 and Fig. 3 show compilations of these data obtained for the HDPE, LDPE, and PP in a steel mold and aged at 20 and 65°C, respectively. They show the contact angle as a function of time by the removal of the HDPE, LDPE, and PP sample from a steel mold. While these curves show a deviation from the behavior observed in the absence of mold-release agent, HDPE shows more difference than PP (Fig. 2, 3). In addition, almost similar phenomenon appears at the temperature of 65°C. On the other hand, a measurement is conducted on the contact angle between LDPE, HDPE, PP and coupling agent (Fig. 4, 5, 6). They show the measurements for the LDPE, HDPE, and PP pressed in mold coated with a silicone fluid mold-release agent. As a result, in the coupling agent drop on PP film the value of contact angle by AOFS (amino functional silane) is the highest whereas that of contact angle by SEFS (hexamethyl disilazane) is lower than the value of contact angle by MEFS (methacrylate functional silane) as time both the AOFS and MEFS keep almost uniform angle (Fig. 4). But the value of these, in fact, are not in accord with the strength of composite which used these coupling agents[4~6]. Furthermore, polyethylene shows similarity with polypropylene in these cases. The coupling agent drop on LDPE film, the value of contact angle by AOFS is a little higher than that of contact angle by MEFS. But it is observed that the value of contact angle on SEFS drop is getting lower remarkably as the time (Fig. 5). In the contact angle of HDPE and coupling agent, both the AOFS and MEFS show considerably low value while SEFS, as in case of LDPE, gets very low value as the time (Fig. 6). The PE also is not consistent with the strength of composite made by treating these coupling agents. The contact angle of glass and coupling agent, in case of AOFS drop, shows the best contact effect and a stable status (Fig. 7). But in case of SEFS and MEFS, both of them are placed far behind these examples. When AOFS is used as coupling agent and LDPE, HDPE, and PP as base polymer, the composite shows good strength more than the composite made by treating fiberglass with MEFS. The fact that when it is treated with SEFS, still shows better value than it is treated with MEFS is also reveals consistency with the values previously reported[4~6]. From this studying on contact angle, it is presumed that the effect

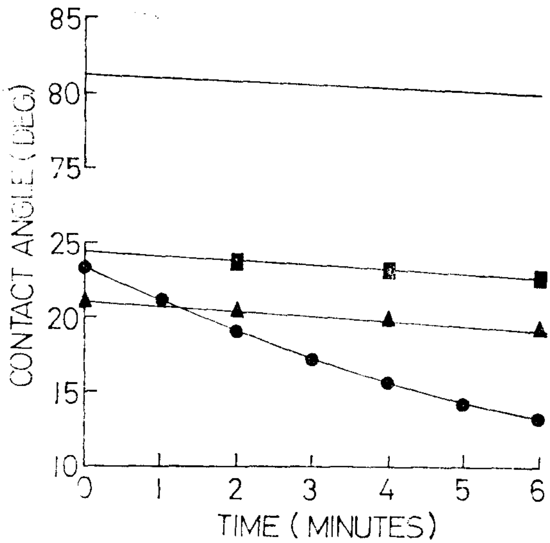

Figure 6. Contact angle measurements of several coupling agents on the propylene.
— ; water ■ ; AOFS
▲ ; MEFS ● ; SEFS

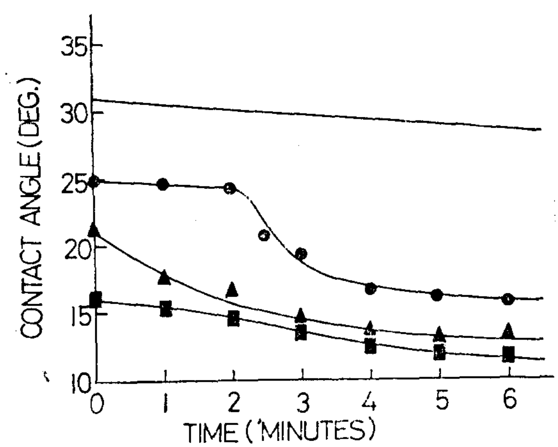

Figure 7. Contact angle measurements of several coupling agents on the glass.
— ; water ● ; MEFS
▲ ; SEFS ■ ; AOFS

of coupling agent does not coincide with matrix but depends on glass.

Conclusion

Polymer matrix shows no remarkable change from aging, but a little change is seen on the contact angle due to aging. The measured value of contact angle of the coupling agent in polymer matrix is not in agreement with the value of the strength of composite manufactured with corresponding material treated by the same coupling agent. However, the measured value of contact angle between glass and coupling agent is almost in agreement with the value of strength of the composite manufactured by treating these coupling agent. That is, when the treatment is conducted in an order such as AOFS>SEFS>MEFS, superior strength is appeared.

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