

단섬유강화 Maleic Anhydride-g-Polyethylene

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Aramid Fiber Filled Maleic Anhydride-g-Polyethylene

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요 약 : roll mill을 사용하여 maleic anhydride(MAH)-g-polyethylene(PE)(g-PE)에 aramid 단섬유를 보강시킨 복합재료를 제조하였다. 섬유의 loading이 작은 범위에서는 복합재료의 탄성율과 강도가 matrix 보다 작아지는 이른바 희석효과가 나타났으며, 강도보강은 10wt% 이상에서 나타났다. 또한 희석효과는 g-PE의 탄성적 본질에 기인한 것으로 보이며, g-PE의 탄성은 grafting 과정에서 야기된 연쇄간 가교화 반응에 의한 것임을 유변물성측정에서 알 수 있었다. 아울러 섬유함량의 증가와 더불어 복합재료의 점도 및 완화시간이 길어짐을 볼 수 있었다.

Abstract : Maleic anhydride(MAH)-g-polyethylene(PE)(g-PE) was reinforced with short aramid fiber on a laboratory open roll. Dilution effect, i.e., strength of the composite lower than the matrix, was observed at low, and strengthening was obtained at $\geq 10\text{wt}\%$ loading. This was interpreted in terms of elastic nature of the g-PE, which on the other hand, was introduced by crosslinking at the stage of grafting, as evidenced from the rheology measurement. Melt viscosity and relaxation time increased with the increase of fiber loading.

INTRODUCTION

It is of practical significance that crosslinking of polyethylene(PE) and polypropylene(PP) provides the resins with improved thermal and dimensional stability and strength at elevated temperature.^{1,2} A number of technique including chemical, radiation-induced crosslinking, and dynamic curing etc. have been developed in the past.^{3,4} These techniques mainly concern the optimum conditions for cure, change of properties, and final product behavior

etc..

Grafting of maleic anhydride(MAH) onto PE provides the resin with polarity. In addition the grafting is carried out with peroxide initiator, and consequently crosslinking is accompanied.⁵⁻⁷ Therefore, the effect of the grafting is twofold, i.e., polar modification and crosslinking.

The addition of short fibers to thermoplastics has produced a new class of engineering materials which have become commercially important over the last several decades. These materials possess

improved stiffness, strength and heat distortion temperature over the unfilled thermoplastics.^{2,8} In the past, glass fibers have most widely been encountered for thermoplastic reinforcement.⁸⁻¹¹

Kevlar is a wholly aromatic polyamide, and among the current reinforcing fibers, it has the lowest specific gravity with highest strength-weight ratio.^{12,13} Moreover, it is much more flexible than carbon or glass fiber, and this leads to less breakage during processing.

This paper considers the reinforcement of MAH grafted high density PE(g-PE) with short aramid fibers. With MAH grafting onto the PE, improved interfacial adhesion with polar fiber is expected. Composites were prepared in open mill. Fiber orientation and hence property anisotropy were determined using scanning electron microscopy (SEM) and Instron tensile tester. Melt properties were measured using a rheometer.

EXPERIMENTAL

Materials and Grafting

PE used was high density PE(Daehan Petrochemicals, E-308, sp.gr. 0.956, M.I. 0.8 g/10 min). Aramid fibers used were du Pont Kevlar 49(sp.gr. 1.45). Fibers were chopped to 5 mm, and this gave original aspect ratio of 420.

Grafting of maleic anhydride(MAH) onto PE was carried out in xylene with benzoyl peroxide (BPO).⁵⁻⁷ A mixture of BPO(0.2 part) and MAH dissolved in xylene(100) was added dropwise to the solution of PE(10) in xylene for the first 3½ hr of 4 hr reaction. The reaction was carried out at 120°C with mild agitation in N₂. Upon completing the reaction, the mixture was cooled to room temperature and washed with methanol several times and dried in vacuum overnight. Evidence for grafting was obtained from FTIR measurement. The grafting ratio determined both from weight increase[eq. (1)], and acid value measurement [eq. (2)] gave essentially identical values of c. a. 1.8 wt%.

$$\text{MAH}(\%) = \frac{\text{wt of dried sample} - \text{wt of PE}}{\text{wt of PE}} \quad (1)$$

$$\text{MAH}(\%) = \frac{\text{acid number} \times 98}{2 \times 561} \quad (2)$$

where

$$\begin{aligned} \text{acid number (mg KOH/g)} \\ = \frac{\text{ml KOH} \times \text{N KOH} \times 56.11}{\text{g of polymer}} \end{aligned} \quad (3)$$

Composites were prepared along the following procedure. The g-PEs were first dissolved in xylene, 120°C, and the chopped fibers were slowly added to the solution with mild agitation. Extreme care was taken to evenly spread the fibers in the solution. At relatively high rpm, fibers were crowded, and only at extremely low rpm fiber dispersion was satisfactory. Fiber suspension was then poured into acetone to extract the xylene out, followed by filtration and drying.

Dried sheets were rolled up in a laboratory open mill(150×330 mm) at 140 ± 0.5°C, with nip gap 1.5 mm, and roll speed ratio, 1 : 1.2. When we attempted to add the fibers directly on the g-PE sheet on the roll, acceptable fiber dispersions were not achieved, It was possible with PE sheet.

The rolled-up sheets were compression molded using a hot press at 150°C, 1200 psi for 10 min. Property measurements were done using the compression molded specimens.

TEST

SEM micrographs and tensile tests(Instron) were made in longitudinal(L) and transverse(T) directions. In roll mixing, fibers are aligned along the roll direction. Though the rolled fibers are, to some extent, randomized during the compression, the original roll direction is defined L, and its perpendicular direction T, in this paper. Melt properties were measured using a RDS(Rheometric Dynamic Spectrometer, type II) rheometer at 250°C, where orientation was assumed random.

RESULTS AND DISCUSSION

SEM Micrographs

The strengthening effect of fiber is governed by a number of facts such as fiber aspect ratio, dispersion, orientation, bonding level between fiber and matrix etc. in addition to fiber fraction.^{14,15} Among them, fiber orientation is the key parameter to control the property anisotropy,¹³ and is mainly governed by the type of manufacturing process and processing condition. In mill operation, fiber is aligned along the mill direction, and the degree of orientation generally increases with the number of passage and roll speed ratio.¹⁶⁻¹⁸ With smaller nip gap at constant speed ratio, better orientation is achieved due to the increased rate of shear. However, smaller nip gap and larger speed ratio possibly yields fiber breakage, and therefore optimum operation condition exists for given fiber-matrix combination.¹⁷

Figure 1 shows the fractured surfaces of the co-

posites, prepared by roll mixing, followed by compression molding. Though not satisfactory, orientation anisotropy is obvious and fiber dispersion is fairly good. It may be inferred that the fiber orientation achieved in mill is, more or less, randomized at the stage of compression. Kinematically, compression between two parallel plates corresponds to squeezing flow, and gives radial alignment of the fibers on the same plane. Holes left upon fiber pull-out, due to the poor interfacial adhesion are also seen.

Mechanical Properties

Tensile properties of the composites as a function of fiber loading are shown in Figs. 2 to 4. At low fiber loadings modulus (Fig. 2) and tensile strength (Fig. 3) of the composites are lower than that of matrix. In L direction, modulus and strength of the composite become greater than the matrix at 5 and 10 wt% loadings, respectively, beyond which strengthening effect is observed. In T direction, the matrix value of modulus and stre-

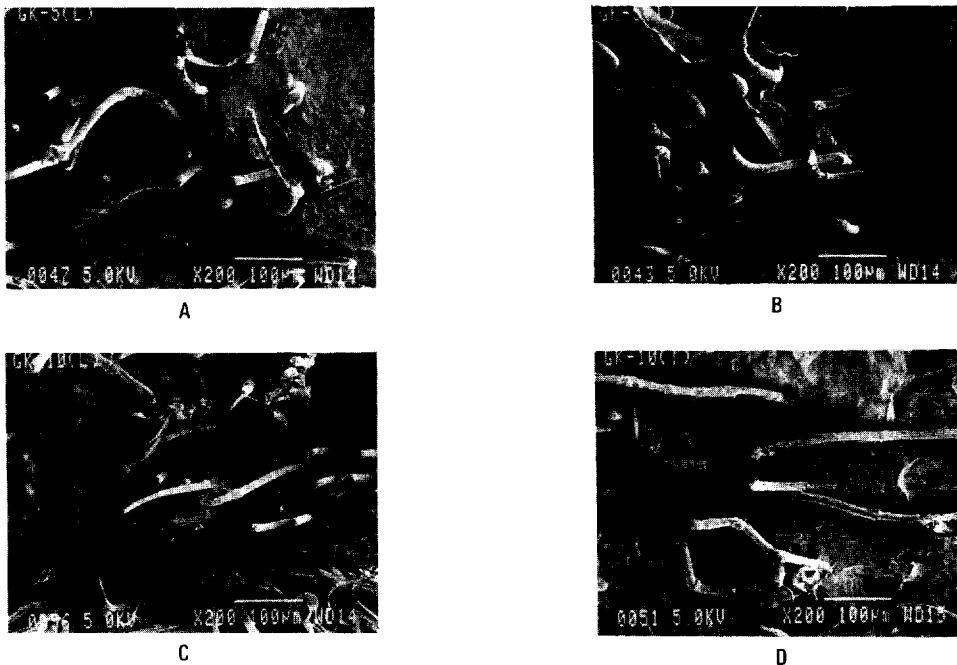


Fig. 1. SEM micrographs of cryogenically fractured surfaces of g-PE/Kevlar composites : (a) 5wt% L, (b) 5 wt% T, (c) 10wt% L, (d) 10wt% T.

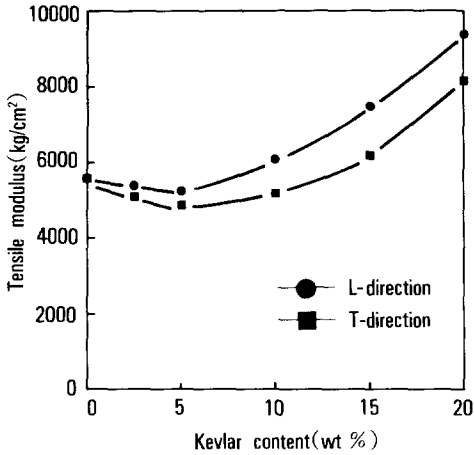


Fig. 2. Tensile modulus vs. Kevlar content for g-PE/Kevlar composites.

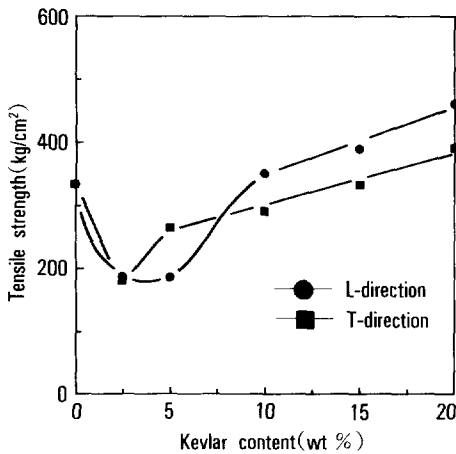


Fig. 3. Tensile strength vs. Kevlar content for g-PE/Kevlar composites.

ngth are recovered at higher fiber loadings than those of L direction. Tensile elongation shows drastic drop up to 10 wt% fiber loading in both directions, and it is kept almost constant beyond the concentration.

The fact that the composite strength is lower than the matrix strength at low loading is not unusual, especially in short fiber reinforced elastomer, and hybrid composites.¹³ The effect is known as dilution effect.¹⁵ Physically, at low fiber loadings, there are not enough fibers to control matrix elo-

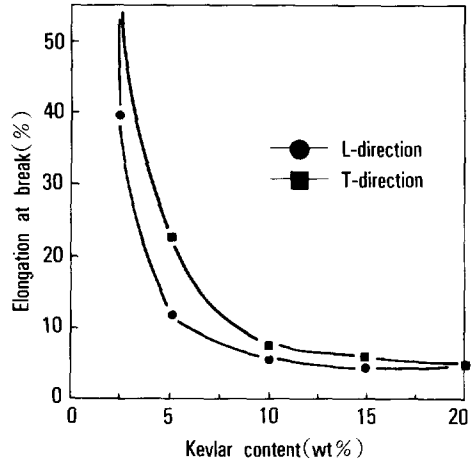


Fig. 4. Elongation at break vs. Kevlar content for g-PE/Kevlar composites.

ngation, and fibers would be subject to high strain, typically with elastomeric matrix, with only small load and break. Consequently, the composite strength could be lower than that of matrix.

Such dilution effect is not observed in typical thermoplastics such as PE. However, at the stage of MAH grafting onto the PE in the presence of peroxide, interchain crosslinking should occur and this provides the resin with elastic character. In fact, it is nowadays well known that MAH grafting onto PE leads to crosslinking.^{5-7, 19} With crosslinking, the matrix becomes more elastic, and the dilution effect, which has often been observed in elastomer composites, is observed. It should be mentioned that the sign of crosslinking is seen from melt properties to follow.

As one of the reviewer pointed out the phenomenon we referred to as dilution effect could be interpreted in terms of fracture mechanics. That is, at low fiber loading, matrix strength dominates the composite strength, and the effective cross section of matrix is reduced by the presence of the fiber. This should lead to the reduced load carrying capacity of the composite below that of matrix itself. For further details, the reader is referred to ref. 20.

Though not great, modulus and strength in L

direction is greater than in T direction throughout the concentrations tested. The anisotropy, however, increase with fiber loading is insignificant due probably the difficult fiber orientation with crosslinked matrix.

Melt Properties

The complex viscosities of the composites as well as the unfilled matrix(g-PE) and virgin PE are shown in Fig. 5. The viscosity function of virgin PE is typical of thermoplastics tending Newtonian at low frequency. The drastic increase of low shear viscosity, over one order of magnitude when compared with the virgin one, directly indicates crosslinking. Effect of branching from grafting may also be considered only in terms of increased specific interchain interactions, however, the effect should be marginal at high temperature(250°C). With the significant increase of low shear viscosity, the flow curve of g-PE becomes almost linear in log-log plot, a typical character of elastomeric materials.²¹

With fiber loadings, the viscosity increases monotonically and approaches straight line. However, the straightening effect of fiber addition comes not from the elastic nature, but from the viscous nature or filler effect. This may be explained from the fact that the fiber addition induces Weissenberg

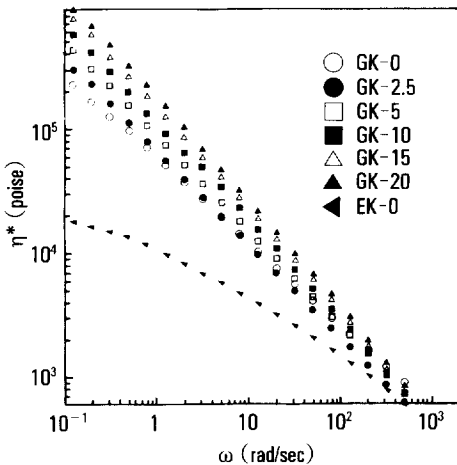


Fig. 5. Complex viscosity vs. frequency for g-PE/Kevlar composites.

effect(normal stress effect), yet with reduced die swell (elastic recoil).⁸ It should be emphasized that viscosity rise of g-PE over PE is mainly from elastic effect i.e., crosslinking. This is seen in G' vs G'' plot(Fig. 6), where data points of g-PE are located far above the diagonal, and those of PE far below the diagonal.

Figure 7 shows the relaxation spectrum²² of the composite, together with g-PE and virgin PE for comparison. The spectrum was calculated follo-

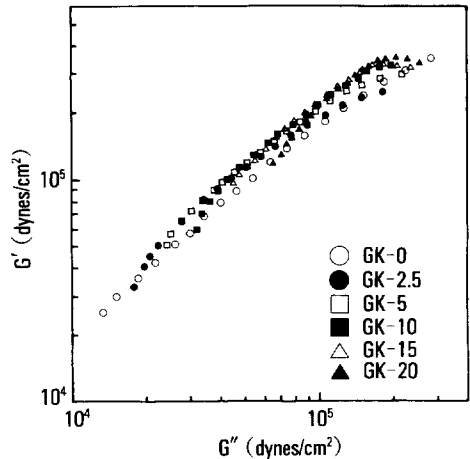


Fig. 6. Storage modulus vs. loss modulus for g-PE/Kevlar composites.

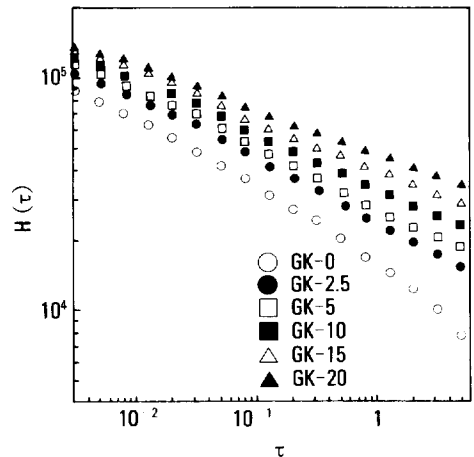


Fig. 7. Relaxation spectrum for g-PE/Kevlar composites.

wing the first order approximation by Ninomiya and Ferry.²³

$$H(\tau) = (2/\pi) [G''(\omega) - a/(a-1)^2 \{G''(a\omega) + G''(\omega/a) - 2G''(\omega)\}]$$

where $\tau=1/\omega$, and a was set to 1.259. It is seen that g-PE extends much longer relaxation time than virgin PE, and the addition of fibers gives the same effect, but the effect is less pronounced. Practically, the relaxation spectrum suggests process time for melt processing. Fiber addition should need longer cycle time compared to the unfilled resin.

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