J. of Korean Ind. & Eng. Chemistry,
Vol.3, No.1, March 1992, 81-87

Melt Rheology and Property of Short Aramid Fiber Reinforced Polyethylene Composites

Chi Hoon Choi, Young Sook Ok, Byung Kyu Kim, Chang Sik Ha, Won Jei Cho, and Young Jo Shin

Dept. of Polymer Science and Engineering,
Pusan National University, Pusan 609 - 735, Korea
(Received October 21, 1991; accepted December 10, 1991)

아라미드단섬유강화 폴리에틸렌복합재료의 용융특성 및 물성

최 치 훈 · 옥 영 숙 · 김 병 규 · 하 창 식 · 조 원 제 · 신 영 조

부산대학교 공과대학 고분자공학과
(1991년 10월 21일 접수, 1991년 12월 10일 채택)

Abstract: Polyethylenes were reinforced with short aramid fibers on an open roll. Fiber orientation and the anisotropy of physical property were studied using scanning electron microscopy and tensile tester, together with the melt properties from an RDS rheometer. It was found that fiber orientation was obtained in roll operation, and the anisotropy of property became greater with the increase of fiber loading. Melt viscosity measurements indicated that the viscosity increases with fiber loading, with the effect much more pronounced at low loading and low frequency.

요 약: 폴리에틸렌에 아라미드단섬유를 보강시킨 복합재료를 roll mill을 사용하여 제조하였다. 섬유배향과 물리적 성질의 이방성을 주사전자현미경과 인장시험기로, 유변특성을 RDS 를 사용하여 측정하였다. 섬유의 배향은 roll 작업으로 어느 정도 이루어 졌으며, 섬유 loading 이 증가할수록 기계적강도의 이방성도 증가하였다. 섬유 loading 에 따른 복합점도의 상승은 저주파수 영역에서 뚜렷이 관찰되었으며, 특히 섬유 loading 이 작은 범위에서 현저하였다.

1. INTRODUCTION

Aramid fibers possess unique properties, and among the current reinforcing fibers, Kevlar 49, one of the commercially important aramid fibers, has very low specific gravity and high tensile strength - to - weight ratio[1-3]. It is inherently resistant to flame and high temperature as well as to organic solvent. Moreover, aramid fiber is flexible over the glass and graphite fiber, and has been extensively used for elastomer reinforcement for V - belt and hose production [4-6].

To date, however, aramid fibers have been employed mainly for thermosetting resin, especially for epoxy and polyester[3].Fairly recently, aramid fibers have been incorporated with a number of thermoplastic resins[1-3,7].

Like in thermosetting reinforcement, effects of matrix, fiber loading and orientation, and the interfacial bonding between fiber and matrix on the reinforcement were the major concerns in thermoplastic composites.

Among many of the thermoplastic resins, polyethylene(PE) and polypropylene(PP), being as commodity polymers, often find applications where dimensional stability and strength at elevated temperature are required, such as hot water pipeline[7].

With regard to short aramid fiber reinforced PE, Takayanagi et al[1], and Petsalas and Andreopoulos[7] reported the effect of fiber surface modification on the mechanical and thermomechanical properties of composites. They prepared samples from compression molding, and fiber orientation was virtually assumed random.

When short fibers are incorporated in thermoplastic matrix, it is of practical advantage that the processing can be done on a conventional unit such as extruder and roll mill[8,9]. When extruder is considered, the equipment should be designed for improved dispersion and minimum fiber breakage during processing. Typically, resin is fed upstream, melted, and fiber is added downstream.

From a practical point of view, this paper considers the preparation of PE/Kevlar composites using an open mill. In roll operation, fibers are oriented along the mill direction, and consequently the anisotropy of property is expected. In addition, melt properties of the fiber - filled composites were measured using a rheometer. Such data should favorably be made use of for extrusion and injection molding. Mechanical properties were measured both in longitudinal(L) and transverse(T) direction, and the fiber orientation was viewed from scanning electron microscopy(SEM).

2. EXPERIMENTAL

2. 1. Materials

Matrix was the high density PE, manufactured by Daehan Petrochemical (E -308, sp.gr. 0.956, melt flow index 0.8 g/10 min). Resin was dried for 5 hrs at 80℃ under vacuum before use. Aramid fiber used was Du Pont Kevlar 49 (sp.gr.1.45). Fibers were chopped using a scissors to 5 mm, leading to a aspect ratio of 420.

2. 2. Preparation

Composites were prepared on a laboratory open mill (150 × 330mm) at 140 ± 0.5 ℃, with a nip gap of 1.5 mm and roll speed ratio of 1 to 1.20. Upon heating up the roll to the desired temperature, PE was fed and run for several min to lower the viscosity. Fiber was subsequently added on the PE sheet. Extreme care was taken to evenly spread the fibers on the sheet. During the experiment it was observed that the fiber orientation was mostly achieved during the first 5 or 6 passages. Upon completing the compounding, samples were air cooled. Test specimens were prepared by compression molding, using a hot press at 150 ℃, 1200 psi for 10 min. The mold specimens were 10 × 10 × 0.2 (cm) in dimension.

2. 3. Tests

SEM micrographs were taken from the cryogenically fractured surfaces of the compression molded specimen. Samples were fractured along(L) and perpendicular(T) to the roll direction.

Tensile specimens and test were made following the procedure described in ASTM D638M. Specimens were elongated on a Instron tensile tester at a crosshead speed of 80 mm/min. Tests were run at room temperature, and at least 5 runs were made to report.

Melt properties of the composities were measured using an RDS(Rheometrics Dynamic Spectrometer, RDS II) at 250 ℃. Frequency sweep was done at 15 % strain level, the highest level where the linear viscoelastic behavior is maintained.

3. RESULTS AND DISCUSSION

3. 1. SEM Micrographs

The strengthening effect of fiber is governed by a

number of facts such as fiber aspect ratio, degree of fiber dispersion and orientation, bonding level between fiber and matrix etc., in addition to fiber volume fraction[10]. Among them, fiber orientation is the key parameter to control the anisotropy of property, and is mainly governed by the type of process and processing condition to prepare the composite. 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 which generates shearing action. 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.

Figure 1 shows the fractured surfaces of the composites, prepared by roll mixing, followed by compression molding. Though not satisfactory, orientation anisotropy is obvious and fiber dispersion is fairly good. It should be inferred that the 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 shear plane. Fiber fullout is also noted and this is probably due to the poor interfacial adhesion.

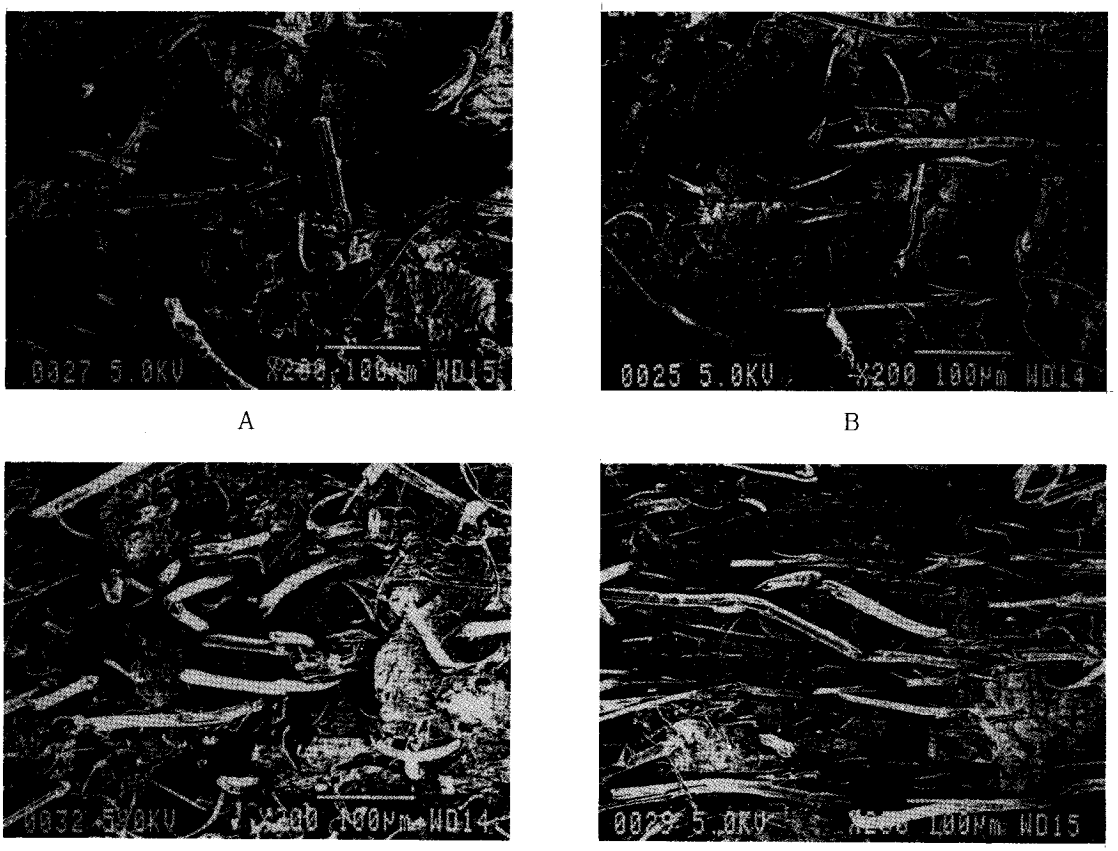

Fig. 1. SEM Micrographs of cryogenically fractured surfaces of PE/Kevlar composites. (a) 5wt% L, (b) 5wt % T, (c) 10wt% L, (d) 10wt% T

3. 2. Mechanical Properties

Figures 2 - 4 show the mechanical properties of the composites. Tensile modulus in L direction almost linerly increases with fiber loading up to 20 wt%, beyond which an abrupt increase is seen, and the value at the highest loading was favorably compared with the one reported by others[3].

Modulus in T direction holds the matrix value up to 10 wt% loading, and strengthening effect is seen beyond the 10% loading. It is also noted that the anisotropy in modulus becomes larger as the fiberl

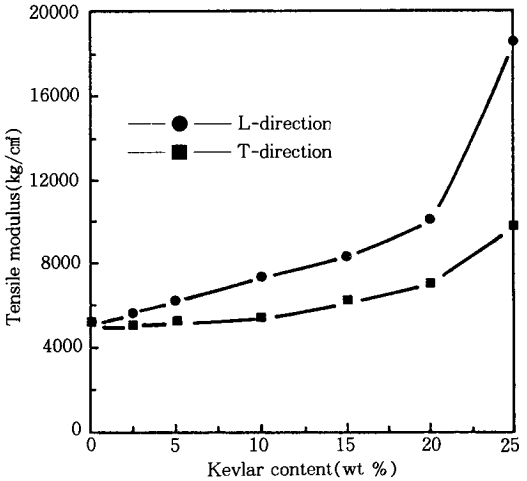

Fig. 2. Tensile modulus vs. Kevlar content for PE/ Kevlar composites.

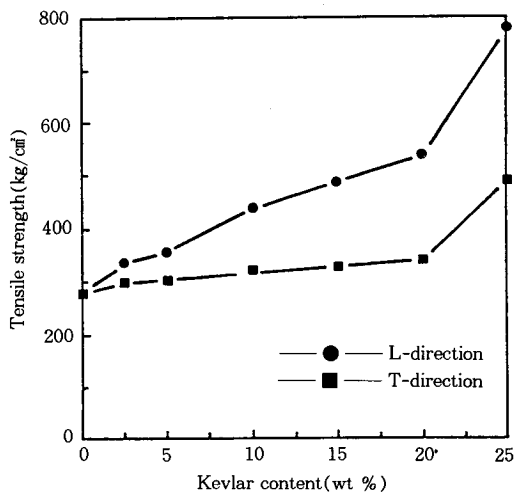

Fig. 3. Tensile strength vs. Kevlar content for PE/ Kevlar composites.

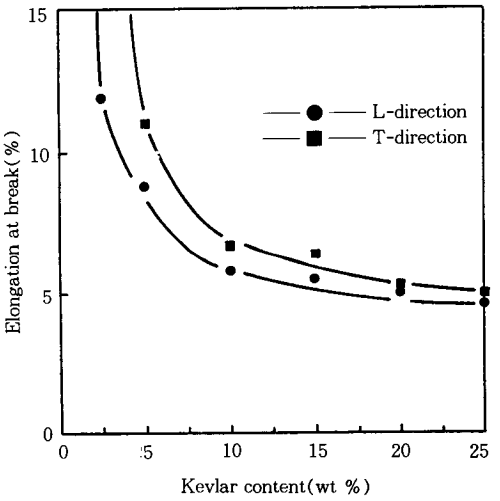

Fig. 4. Elongation at break vs. Kevlar content for PE/Kevlar composites.

oading increases. This should imply that the fiber orientation is more feasible at higher fiber loading [11,12].

Tensile strength(Fig.3) shows similar trend with the modulus dependence on fiber loading. Anisotropy between L and T direction is obvious, and it becomes larger at higher fiber loading. Elongation at break(Fig.4) shows a drastic reduction up to about 10% loading.

Though marginal, elongation at break in L is smaller than in T direction, as expected. In fiber filled composite, strengthening effect is directly related to the fracture elongation[12]. At the minimum fiber loading where strengthening is achieved, fiber would control the matrix elongation, and a drastic reduction in elongation is observed[6,11].

3. 3. Melt Properties

Short fiber reinforced thermoplastics are commercially important engineering materials, which can be processed by injection molding to speed up the rate of production[8,9]. In this regard, the melt properties of the thermoplastic composites have been extensively studied during the last couple of decades, with an emphasis on the glass fiber filled PP, polyester, and nylon[13-15]. Capillary type or other steady flow rheometer was usually employed.

The effect of fiber concentration on viscosity has been studied by a number of workers[16-18]. Earlier study[18] claimed that fibers do not exert effect on the flow curve of the matrix. This has been first questioned by Hill[16], who showed that the shear viscosity can be greatly affected by the presence of small fraction of long fibers. It is nowadays generally agreed that the shear and elongational viscosity increases with fiber (long or chopped) addition, and the effect is most pronounced at low rate of shear and elongation[8,13]. In addition, with fiber introduction, drastic increase of normal stress, yet with large reduction in extrudate swell was also generally observed[13]. Crowson et al[8], who measured the melt viscosity of short glass fiber reinforced PP using a capillary rheometer, proposed the possible mechanism from fiber alignment. Following these authors, shear flow has the effect of partially disorienting the fibers, the effect being more pronounced at low flow rate.

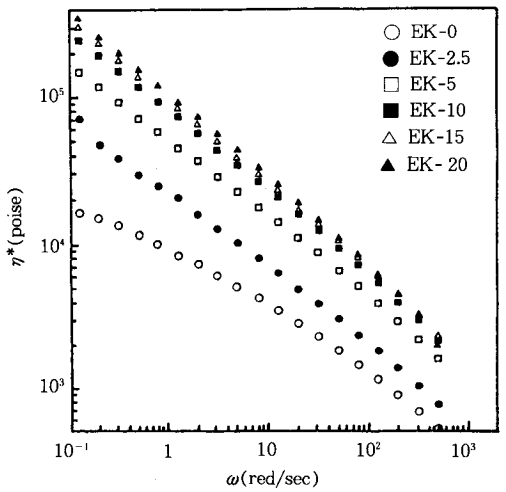

Fig. 5. Complex viscosity vs. frequency for PE/Kevlar composites.

Figure 5 shows the complex viscosities of the PE/Kevlar composites prepared in our experiments.

A significant increase in viscosity with fiber addition is noted, with the effect more pronounced at initial loading and low rate of shear, showing viscosity yield at ≥ 2.5 wt%. As the fiber loading is increased over 10 wt%, the effect is less pronounced, due probably to the segregation effect at high concentration, which was also been observed from glass fiber reinforced PE and other system[13]. A notable difference between the present work and earlier ones using glass fibers should be the existence of viscosity yield. The reason is not clear.

At high frequencies, the viscosity function is linear in the log - log plot, and the slope approaches - 1 as fiber loading increases. This indicates that the power - law index(n) approches zero, and the velocity profile, for example in tubular flow, becomes blunt, and plug flow type velocity profile is expected[9].

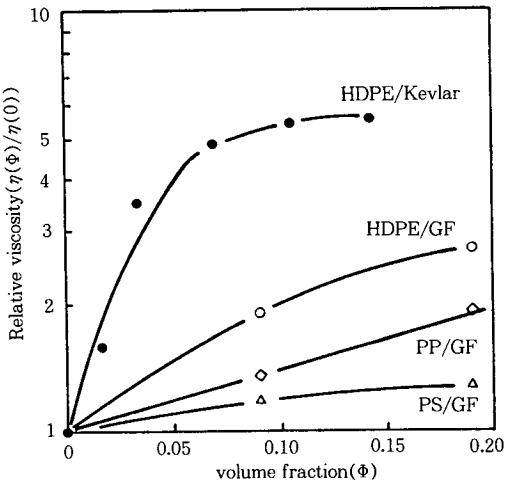

Fig. 6 Relative viscosity $\eta(\Phi)/\eta(0)$(10 sec^{-1}) vs. volume fraction of aramid fibers(GF data from ref. 13).

Figure 6 shows the effect of fiber loading on viscosity, in terms of relative viscosity(η(composite)/η(matrix)), together with the experimental results by others for glass fiber reinforced thermoplastics [13]. Here, viscosity was compared at $\omega = \gamma$(10 rad/s or and 10/s) assuming $\eta^* \simeq \eta$. Though the trend is essentially similar, the present results give much more pronounced effect on viscosity rise. This probably is again due to the flexible nature of Kevlar over the glass fiber.

Dynamic(η') and loss part(η'') of the complex viscosity are shown in Figs 7 and 8, respectively. η' corresponds to energy loss due to viscous dissipa-

tion, and η'' to elastic energy storage in a cyclic deformation. At 2.5 wt% loading, yield behavior is more clearly seen in η' data especially, than in η^* or η''. At higher fiber loading the flow curves are nearly a straight line, which is a typical characteristic of elastomers and crosslinked PE. However, for elastic materials, the deformation even at low rate of shear is strongly elastic, and consequently contribution of η'' to η^* is dominant than that of η' to η^*. However, the relative magnitude of η' and η'' of the present system is typical of thermoplastic materials, i.e., $\eta \gg \eta''$ at low frequencies.

This should imply that the rise of viscosity with fiber loading should be related to the increase of hydrodynamic volume[19,20]. That means, with the addition of fibers, the actual volume occupied by the fibers under motion is greater than the fiber volume. At high fiber concentration, fibers are subject to crowding, and the rate of viscosity ascent decreases. Our experimental results agree with these tendencies.

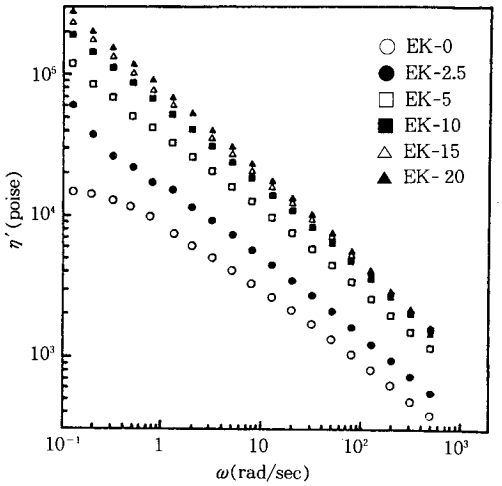

Fig. 7. Dynamic viscosity vs. frequency for PE/Kevlar composites.

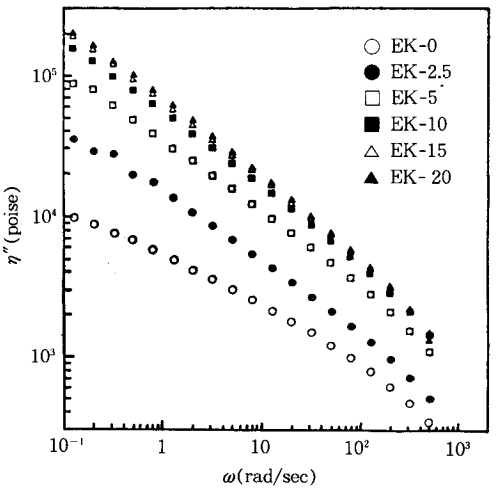

Fig. 8. Loss part of complex viscosity vs. frequency for PE/Kevlar composites.

감사의 글

본 연구는 1990년도 교육부 신소재분야 연구비 지원으로 진행되었기에 이에 감사를 드립니다.

REFERENCES

1. M. Takayanagi, T. Kajiyama, and T. Katayose, *J. Appl. Polym. Sci.*, **27**, 3903(1983).
2. P.K. Mallick, Fiber Reinforced Composites, Marcel Dekker, New York, 1988.
3. Handbook of Composites, G. Lubin ed., Van Nostrand Reinhold, New York, 1982.
4. Engineering Materials Handbook, Vol. 1 Composites, ASM International, Metals Park, OH, 1987.
5. S.R. Moghe, *Rubber World*, **187**(5), 16(1963).
6. S.R. Moghe, *Rubber Chem. Technol.*, **57**, 491 (1983).
7. H.J. Petsalas and A.G. Andreopoulos, *J. Appl. Polym. Sci.*, **38**, 593(1989).
8. R.J. Crowson M.J. Folkes, and P.F. Bright, *Polym. Eng. Sci.*, **20**, 925(1980).
9. R.J. Crowson and M.J. Folkes, *ibid*, **20**, 934 (1982).
10. J.V. Milewski, *Plastic Compounding*, **53**, 333, (1982).
11. L.A. Goettler, R.I. Leib, and A.J. Lambright, *Rubber Chem. Technol.*, **52**, 839(1979).
12. L.A. Goettler and K.S. Shen, *ibid*, **56**, 619 (1983).

13. Y. Chan, J.L. White, and Y. Oyanagi, *Journal of Rheology*, **22**(5), 507(1978).
14. W.V. Titow and B.J. Lanham, Reinforced Thermoplastics, Applied Science, London, 1975.
15. Y.Oyanagi and Y.Yamaguchi, *J. Soc. Rheol. Jpn*, **3**, 393(1975).
16. C.T. Hill, 33rd ANTEC, Tech. Papers, p. 9 (1975).
17. D. McNally, *Polym. Plastic Technol. Eng.*, **8**, 1015 (1977).
18. J.M. Charrier and J.M. Rieger, *Fiber Sci. Technol.*, **7**, 162(1974).
19. L.A. Utracki, *Rubber Chem. Technol.*, **57**, 507 (1984).
20. J.L. White, Polymer Engineering Rheology, Wiley Interscience, New York, 1990.