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Preparation and crystallization behavior of UHMWPE/LLDPE composites

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Summary : UHMWPE fiber reinforced LLDPE composites were prepared to develope the impact resistant materials. The crystallization kinetics of LLDPE with UHMWPE fiber was investigated to understand the interfacial adhesion and composite performance. The crystallization behavior of LLDPE depends on the crystallization temperature and existence of UHMWPE fiber. LLDPE matrix crystallization was affected by the inclusion of UHMWPE fiber via preceded transcrystallization on the fiber surface. The interfacial adhesion of composites was changed by cooling rate control with different crystallization behavior.

Introduction

Ultrahigh molecular weight polyethylene(UHMWPE) fiber is one of the high performance fibers which has the lowest specific gravity, 0.97g/cc, currently available for impact resistant composites[1]. However, this unique reinforcement has disadvantages of poor wettability to matrix resins as well as low melting temperature (147°C). Therefore, among various matrix resins, only a few polymer can be used as the matrix for UHMWPE fiber composites. Some studies were tried to use the polyethylene as the matrix of UHMWPE fiber[2-3]. In this case, “single polymer composites” can be prepared with different morphologies of polyethylene as the matrix and as the reinforcement. Up to now, however, only a high density polyethylene(HDPE) has been studied as a matrix. But the processing temperature of HDPE(140 ~ 145°C) cause the partial melting of UHMWPE fiber, thus its mechanical properties were reduced significantly.

In this study, linear low density polyethylene(LLDPE) resin which has low melting temperature(123°C) was used as a matrix for UHMWPE fiber composites. LLDPE resin can be expected to achieve the good adhesion with UHMWPE fiber and to give no damages to the fiber when fabricated into the composite. Moreover its high toughness yields a good impact resistant composite with UHMWPE fiber as well as the advantages of thermoplastic composite processing. Purposes of this study are to characterize the crystallization behavior of LLDPE matrix with UHMWPE fiber and to investigate the interfacial adhesion of UHMWPE/LLDPE composites.

Experimentals

The matrix resin, LLDPE grade 3245 supplied by Hanwha Chemical Co., was used in the form of film with thickness of 60μm. Its density was 0.923g/cc and number average molecular weight was 39,200, while melt index was 2.2dg/min. UHMWPE fiber,

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Spectra-900® supplied by Allied Signal Co., was used in this study. UHMWPE fibers were cleaned by soxhlet extractor with n-Hexane for 24 hours, and rinsed with deionized water several times followed by drying under vacuum at 60°C for 24 hrs. To prepare the composite specimen, film prepreg of UHMWPE/ LLDPE was used which has the fiber contents of 50wt% with stamping LLDPE films to UHMWPE fibers at 115°C.

Differential scanning calorimetry(DSC) was carried out to find out the crystallization kinetics of LLDPE matrix and its composite using DuPont 910 DSC cell. As the isothermal experimentals, LLDPE resin and UHMWPE/LLDPE composite samples were melted at 130°C for 5min. and then cooled rapidly to the predetermined crystallization temperature. Four temperatures of 117°C, 118°C, 119°C and 120°C were chosen as the isothermal crystallization temperature on the basis of crystallization onset temperature. Since it is very difficult to control the temperature upto 1°C resolution, much careful attention was given to precise controling the temperature profile of the device. At each isothermal temperature, specimens were sustained for 6 hours and heat flows as a function of time were recorded. The crystallization behaviors of LLDPE and UHMWPE/LLDPE composite were compared in terms of Avrami parameters.

Cooling rate control was performed to examine the change of the crystallization of LLDPE matrix and its composites. Firstly, LLDPE resin was heated up to 130°C and dwelled for 5min to remove any thermal histories in temperature controlled micro-oven(Umetric programmable oven 359L). And then it was cooled with the predetermined cooling rate such as 1°C/min, 10°C/min, 20°C/min, and quench cooled with ice water. The same procedure was applied to UHMWPE/LLDPE composites. The changes in morphological feature of crystallized samples were observed with the polarized optical microscope(Leitz Laborlux 12 POL S). The single fiber pull-out tests were carried out to measure the interfacial shear stress of micro-composite specimen prepared with attaching very small resin melt to a fiber. The interfacial shear stress was obtained by pulling out a fiber from the micropiece at a rate of 1mm/min using tensile tester(Instron model 1122). The fractured surface of pull-outed sample was observed with SEM(JEOL JXA-840A).

Results and Discussions

Fig.1 shows the result of DSC measurement for LLDPE resin with 5°C/min heating and 1°C/min cooling rate, respectively. The melting peak appears at the range of 55°C to 127°C. The broad melting peak may indicate the existence of imperfect crystals or comonomers such as butene or octene which melts at the relatively low temperature[4]. In cooling process, the crystallization peak is found at 115°C and the onset of crystallization starts at 117°C. The full melting temperature(127°C) of LLDPE resin is lower than melting onset temperature(142°C) of UHMWPE fiber.

The results of isothermal experimentals were analyzed by integration of the area under the crystallization peak with the isothermal time. Thus the results were plotted with the relative crystallinity as a function of time as shown in *Fig.2*. In which the higher the isothermal temperature, the slower occurred the crystallization of LLDPE due to the extent of ease in the nucleation[5]. Most of crystallization was finished within 40minutes at 117°C isothermal condition, while relatively slow crystallization within about 140minutes was occurred at 120°C. By some reports, crystallization time often changes from minutes to days over a 3°C temperature range in a linear polyethylene[5].

The kinetics of polymer crystallization can be analyzed using Avrami model for the volume fraction crystallized as a function of time. Avrami model can be expressed in the well-known double logarithmic form[6] as follows :

$$\log[-\ln(1-X(t))] = \log(K) + n(\log t)$$

where, X(t) is the volume fraction crystallized or relative crystallinity at time t.

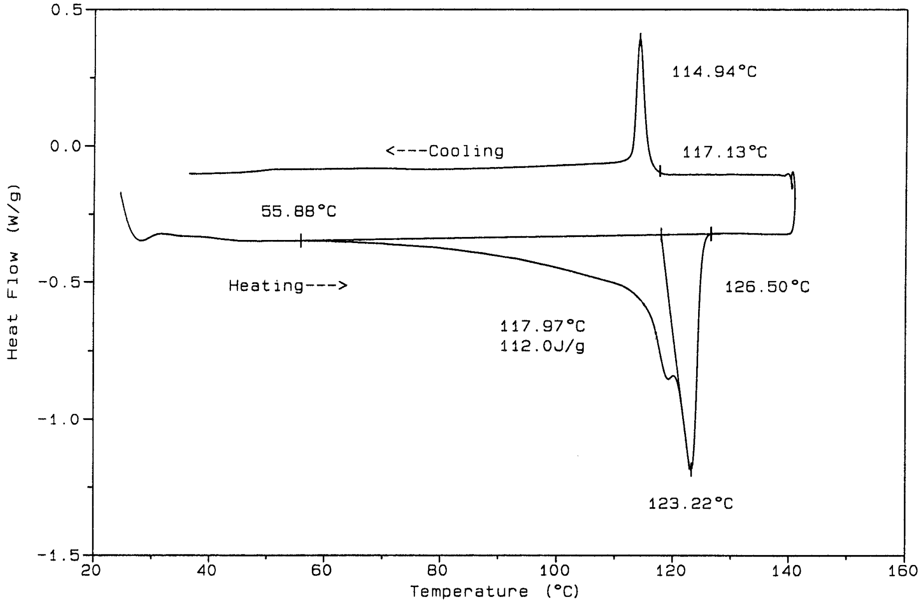

Fig. 1 DSC thermogram of LLDPE resin

Avrami exponent(n) is related to growth mechanism and geometry, while rate constant(K) contains nucleation and growth parameters. Systems obeying Avrami kinetics display almost linear behavior when log[-ln(1-X(t))] is plotted as a function of log(t) as shown in *Fig.3*. From the curves in *Fig.3*, n and log(K) can be determined by slope and interceptions, respectively. The values of n and K are presented at Table 1. In Table 1, the average value of n is about 1.97 indicating the formation of very fine spherulitic or disk-shape crystals athermally from the melts of unfractionated polyethylene. The average value of log(K) in Table 1 is about -16 which is dependent upon both the number and growth rate of the crystal. These values of n and log(K) can be compared to those of UHMWPE/LLDPE composites discussed later.

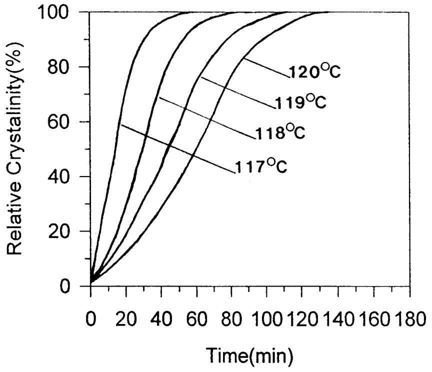

Fig.2 Relative crystallinity of LLDPE resin as a function of time

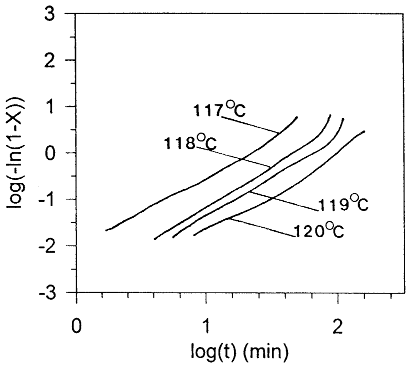

Fig.3 Relation of log{-ln(1-X(t))} vs. log(t) in crystallization of LLDPE resin

Table 1. Avrami parameters of LLDPE resin

Temperature (℃)	n	log(K)
117	1.971	-13.261
118	1.997	-16.283
119	1.952	-16.713
120	1.960	-19.410
Average	1.970	-16.392

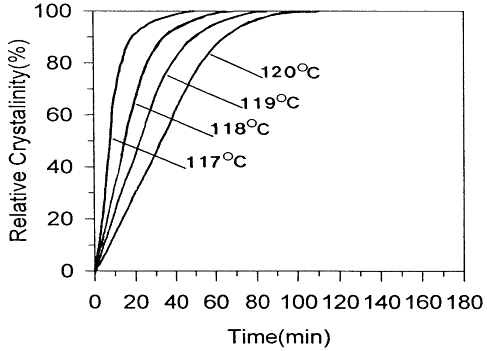

Fig.4 Relative crystallinity of UHMWPE/LLDPE composite as a function of time

Plots of isothermal crystallization for UHMWPE/LLDPE composite are presented at *Fig. 4*. Most of crystallization in composite occurred in shorter time at the same isothermal temperature compared to LLDPE resin. Crystallization rate of the composite seemed to be accelerated with the existence of fiber compared to the homogeneous crystallization of LLDPE resin only. It means that the incorporation of fiber reinforcements affect the nucleation and growth behavior of the crystallization. The seeding effect of UHMWPE fiber seemed to contribute the rate of the nucleation and growth of crystallization.

Avrami equation has also been used to analyze the crystallization behavior despite the additional complications that UHMWPE fiber imposes. In this case, Avrami parameters seemed to lose their exact mechanistic meanings. However, the trends of variations in their values are very useful to understand the crystallization behavior of the composite. Avrami relation between log{-ln(1-X)} and log(t) of UHMWPE/LLDPE composite is shown in *Fig. 5*. Values of n and log(K) of the composite are presented at Table 2 for

Table 2 Avrami parameters of UHMWPE/LLDPE composites

Temperature (℃)	n	log(K)
117	1.486	-9.449
118	1.482	-11.075
119	1.493	-12.402
120	1.465	-12.572
Average	1.482	-11.375

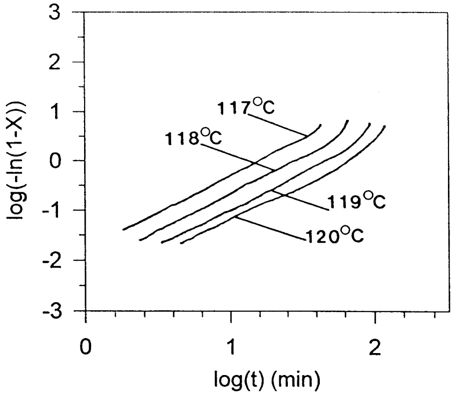

Fig.5 Relation of log{-ln(1-X(t))} vs. log(t) in crystallization of UHMWPE/LLDPE composite

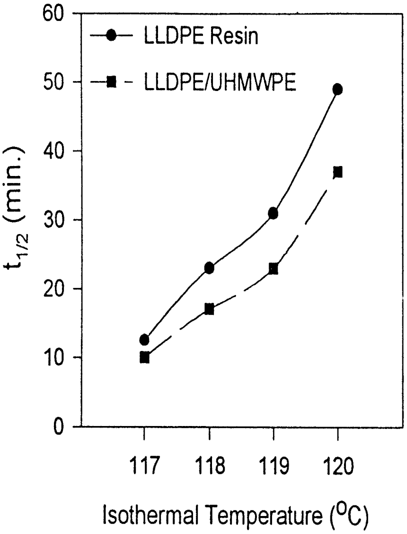

Fig.6 Crystallization half time($t_{1/2}$) of LLDPE resin and UHMWPE/LLDPE composite

each isothermal temperature. n values of composite are smaller than those of LLDPE resin implying the changes in nucleation process. It has been reported that n is largely affected by the seed content. As the seed content increases, n value decreases from 2 or 3 to about 1.5 in crystallization of linear polyethylene[5]. Accordingly, decrease of n value in the composite is attributed to the seeding effect of UHMWPE fiber. Furthermore, as the fiber surface acts as seed, the crystallization in the presence of fiber causes the formation of a transcrystalline region on its surface[7]. Since transcrystallization leads the shape of crystal to 1 or 2-dimensional geometry, resulted values of n are lowered in composites than those of LLDPE resin.

Values of log(K) in composites are increased largely because of relatively fast crystallization. The kinetics of crystallization can be quantified by a crystallization rate, which can be taken to be the inverse of the crystallization half-time ($t_{1/2}$), defined by the time for half the area

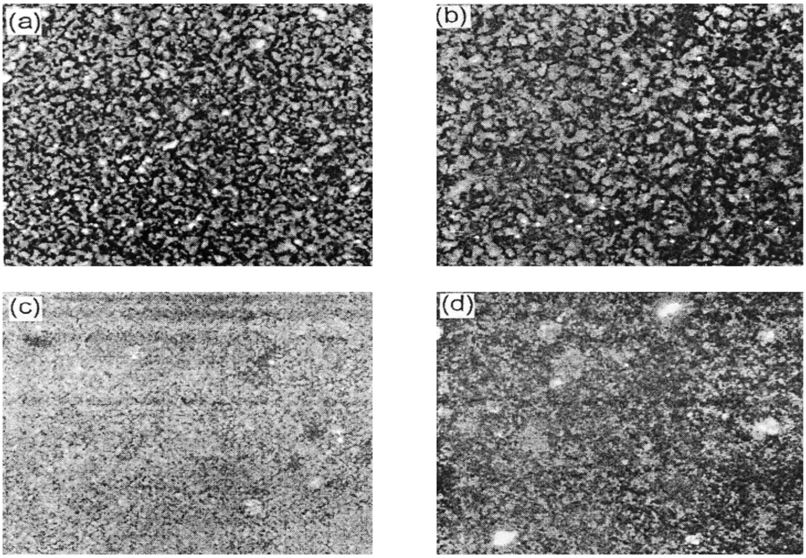

Fig. 7 Polarized optical micrographs of LLDPE resin as cooling rate varied :
(a) 1 °C/min, (b) 10 °C/min, (c) 20 °C/min and (d) quench cooled

under the isothermal crystallization peak. In *Fig.6*, the crystallization half time($t_{1/2}$) decreases to certain extent with UHMWPE/ LLDPE composites. Especially at 120°C isothermal condition, difference in time for crystallization decreases significantly. This also implies that the nucleation and growth process of crystallization has been affected greatly by the incorporation of fiber. The crystalline morphologies of LLDPE resin and UHMWPE/LLDPE composite have been observed with the polarized optical microscope. The observed morphological feature of LLDPE matrix at each condition is shown in *Fig. 7*. The crystalline texture(a), observed at the condition of 117 °C isothermal crystallization, shows a fine and granular texture without recognizable spherulites of a significant size. Nearly amorphous feature is observed in the specimen quench cooled with ice water(d) where almost no spherulite is presented.

The features of fiber incorporated specimen are shown in *Fig.8*. With the composite specimen, microscopical observation shows that the nucleation sites are so densely located on the fiber surface that polymer crystals are constrained to grow linearly outward from the fiber surface. Thus transcrystalline morphology was appeared near the fiber surface distinctly different from that in the bulk of polymer[7]. The transcrystalline region has a thickness mounts up to 2~3μm protruding from the fiber surface along its axis. Even in rapidly cooled specimen with cooling rate of 20°C/min(c), small transcrystalline region can be observed along the fiber surface although the spherulitic crystal may hardly be found in bulk matrix.

From the observation of specimen cooled with 20°C/min, starts of transcrystallization might proceed the spherulitic crystal growth. Since fiber reinforcement offers the nucleation seed, transcrystallization occurred on the fiber surface before spherulitic

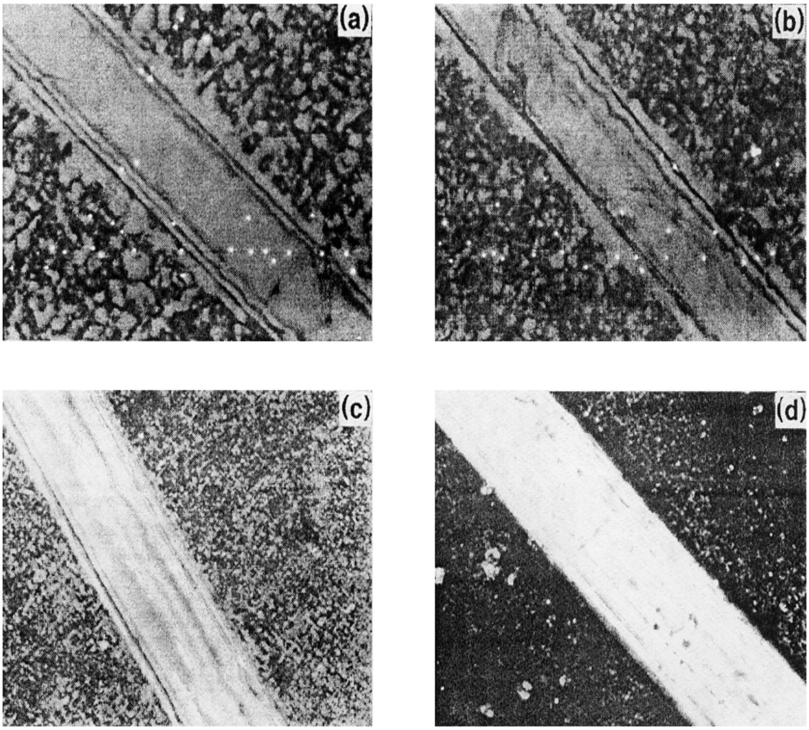

Fig.8 Polarized optical micrographs of UHMWPE/LLDPE composite as cooling rate varied : (a)1 °C/min, (b) 10 °C/min, (c) 20 °C/min and (d) quench cooled

Table 3. Interfacial shear strengths of UHMWPE/LLDPE composites as cooling rate

cooling rate	1～10℃/min.	20℃/min.	quench cooled	UHMWPE/vinylester composite (reference)
Interfacial shear strength	9 ～ 13MPa	7 ～ 10MPa	5 ～ 8MPa	1.5 ～ 6MPa

crystallization in bulk matrix. This nucleation effect of fiber agrees well with the shorter crystallization half time($t_{1/2}$) of fiber incorporated specimens as previously described. However, almost no transcrystalline is found in quench cooled specimen(d) with ice water which contains only an amorphous feature in bulk state even on the fiber surface.

Table 3 shows interfacial shear strengths measured from the fiber pull-out tests. They are very high values compared to those of typical UHMWPE composites with thermoset matrices even in the case of using properly surface treated fibers. Matching of the solubility parameters between adherends is very important to form a strong interfacial adhesion, especially in thermoplastic composite with inert surface, which has been explained with Hildebrand's mixing enthalpy[8]. The solubility parameters of UHMWPE and LLDPE are very similar as in the range of 7.9 - 8.1 $(cal/\ cm^3)^{1/2}$ [9]. Thus it could be said that very high interfacial strengths in UHMWPE/LLDPE composites are attributed to the molecular interdiffusion from similarity in solubility parameters between them.

However, interfacial shear strengths of UHMWPE/LLDPE composite also affected by cooling rate as shown in Table 3. It means that the crystallization of LLDPE matrix and the formation of transcrystalline region around the fiber have an significant influence on the interfacial adhesion. Since well-developed spherulites or transcrystalline region can restrict the pulling out of the fiber and the interphase failure, the cooling rate controlled specimens show very high interfacial strengths. But the quench cooled specimen, since there was little or no matrix spherulites or transcrystalline around the fiber, has lower value of interfacial shear strength. Therefore, changes in interfacial shear strengths with the cooling rate are associated with the radial shrinkage force of transcrystalline region on the fiber surface which tighten the fiber to resist the pull-out motion.

The fracture surfaces after fiber pull-out tests were illustrated in Fig. 9. However, no significant difference is found in fracture surfaces between the cooling rate controlled samples((a), (b)). At the interface region, the features of shear failure is found with mixed fractography of hackles, matrix globules and fiber breakages, which has been produced from strong interfacial bonding. Merely quench cooled specimen(c) displays some differences such as dominant resin failure and smooth surface covered with resin without fiber breakages. It means that most of failure in quench cooled specimen occurred at the resin or interface region without great resistance due to almost no transcrystalline and matrix crystalline.

Conclusions

From the investigation of crystallization behavior during the preparation and interfacial adhesion of UHMWPE/LLDPE composites, following conclusions can be made:

a) The crystallization behavior of LLDPE resin was changed with the inclusion of UHMWPE fibers which cause the faster crystallization rate.

b) In composites, transcrystallization on UHMWPE fiber surface which preceded bulk crystallization of LLDPE matrix was observed and changed with cooling rate.

c) Prepared UHMWPE/LLDPE composites show very high interfacial strength due to the strong interfacial adhesion from molecular interdiffusion and transcrystallization of matrix resin on the fiber surface.

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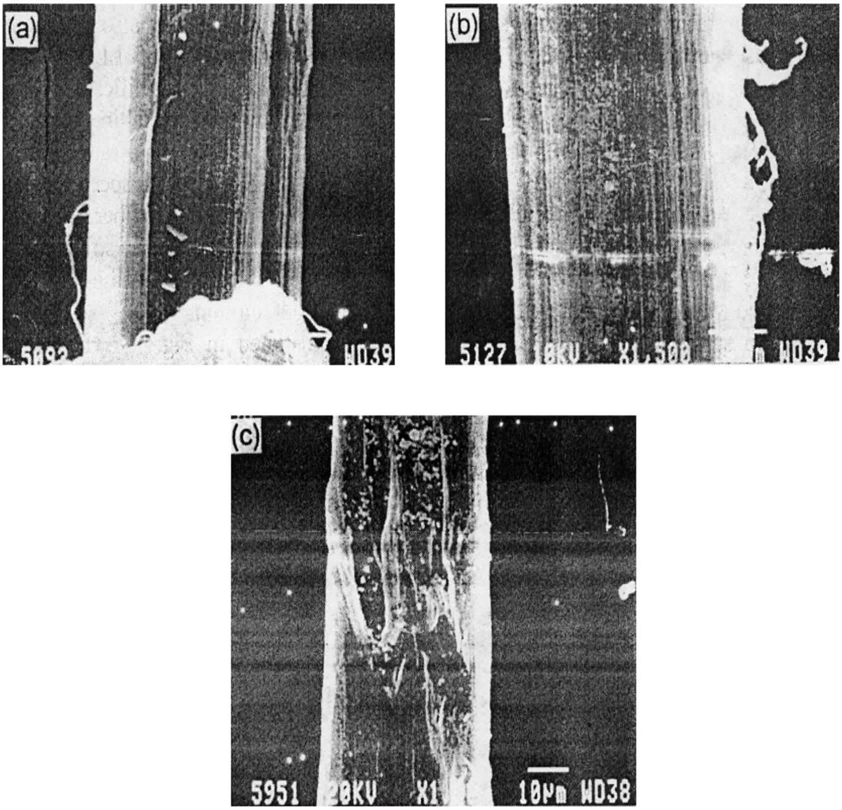

Fig.9 Fracture surface of UHMWPE/LLDPE composites after fiber pull-out test as cooling rate varied : (a) 1 °C/min., (b) 20 °C/min. and (c) quench cooled