Effect of Electric Irradiation on the Mechanical Properties of Polypropylene/Vapor Grown Carbon Fiber Composites Prepared by Melt Compounding

TANOUE Shuichi*, NITHIKARNJANATHARAN Jittiwat, SUZUKI Takeo,
UEMATSU Hideyuki, IEMOTO Yoshiyuki

Graduate School of Engineering, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507, JAPAN

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Abstract

In this study, we discussed the effect of the electric irradiation on the properties of Polypropylene (PP)/Vapor-grown carbon fiber (VGCF) composites prepared by melt compounding using a twin-screw extruder. Ethylene-propylene random copolymer was included in PP. Graft copolymer of maleic anhydride of polypropylene (MA-PP) was employed as an additive agent. The Young's modulus of PP and PP/MA-PP increased with the irradiation dose. On the other hand, the increments of Young's modulus of PP/VGCF and PP/MA-PP/VGCF to irradiation dose were smaller than those of PP and PP/MA-PP. The effect of electric beam on the yield stress coincided to that of Young's modulus. According to the X-ray diffraction results, the crystallinity of PP is almost independent of electric irradiation. Thermal conductivity of the composites was also independent of the electric irradiation even if the thermal conductivity increased by adding of VGCF. It is clear that the dispersion and shape of VGCF would not be broken by the electric irradiation. We concluded that the Young's modulus could be increased with irradiation beam due to cross-linking of amorphous ethylene component and maleic anhydride component and the chemical reaction was inhibited with VGCF because the mobility of the amorphous chain could be constrained by VGCF.

Key Words: Polypropylene, Vapor grown carbon fiber, Melt compounding, Electric irradiation

1. Introduction

One of the methods for giving high performances to a plastic is to mix the reinforcement such as glass fiber and filler, or other functional material to the plastic. When the nano-filler whose size is nano-order is mixed with the matrix, we expect the expression of several functions, e. g. the increase of tensile strength, the improvements of thermal properties and the gas barrier effect even if the small amount of nano-filler is mixed in the polymer [1]. One example of the polymer/nano-order composite systems with high performance is the polymer/clay nanocomposite using layered montmorillonate. Kojima et al. [2] introduced the study of the nanocomposites of polyamide-6 (PA6) with clay prepared by the polymerization. They demonstrated the several improvements of the properties by adding the small amount of clay (usually 1 to 5 wt%). The reactive method such as polymerization or stirring in a solution has the advantage in order to obtain the nanocomposite with well dispersed nano-filler. However, the melt compounding is more industrially useful than the reaction method because there are

some advantage points in melt compounding, e.g. 1) It is rapid, less than about 10 min, 2) It is possible to use existing equipment such as a twin-screw extruder. Many studies of polymer/clay nanocomposites using several kinds of polymers were carried out by several researchers [3–6].

From an industrial point of view, multi walled carbon nano-tube (MWNT) which is large aspect ratio has been focused because the handling is easier as compared with single walled carbon nano-tube (SWNT). For example, Isayev et al. [7] prepared polyetherimide (PEI)/MWNT composites by melt compounding using an ultrasonically assisted twin screw extrusion process. They found that ultrasound has an effect on the tensile strength and Young's modulus of the nanocomposites. Meincke et al. [8] prepared the conductive polycarbonate (PC) composite using a high density polyethylene (HDPE) and MWNT by melt compounding using a masterbatch process. The electrical conductivity of this composite was maximum value at MWNT content of 30 wt%, and this depends on the screw rotation speed and mixing time on melt compounding process. Potshke et al. [9] studied the melt

* Corresponding author: E-mail: tanoue@matse.u-fukui.ac.jp, Tel: +81-776-27-8969, Fax: +81-776-27-8767

rheological properties of polycarbonate (PC)/MWNT composites prepared by melt compounding using a masterbatch process. The non-linearity of rheological properties of the PC/MWNT composite melts at low frequency can be seen at the MWNT content more than 2 wt%. This threshold value is equal to that of electric conductivity in the composites with percolation structure of MWNT. Villmow et al. [10] discussed the MWCNT dispersibility in polylactic acid (PLA) matrix by melt compounding using a co-rotating twin screw extruder. Vapor-grown carbon fiber (VGCF) and vapor-grown carbon nano-tube (VGCNT) which is kinds of MWCNT have been also used in generalized system. Koyama et al. [11] studied the polypropylene (PP) /VGCF composite monofilament by melt compounding. The tensile properties of PP/VGCF composite monofilament were improved by adding the small amount of VGCF (1wt% in the study) in PP matrix. Koyama et al. [12] also studied the effect of process conditions on the properties of Polyamide 6 (PA6)/VGCF composites by melt compounding. They found that the matrix viscosity and the screw rotation speed were found to influence the mechanical properties of PA6/VGCF composites. Yang et al. [13] studied dynamic mechanical and thermal analysis of aligned vapor grown carbon-nanofibers (VGCNFs)-reinforced HDPE by preparing the composite tapes on the drawing process. Dynamic mechanical analysis showed dual increase of storage modulus and loss modulus with draw ratio, i.e. orientation state of VGCNFs in the composite tapes. Therefore, the performances of polymer materials can be improved by adding the small amount of MWNT.

On the other hands, the electric irradiation is one of the useful operations for improvement of the mechanical properties of the plastic. In general, the tensile properties of the polymer can be controlled by irradiating of electric beam because the cross-linking reaction or the degradation of polymer chain would occur. Some degradation occurs by the electric irradiation in case of PP though the polymer chain of PE could be cross-linked. Therefore, some additives are needed for improvement of mechanical properties of PP by the electric irradiation [14, 15]. In addition, the moldability of the polymer for film molding process is improved by the electric irradiation operation. [16]

The effect of electric irradiation on the crystal structure, IR absorption and photoluminescence spectra of PP/MWCNT composites was studied by Diyakon et al. [17]. However, there is little study examples about the effect of electric irradiation on the mechanical properties of PP/MWCNT or PP/VGCF composites. In this study, we investigated the effect of electric irradiation on the properties of PP/VGCF composites prepared by melt compounding using a twin-screw extruder. In order to avoid the degradation of PP chain, we used the copolymerized PP and the graft copolymer of maleic anhydride of polypropylene (MA-PP) as an additive agent. We discussed the effect of electric beam on the chemical reaction and the shape and dispersion of VGCF.

2. Experiments

2.1 Materials

The commercialized PP used in this study was kindly supplied by Sumitomo Chemicals Co. LTD, Japan. Ethylene-Propylene random copolymer was included in homo PP at 15 wt%. We selected VGCF-S, which was purchased from Showa Denko, Co. Ltd, Japan. The dimensions of this VGCF are the diameter of 100 nm and length of $10\mu\text{m}$, and its aspect ratio that is the ratio between the length and diameter is 100. As an additive agent, MA-PP, Umex 1010, which was purchased from Sanyo Kasei Co. Ltd, Japan, was employed as an accelerator of the cross-linking reaction between MA-PP and other material (PP or VGCF-S) because MA-PP has double bond in the carboxylic group. The properties of materials used in this study are listed in Table 1.

2.2 Melt Compounding

Table 2 shows the compounding ratio of the PP/VGCF composites prepared in this study. The VGCF contents of PP/VGCF and PP/MA-PP/VGCF were set up at ca. 2 wt%. PP, MA-PP and VGCF were mixed in a co-rotating twin-screw extruder (S1 KRC kneader by Kurimoto, Ltd., screw diameter of 25 mm, screw length/diameter ratio of 10.2). The PP and VGCF were added separately by feeders from the hopper of the extruder. Before melt compounding, VGCF was dried at 60°C for at least 24 h under vacuum. PP and MA-PP were first dry-mixed by shaking in a

Table 1 Materials used in this study.

Materials	Supplier	Specification
Polypropylene (PP, AZ564)	Sumitomo Chem.	MFR = 30 g/10min (230°C) $M_n = 42,000$, $M_w = 179,000$ Propylene-ethylene random copolymer is included in PP at 15 wt%.
Vapor-grown carbon fiber (VGCF, VGCF-S)	Showa Denko	Diameter = 100 nm Length = 10000 nm
Graft copolymer of maleic anhydride polypropylene (MA-PP, Umex 1010)	Sanyo Kasei	$M_w = 30,000$ MA-PP contains 10 wt% of maleic anhydride.

Table 2 Compounding ratio.

Case	Matrix polymer		VGCF (phr)
	PP (phr)	MA-PP (phr)	
1	100	0	0
2	90	10	0
3	100	0	2
4	90	10	2

plastic bag, before using a feeder for feeding into the top hopper of the twin-screw extruder. Compounding was carried out at a constant barrel temperature of 200°C, a screw rotation speed of 150 rpm and a feed rate of 1 kg/h for each sample.

2.3 Preparation of the specimens

The specimens for tensile testing (JIS K7162, Type 1BA) were prepared by the injection molding machine (NP7 Real Mini by Nissei Plastic Industrial Co., Ltd, Japan) owned by Industrial Technology Center of Fukui Prefecture. The barrel temperature was from 160°C to 200°C, the molded temperature was 40°C and the injection pressure was from 72 MPa to 105 MPa. The specimens for measurement of thermal conductivity were prepared by compression molding at a temperature of 200°C and compression pressure of 19.6 MPa. The size of these specimens is 150 mm × 130 mm × 1 mm in each case.

2.4 Electric Irradiation

Before doing the electric irradiation, the molded samples were dried under a vacuum at the temperature of 50°C for at least 24 h. And the dried samples were sealed immediately in the plastic bag in order to avoid the contact between an air and the samples. The electric irradiation was carried out by using the electron accelerator which can irradiate the electron beam with 10 MeV, in Nuclear Fuel Industries, Ltd., Japan. In this system, the dose is 35 kGy in the once electric irradiation. In this study, we controlled the strength of the electric irradiation (dose) by the number of times (0, 1, 2 and 3 times) in each blended system. The electric irradiation was carried out at room temperature. The interval time was taken enough so that the temperature of the sample may become almost the room temperature.

2.5 Testing and measurement

In order to discuss the tensile properties, tensile tests were carried out at room temperature according to JIS K7162 with a SHIMAZU Autograph AGS-J (Kyoto, Japan). And the tensile test was conducted in dumbbell specimens according to JIS K7162. Young's modulus was measured with an extensometer. The crosshead speed was set up at 1 mm/min for measurement of Young's modulus, and 50 mm/min for measurement of yield stress and strain at yield point. Typically, data from five specimens were averaged and standard deviation to determine mechanical properties. In order to discuss the dispersion state of VGCF in the matrix, the surface morphology of injection molded specimens that fractured during tensile testing was observed with a Hitachi S-2600H at an acceleration voltage of 20 kV. All samples were coated with Au.

In addition, in order to discuss the internal structure of injection

molded specimens for tensile testing, wide-angle X-ray spectra of the injection molded specimens were recorded with a Rigaku SWXD-FK X-ray diffractometer (Cu Ka radiation with $\lambda = 1.5406$ Å; Tokyo, Japan). X-ray diffraction (XRD) measurements were carried out in a 2θ scan range of 10~25° at a scanning rate of 0.5°/min and at room temperature. And the thermal conductivity of the composites was measured by the hot-wire method using a Kyoto Denshi Kogyo QTM-500 quick thermal conductivity measurement equipment (Kyoto, Japan) at room temperature. The measurement of thermal conductivity was carried out 5 times by changing the location of measurement on the surface of the specimens for the measurement of the thermal conductivity.

3. Results and Discussions

3.1 Tensile testing results

First, we discuss the relationship between the tensile properties and the irradiation dose for various PP/VGCF composites. Figure 1 shows the relationship between the Young's modulus and dose for various composites. The width of error bars in the results show the region of standard deviation. The Young's modulus increases by adding VGCF in the composite, this is nothing special. In addition, the Young's modulus increases by adding MA-PP as an additive. When we focus the effect of the electric irradiation, the Young's modulus also increases with dose on the whole. There may be three reasons for getting these results, 1) PP molecules or PP and VGCF may be bridged by the electric irradiation, 2) the electric irradiation may be similar to the weak annealing process because temperature of the composite increases by the electric irradiation, 3) the component of Ethylene-Propylene random copolymer in PP may have the some influences, maybe the cross-linking of ethylene

Fig. 1 Young's modulus as a function of irradiation dose for various PP or PP/VGCF composites.

component in this copolymer, on the performance of composites after the electric irradiation. In this study, the dose per one irradiation operation was 35 kGy because of the apparatus limitation. Then, the crystallization on the electric irradiation would be small because the temperature increasing of PP on one operation of the electric irradiation was theoretically about 20°C. We tried to estimate the crystallization rate of PP at room temperature and room temperature plus 20°C by using the temperature dependence of the crystallization given by the empirical relation [18]. In this estimation, we assumed that the room temperature was 20°C. The crystallization rate of PP at 20°C was $1.07 \times 10^{-3} \text{ s}^{-1}$, and that at 40°C was $8.02 \times 10^{-2} \text{ s}^{-1}$. These values were quite smaller than the maximum crystallization rate of PP that is 0.55 s^{-1} at 65°C [18]. Then, we can conclude quantitatively that the electric irradiation would have a little influence on the crystallization of the specimens. Therefore, the effect of the crystallization in the electric irradiation operation on the Young's modulus of the composites will be small. The important point to note is that the Young's modulus of PP and PP/MA-PP increased by irradiating of electric beam, however the increments of Young's modulus of PP/VGCF and PP/MA-PP/VGCF to irradiation dose were smaller than those of PP and PP/MA-PP. In other words, it is suggested that the chemical reaction could be inhibited with VGCF. The increment amount of Young's modulus for PP and PP/MA-PP by adding of VGCF almost agreed except for PP at 105 kGy. This result implies that the synergistic effect of blending of MA-PP and VGCF is extremely low. Therefore, the chemical reaction of MA-PP and VGCF did not occur. The increase of Young's modulus of PP and PP/MA-PP means that the polymer chain could be reacted by irradiating of electric beam.

Figure 2 shows the yield stress as a function of the dose for various composites. The width of error bars in the results show the

Fig. 2 Yield stress as a function of irradiation dose for various PP or PP/VGCF composites.

region of standard deviation. In case of PP/MA-PP/VGCF composite at 105 kGy, we show the maximum stress in Figure 2. The yield stress of PP and PP/MA-PP increased with irradiation dose until 70 kGy. On the other hand, the increments of yield stress of PP/VGCF and PP/MA-PP/VGCF to irradiation dose were smaller than those of PP and PP/MA-PP though that of PP and PP/MA-PP increased with adding of VGCF. Therefore, we found that this result was the same as Fig. 1. This result is reasonable due to increasing of Young's modulus. It is an important point that the increment of yield stress is lower than that of Young's modulus. In VGCF system, the increasing effect of yield stress is especially weak. The yield strain of the composites as a function of dose was shown in Fig.3. The width of error bars in the results show the region of standard deviation. The yield strain decreased with increasing of dose and VGCF. The same tendency was shown in the elongation at break (not shown here). The fracture cross-section of the specimens after electric irradiation treating or adding VGCF was comparatively smooth. This implies that the deformation of the composite in the micro level would not be uniform because the structure of the composites would become unhomogeneous by irradiating the electric beam or adding VGCF. It is reasonable to suppose that the unhomogeneous structure was developed with irradiation beam and adding of VGCF. In addition, the result leads to our presumption that the chemical reaction locally arose by irradiating electric beam in PP and PP/PP-MA system.

By the way, according to the tensile testing results shown in Figs. 1 and 2, the increments of Young's modulus and yield strength of PP/MA-PP to irradiation dose are a little larger than those of PP except for the case of irradiation dose of 105 kGy. However, at the present stage, it would not be clear which component is effective on the cross-linking reaction in the composites by propylene-ethylene random copolymer in PP or maleic anhydride group in MA-PP.

Fig. 3 Yield strain as a function of irradiation dose for various PP or PP/VGCF composites.

This clarification is one of the future works.

3.2 X-ray diffraction results

In order to consider the effect of the irradiation beam and VGCF on the structure of PP and PP/MA-PP, the internal structure was investigated indirectly. Figure 4 shows the X-ray diffraction results on the fracture cross section of the injection molded specimens at various values of dose. The two prominent peaks are observed in the 2θ range of $10\sim 25^\circ$ for each composite, those are $2\theta = 14.25^\circ$ and 17.05° . These peaks would correspond to the (110) and (040) lattice plane, respectively. And the weak peak is observed at $2\theta = 18.8^\circ$, corresponding to the (130) lattice plane. Especially, the intensity of peak in $2\theta = 17.05^\circ$ increases by adding VGCF. This tendency can be seen in other studies [12], i.e. the addition of VGCF does affect the crystal structure of PP matrix and there is a preferential growth of PP crystallites along the b -axis during nucleation. Next, we discuss the relationship between the peak position and the dose. The peak intensity would be a maximum at the dose of 70 kGy except for the case of PP/MA-PP composite. In addition, the peak intensity at $2\theta = 14.25^\circ$ of PP and PP/VGCF composite at the dose of 105 kGy is a little (less than about 5%) smaller than that at 70 kGy. In case of PP/MA-PP/VGCF composite, the decreasing rate of peak intensity at $2\theta = 14.25^\circ$ is a little large, about 40%. The crystalline structure of the composite may be broken by the strong electric irradiation. However, the electric irradiation would have little effect on the crystalline structure of the composite because the locations of the peak are almost independent of the value of dose. Therefore, it is obviously difficult to consider that the reason of the slight improvement of

Young's modulus of PP/VGCF composite by electric irradiation is the creation of crystalline structure in PP/VGCF composites by temperature increasing of the composites in the electric irradiation. The result of X-ray diffraction means that the structure and degree of crystallization almost could not be change with irradiation beam and VGCF. In other word, the degree of amorphous chain is almost constant though VGCF was added to PP or PP was irradiated by the electric beam. Therefore, it is clear that the Young's modulus increased with the chemical reaction of ethylene component and adding of VGCF because the glass transition temperature (T_g) of PP including ethylene copolymer is about -50°C . It should be also explained that the amorphous MA-PP chain, of which T_g is about -10°C , could be reacted with ethylene component because the crystallinity of MA-PP is low due to adding maleic anhydride. A further important point is that the composite became fragile because the elastic component constituted with amorphous chain is locally enhanced.

By the way, as shown in Figs.1 and 2, the Young's modulus and yield strength of PP and PP/MA-PP at the dose of 105 kGy were smaller than those at the dose of 70 kGy. One possibility the reason why these were occurred is that the degree of breaking the amorphous structure would be larger than that of cross-linking reaction in PP matrix. Another possibility of the reason is that the cross-linking reaction in PP matrix may be reduced by the large electric beam. In addition, the yield stress and yield strain of PP/VGCF composites were almost independent of the dose because the chemical reaction would be inhibited with VGCF. Then, the yield stress and yield strain of PP/MA-PP/VGCF, which showed the maximum yield stress and minimum yield strain at 105 kGy in our study, may be constant values when the dose add to over 105 kGy. The detail discussions about the properties at high irradiation dose are one of the future works.

3.3 SEM observations

Figure 5 shows the SEM photos of the fracture cross-section of PP/VGCF composites after tensile tests. The white parts show VGCF, and the dark ones show the matrix polymer. VGCF in the composite is dispersed well in a whole by melt compounding although there are some aggregates in the composites shown by the broken line circles in these photos. The fracture cross-section seems to be smooth when the irradiation dose increases. Taking into consideration the tensile strength results, this implies that the composite may become stiff because the some cross-linking reaction in the composites may cause by the electric irradiation. Then, the breaking state of VGCF on the fracture cross-section in the composite would not be changed by the electric irradiation. At least, there would be no effect of the electric irradiation on the degradation of VGCF. Figure 6 shows the SEM photos of the fracture cross-section of PP/MA-PP/VGCF composites after tensile tests. To add the MA-PP in the composite has little influence on the

Fig. 4 XRD diffraction results for the injection molded specimen of each PP or PP/VGCF composites. (a) neat PP, (b) PP/MA-PP composites, (c) PP/VGCF-S composites, (d) PP/MA-PP/VGCF-S composites.

Fig. 5 SEM photos of the fracture cross-section of the injection molded specimens after tensile testing for PP/VGCF-S composites at various irradiation dose.

Fig. 6 SEM photos of the fracture cross-section of the injection molded specimens after tensile testing for PP/MA-PP/VGCF-S composites at various irradiation dose.

dispersion state of VGCF in the composites. The fracture cross-section seems to be smooth when the irradiation dose increases. This is the same result in case of PP/VGCF composite. The domain structure of ethylene component could not be observed from SEM observation. According to the testing results of tensile testing, XRD and SEM observation, the domain structure of cross-linking ethylene component in the composite may be similar to the separated domain structure of ethylene components with submicron order size in PP matrix from TEM photos shown by Shiromoto and Koyama [19].

Fig. 7 Thermal conductivity of the compression molded specimens as a function of irradiation dose for various PP or PP/VGCF composites.

3.4 Thermal conductivity

Figure 7 shows the relationship between the thermal conductivity of the solid composites and the dose at room temperature. The width of error bars in the results show the region of standard deviation. The thermal conductivity increases by ca. 70% by adding 2wt% VGCF in PP. The addition of VGCF contributes to the improvement of the thermal conductivity of PP based composites. Overall the thermal conductivity of the composites was almost independent of the electric irradiation. Therefore, it is suggested that the dispersion and shape of VGCF was not be changed with irradiation of electric beam.

4. Conclusions

In this study, we investigated the effect of the electric irradiation on the mechanical properties of PP/VGCF composites prepared by melt compounding using a twin-screw extruder. Ethylene-Propylene random copolymer is included in our used PP at 15wt%. Graft copolymer of maleic anhydride of polypropylene (MA-PP) was employed as an additive agent.

The Young's modulus of PP and PP/MA-PP increased with the irradiation dose. On the other hand, the increments of Young's modulus of PP/VGCF and PP/MA-PP/VGCF to irradiation dose were smaller than those of PP and PP/MA-PP. The effect of electric beam on the yield stress coincided to that of Young's modulus. The yield strain decreased with an increase of the irradiation dose. According to the X-ray diffraction results, the crystallinity of PP is almost independent on the electric irradiation. Thermal conductivity of the composites was almost independent of the electric irradiation the even if the thermal conductivity increased by adding VGCF. It is confirmed that the dispersion and shape of

VGCF would not be changed by irradiating electric beam. We have summarized that the Young's modulus could be increased with irradiation beam due to cross-linking of amorphous ethylene component and maleic anhydride component and the chemical reaction was inhibited with VGCF because the mobility of the amorphous chain could be constrained by VGCF.

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