

福井大学審査学位論文

**A Dissertation Submitted to the
University of Fukui for the Degree of
Doctor of Engineering**

**Mechanical Properties and Thermal Conductivity of
Polymer/Vapor Grown Carbon Fiber Composite Prepared
by Melt Compounding Using a Twin-Screw Extruder**

(二軸押出機を用いた溶融混練で作製されたポリマー
／気相成長炭素繊維系複合材料の機械的特性と熱伝導性)

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Nithikarnjanatharn Jittiwat

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Chapter 1

Introduction

1.1 Background

Composite materials have been used in improving the defect of polymer materials. They are mainly composed of two components, a matrix and reinforcement. Polymer materials are composed of two or more constituents combined in such a way that each constituent affects the final property separately, producing new properties unachievable by the single constituent acting alone. Advantages of composites are not only in weight reduction but also in superior excellent mechanical and thermal properties. Hence, numerous studies have begun to focus on the characteristics of reinforcements and composite materials.

From several century composites have research and developed, some with highly valuable properties. With careful combination of the reinforcement and the matrix, researcher can fabricate composites that meet specifically required properties. Composites can be an alternative for conventional applications of polymer materials, such as organoclay and carbon fiber. In addition, composites can provide highly advanced properties that are beyond the capabilities of polymer material.

Composite appeared soon after the introduction of polymer during 19th century. A century ago, the first plastics were modifications of natural materials. Industrial chemists later produced plastics only one from chemical reactions. Since the 1950s, plastics have grown into a

major industry that affects all of our lives – from providing improved packaging to giving us new textiles, to permitting the production of fantastic new products and cutting edge technologies in such things as televisions, cars and computers. Polymer composite has been developed by researchers continue to meet the needs of industry and well-being.

A material is one component of the composite. Polymer are commonly used as matrix materials and mixed with various fiber reinforcements. It is important to understand the characteristics of polymer matrixes. There are two types of major categories: thermoplastic and thermosetting. Thermosetting polymer, such as polyester or epoxy is used as liquid resin, which becomes rigid when they are cooled. The setting process is unrecyclable, so that thermosetting matrices do not become soft under high temperature environments. Thermoplastics, such as polycarbonate and polypropylene, are hard at low temperatures but soft at high temperatures. They have higher fracture toughness and are recyclable. Metal, ceramic and carbon are also used as matrices for some highly specialized purposes. Such as, Carbon fiber matrices are used for high temperature heat exchangers.

The carbon fiber is widely used in popular applications since its functional properties. It is interesting in carbon fiber reinforced because five times stronger than steel while weight can be five times lighter. Due to carbon fibers can have many times higher thermal conductivity than copper, highly thermal conductive composites are benefit for manufacturing. Then, carbon fiber can provide the mechanical properties and thermal conductivity to the polymer composites.

Carbon fiber, especially carbon nanotube, has been considered as one of the good fillers for polymer composites since to control mechanical properties and thermal conductivity. Carbon nanotubes were discovered while studying by-products of are-evaporation synthesis of fullerenes

[1]. These are large macromolecules that are distinctive for their size and possess extraordinary physical properties. They can be depicted as a sheet of graphite rolled up like a cylinder. These network structures have formed much enthusiasm in the recent year and a large amount of research has been devoted to their understanding. It has been found that nanotubes have a very wide range of electrical, thermal and mechanical properties depending on their geometries, such as diameter and length. Vapor grown carbon fiber (VGCF) is a variation of multi wall nanotube (MWNT), which is assembly of concentric single wall nanotubes (SWNTs)-cylinders inside other cylinders.

During the last few years, VGCF has received increasing interesting as a lower cost alternative for conventional carbon fiber. Since the VGCF grows for only a few minutes in a reactor, VGCF's size is smaller than traditional carbon fibers because VGCF's diameters are about 20-200 nm and their lengths below 100 μm [2, 3]. VGCF can offer advantages of economy and convenience of processing over polymer composites. Particle fiber reinforced composites can be manufactured by inexpensive and high volume production available processed, such as injection and extrusion. However, there are several issues in using VGCF as reinforcement polymer composites.

Since to competitive mechanical properties, thermal conductivity and the prospect of low cost manufacturing processes, VGCF reinforced composites have received increasing interesting and many studies have been performed to investigate their characteristics with a variety of matrices. Gordeyev et al. [5] produced VGCF reinforced polypropylene (PP) (PP/VGCF) composites and investigated their property changes with respect to draw ratio. Spun and stretched composites with 15 wt% improved tensile strength and tensile modulus. Koyama et al. [6] have reported that the tensile properties of polypropylene (PP)/VGCF composite

monofilament were improved by melt compounding using a twin screw extruder and fiber spinning operation even if the VGCF content is very small (1wt% in this study). Kumar et al. [3] added 5 wt% of VGCF by weight to PP and improved tensile strength by 15% and tensile modulus by 50 %. Copper et al. [7] produced VGCF reinforce polymethyl methacrylate (PMMA) composite and showed well dispersed and network structure of carbon fiber in matrix with mechanical property improvement in the composite. Koyama et al. [8] studied the effect of the matrix viscosity and the screw rotation speed on the properties of polyamide 6 (PA6)/VGCF composites by melt compounding. They found that the matrix viscosity influences on the tensile properties of PA6/VGCF composites using VGCF with high aspect ratio and does not influence on the tensile properties of PA6/VGCF composites using VGCF with low value of aspect ratio. In addition, the screw rotation speed has very few influences on the tensile properties of PA6/VGCF composites using low value aspect ratio. However, it may not clear the net relationship between the tensile properties and the melt viscosity of matrix polymer in this paper because PA6 is crystalline polymer. However, it may not make clear the relationship between the physical properties such as tensile properties and the dispersion state of VGCF in their paper because of containing the effect of VGCF on the crystallization of polymer. Takase et al. [9,10] studied the dispersion state of VGCF in Polycarbonate (PC), which is amorphous polymer, by melt compounding. However, they did not focus the effect of the melt viscosity of polymer matrix on the dispersion state of VGCF.

VGCF as a renewable filler for melt compounding polymer composites is introduced in order to improve their mechanical properties and thermal conductivity as well as economically on composites, which indicates potential for the application of the VGCF filler as mechanical properties and thermal conductivity for polymer/VGCF composites.

1.2 Polymer/carbon nanotube fiber composites

Approaches to the melt compounding of polymer/nanotube fiber composites cover a very broad range of processing technologies, including, in some cases, combinations of different methods. Standard techniques such as extrusion and injection-molding are preferred for economic reasons. A concise review of the literature poses some difficulties due to a lot of experimental parameters that have been explored. The studies, although mostly consistent in themselves, generally evaluate rather different composite systems and low present both an assessment of mechanical properties and thermal conductivity.

Carbon nanotube fiber is distinctive nano size carbon structures with striking mechanical and thermal properties. Carbon nanotubes exist in two forms, a single wall nanotube (SWNT) and a multi wall nano tube (MWNT). Carbon nanotube fiber has special effects, such as larger ratio surface area, high mechanical strength and easily generated reactive sites. However, carbon nano fiber is strongly affected by Van der waal's attraction just due to its small diameter and large surface area. These forces give rise to the formation of aggregates, which in turn, make dispersion of carbon nano fiber in polymer attraction, resulting in improve the mechanical and thermal conductive properties. The methods commonly used to incorporate carbon nano fiber into thermoplastic polymer can be roughly classified into four strategies: (1) melt compounding of carbon nano fiber with polymers [11, 12]; (2) solution mixing or film casting of suspensions of carbon nano fiber in dissolved polymer [13, 14]; (3) in situ polymerization of carbon nano fiber-polymer-monomer mixture [15, 16]; and (4) directly mixing dispersed carbon nano-fiber with water-dispersible polymer latex in aqueous suspension [17, 18].

Nowadays, there has been a growing interest in the applications of VGCF, namely in carbon fiber and polymer matrix composites. As the research on VGCF has mainly been interested with the dispersion and properties of the fiber and the investigation of their applications only recently commenced, the number of publications on this subject is limited. However, the works reviewed cover a wide range of applications.

Hence this process overcomes for compounding VGCF with polymer matrix in order to achieve good dispersion of filler and good functionalization of the outer surface (smaller size but higher contact area) in the composites of polymer/VGCF. Other studies of melt compounding process for preparation of polymer/VGCF composites were carried out by other researchers using other polymer e.g. poly(propylene) [19-20], poly(ethylene) [21], poly(acrylonitrile-co-butadiene-co-styrene) [22], poly(styrene)[23] and poly(methyl methacrylate) [24-25]. Polymer composites containing VGCF have been attracted because of their high mechanical properties and thermal conductivity. The advantage of VGCF compared to conventional carbon fiber is higher aspect ratio, which is important to improve properties of the composites [26]. However, the mechanical properties and thermal conductivity are depended on the effect of viscosity polymer, the size of VGCF and dispersion of VGCF.

1.3 Materials characterization

1.3.1 Polycarbonate (PC)

PC is an interesting and commercially successful class of polymer. The properties of PC are toughness, hard impact and thermal stability. PC is very tough and easily melt compounded, new applications are always being research. PC highly filled with carbon fiber can be made slightly electrical conductivity, thermal conductivity and other operations [27]. Potschke et al [28] have found that multi-walled carbon nanotubes can be dispersed in polycarbonate, leading to highly conductive, filled polymers at loadings of less than 2% nanotubes. In this thesis, we study PC/VGCF in chapter 3 and 4.

1.3.2 Polypropylene (PP)

PP is a carbon chain thermoplastic comprised of propylene homopolymer prepared by stereospecific polymerization in the presence of Ziegler Natta catalysts. The majority of PP is isotactic. PP has good flexibility, low density and resistance to chemicals, scratch, moisture and stress cracking, but decreased dimensional stability, mechanical strength, and resistance to UV light and heat. Among the most versatile polymers, polyolefins such as PP are thermoplastic polymer, made by the chemical industry and used in a wide variety of applications, including packaging, textiles (e.g. ropes, thermal underwear and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, automotive components and polymer banknotes. And PP is used in applications ranging from injection-molded and blow-molded products and fibers and filaments to films and extrusion coating. An addition polymer made from

the monomer propylene, it is rugged and unusually resistant to many chemical solvents, bases and acids.

PP is thermoplastics having a higher consumption because of their well-balanced physical and mechanical properties and their easy processability at a relatively low cost. Mechanical properties of PP are generally modified by melt mixing with carbon fiber [29-31] and CNT fillers [32-35] as well as by melt compounding with other polymer [36-38]. Reinforcement at nanoscale to improve mechanical and other properties including changes in polymer crystallization behavior has been attempted [39-41]. In this thesis, we study PP/VGCF in chapter 5.

1.4 Preparative techniques

1.4.1 Melt compounding

Melt compounding with the filler in the polymer matrix is one of the preparatory processes of the polymer composite. The advantages in the melt compounding are quickly (less than ca. 10 min) and mixing equipment such as twin-screw extruder can be available for preparation of polymer composites. However, it is important to establish the technique for preparation of polymer composites by melt compounding in industry, and many studies of melt compounding process for the preparation of polymer composites have been carried out. The advantages of forming composites by melt processing are interesting. It just downstream production of composite materials, the end-use manufacturers many degrees of freedom with respect to the requirements

of the final product (eg. selection of polymer grade). At the same time, melt processing minimizes capital costs due to its compatibility with existing processes.

1.4.2 Viscosity

Viscosity is defined as the steady-state shear stress divided by the shear rate in a steady simple shear experiment. For a Newtonian fluid, the viscosity is independent of shear rate, and this is also the prediction of the theory of linear viscoelasticity. This means that a molten polymer will exhibit a shear rate independent viscosity at a sufficiently small shear rate, although such a low shear rate may be difficult to access experimentally, especially in the case of polymers with broad molecular weight distribution or long-chain branching. Outside this range, the viscosity is a strong function of shear rate and the dependency of viscosity on shear rate (η) is an example of a nonlinear material function.

1.4.3 Property prediction

Variety models have been objected to predict on the properties of short fiber composites from the fiber and matrix properties. The more useful and generally applicable use the same underlying methods and assumptions. The models assume that: the matrix and fiber are linearly elastic; identical in the size of fiber, shape of fiber and can be characterized by an aspect ratio l/d ; the fiber and matrix are well catch at the surface, and remain that way during unusual. Based on these assumptions, the well-known semi-empirical Halpin-Tsai equations [42] have substantiated to be accurate for prediction of stiffness. Since its relative simplicity, the Halpin-Tsai equations are expanded used, although other refinements or exact theories can be found in review [43-46].

The predictions of the coefficient of thermal expansion for short fiber composites are less frequently found. However, they are generally based on the Schapery-equations [47], as adapted for short fiber materials by Halpin [48]. Same as with the Halpin-Tsai equations, their relative simplicity allows wide utilization. The next step, models to predict the properties of the composite are often used instead of the average fiber length in composite expressions derived earlier to obtain the properties of the composites direction. In short fiber composites, however, fiber length distributions exist as a result of processing. A significant decrease and dispersion in fiber length compared to the initial fiber length is usually observed. A more accurate solution would therefore be to integrate the expressions over the whole range of fiber lengths. For the case of stiffness-prediction, Doshi et al. [49] have shown that differences in final property predictions can occur when taking into account a single fiber length as opposed to the full fiber length distribution. In the case of carbon fibers, a further complication arises as also the fiber strength is dependent on fiber length [50-51]. However, as information on the actual fiber length distribution is generally not available, or can be predicted with existing theories and furthermore requires further calculated effort, most works limit themselves to taking only the average fiber length into account. After accounting for the fiber length, the properties of the final composite are taken as an average of these directional properties over all directions, weighted by the orientation distribution function. This is often called to as ‘orientation averaging’. The directional properties as derived above are used to construct the stiffness and thermal expansion tensors. These tensors can be ‘orientation averaged’ following the method described [52], to derive the final composite properties. In this way, models have been developed to predict elastic modulus and thermal expansion coefficients for arbitrary fiber orientations, showing good agreement with experimental results [53-54]. Variety models have also been proposed to predict strength of short fiber composites, of which some have shown good agreement with experimental results [55-56]. However, most models are limited to random two- or three-dimensional fiber orientation and

their ability to predict strength of composites with arbitrary fiber orientation is limited. The complexity of fiber orientation patterns and fiber length distributions and the structural analysis problems require a model that is able to predict strength for any kind of fiber orientation and length distribution, in any direction and under any loading condition.

1.5 Characterization of composites

Properties of composites are strongly dependent on the properties of their constituent material, their distribution and the interaction among them. The composite properties may be the volume fraction sum of the properties of the constituents or the constituents may interact in a synergistic way resulting in improved or better properties. Apart from the nature of the constituent materials, the geometry of the reinforcement (shape, size and size distribution) influences the properties of the composite to a great extent. The content distribution and orientation of the reinforcement also affect the properties.

Generally, the state of dispersion and exfoliation of particles has typically been established using X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) observation. Choi al. [57] investigation describes fabrication of polymer composites sheets incorporated with VGCF by a solution evaporation and a rolling, and a procedure to determine fiber dispersion, orientation state and electrical and mechanical properties. Characterize of polymer/VGCF composite was investigated by XRD and SEM.

1.5.1 X-Ray diffraction (XRD) analysis

XRD analyze the internal structure of the compound, the specimens were measured by X-ray diffraction technique. Powder diffraction (also called XRD or X-ray diffraction) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline samples. Boris al.[20] investigation PP/VGCF were prepared by melt mixing extrusion, followed by melt drawing. The effect of composition and flow on the morphology was investigated by XRD, higher degrees of crystallinity and crystallization kinetics enhancement. The amount of the orientated crystals increased as a result of VGCF addition, suggesting that the VGCF obstructed the motion of polymer chains. Significant stiffness improvements were observed due to the VGCF and high draw ratios of the filaments.

1.5.2 SEM observation

Scanning electron microscopy (SEM) is a useful tool to confirm deformation processes detected by other methods. In the case of polymer composites the fracture surface of specimens failed during mechanical testing supply the most reliable information about the mechanism of deformation, since these initiate the catastrophic failure of the samples. Some authors [58,59] use in situ deformation measurements in the SEM apparatus. The advantage of this method is that the process is easy to follow. SEM observation allows a qualitative understanding of the dispersion state of the carbon fiber such as VGCF within the polymer matrix.

1.6 Properties

Composites frequently exhibit remarkably improved. Improvements generally include a higher modulus both in solid and melt state, increased strength and thermal stability. The main reason for these improved properties in composites is the stronger interfacial interaction between the matrix and carbon fiber, compared with conventional filled-reinforced systems. Mechanical, thermal and rheological properties are widely searched as a method of evaluation the composites.

1.6.1 Mechanical properties

The focus of this thesis is on mechanical properties. Accordingly, tensile properties of a material are measured to provide information on the mechanical strength of a material. Tests involve the application of a constant rate of uniaxial extension to the sample. The engineering stress, defined as the force normal to the initial cross-section of the test sample is measured as a function of extension, under a constant rate of extension. The chemistry of the hard and soft segments, the degree of phase separation of the carbon fiber and viscosity of polymer can affect the values obtained for Young's modulus, ultimate tensile strength and ultimate elongation. Choi et al. [60] studied the mechanical and thermal property of PC/VGCF composites with 10, 15 and 25 wt%. Microscopic analysis has shown that the VGCF were well dispersed in a PC matrix. The improvement on the PC/VGCF of the composites was attributed to the good mechanical and thermal properties of fillers. Our attention is directed mainly to these processes; carbon fiber fillers were used to study them. Because of their novelty and the enhanced interesting in them we discuss VGCF more in detail in the chapter 3-5

1.6.2 Thermal properties

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. When the temperature increases, an amorphous solid will become less viscous and the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form at some point. The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity. Sanchez-Soto et al. [61] studied the thermal properties of composites PC matrix and polyhedral oligomeric silsesquioxane with phenethyl substituents (Ph-POSS). The Ph-POSS nanocages were added to the PC by direct melt blending at loadings between 0 wt% and 15 wt%. The DSC showed that increasing the amount of nanocages caused a continuous decrease on the composite's T_g . Although little increments on the PC decomposition temperature were found, the presence of Ph-POSS did not improve significantly the thermal stability.

1.6.3 Rheological properties

Dynamic rheological measurements can be defined as the science of the flow deformation of matter. The rheological is very important for both polymer composites. This is true for two reasons. Firstly, flow is involved in the processing and artificial of such materials in order to make useful objects. The fluid rheology is related to polymer processing operations such as the stress level in the extrusion, film blowing and fiber spinning. Abdel-Goad et al. [62] studied PC/MWNT composites were produce with different compositions by diluting a masterbatch

using melt mixing in a DACA-Micro-Compounder. Dynamic rheological measurements of PC/MWNT composites were carried out at 280 °C with a strain-controlled rheometer (ARES, TA Instruments). At a content 0.5 wt% MWNT, a significant change in the frequency dependence of the moduli was observed which indicates a transition from a liquid like to a solid like behavior of the composites. This transition can be related to the formation of a combined network between the nanotubes and the polymer chains.

1.7 Aims of the research

In this study, mechanical properties and thermal conductivity of polymer/vapor grow carbon fiber (VGCF) composites prepared by melt compounding using a twin screw extruder were investigated. The driving force for this work is that VGCF has the economic advantage of conventional carbon fibers. Furthermore, there are very few studies on the VGCF reinforced polymer composites. Since the advent of VGCF, various polymers have been tested as matrices for compounding composites. Among tested matrices, polymer has shown the best compatibility with VGCF the obtained knowledge from PC/VGCF and PP/VGCF composites, such as screw rotation speed, melt viscosity of polymer, VGCF size and VGCF contents form the basis for producing composites.

This study will focus on producing PC/VGCF and PP/VGCF composites, investigating their mechanical properties and thermal conductivity for the VGCF compounding composites. PC/VGCF and PP/VGCF will be melt compounding using a twin screw extruder. The mechanical properties of the composites are determined by the characteristics of the VGCF and

matrix material, the state of the VGCF small quantity of aggregates and dispersion. As seen in earlier studies, the key issues of compounding VGCF reinforced polymer composites are structure, dispersion, VGCF contents and aspect ratio of VGCF in polymer matrices. It can be inferred that well composites show good dispersion, VGCF contents and aspect ratio of VGCF. VGCF dispersion, VGCF contents and aspect ratio of VGCF will be investigated by scanning electron microscopy (SEM).

In chapter 3, we discussed about the properties of polycarbonate (PC)/vapor grow carbon fiber (VGCF) composites by melt compounding using a twin screw extruder. In part 1, we observe the preparation of PC/VGCF composites various PC matrices which have different melt viscosity each other in order to discuss the effect of matrix melt viscosity on VGCF dispersion state and the properties of composites. In addition, we discuss the effect of the size and content of VGCF on the mechanical and thermal properties of the PC. In part 2, we observed the relationship between the rheological properties and the thermal properties is investigated. Especially, the effect of the viscosity of matrix polymer on the dispersion of VGCF has been hardly investigated. In this study, we investigated the effect of the viscosity of matrix polymer on the thermal conductivity of VGCF composite from the view point of rheological properties of PC/VGCF.

In chapter 4, we investigate the effect of screw rotation speed on PC/VGCF composites by melt compounding from the view point of mechanical properties and thermal conductivity. The rheological behavior and thermal conductivity are reported for composites based on different of VGCF aspect ratios, melt viscosity of PC and screw rotations speed. We selected a range of screw rotation speeds from several functions of melt compounding with a twin-screw extruder.

In chapter 5, we discussed the effect of the electric irradiation on the properties of Polypropylene (PP)/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 resulting mechanical properties and thermal conductivity of these PP/VGCF composites were evaluated. In addition, we also investigated the effect of different of the electric irradiation on the properties of PP/VGCF and PP/MA-PP/VGCF composites prepared by melt compounding.

In the final chapter, we briefly summarize the main results obtained during the work, but refrain from their detailed discussion, because the most important conclusions were drawn and reported at the end of each chapter. This chapter is basically restricted to the listing of the major thesis points of the work. The large number of experimental results obtained in the research supplied useful information and led to several conclusions, which can be used during further research and development related to the optimization of properties of polymer in particulate filled and VGCF composites. Research continues in this field at the laboratory and we hope to proceed successfully further along the way indicated by this Thesis.

In the relationship of the chapter 1 to chapter 6 are created by Figure 1.1. The Figure 1.1 shows the step of the research study first chapter 1 introduction. Next chapter 2 experimental procedure is preparation sample of polymer/VGCF and measurement of research concerned. After that, we separate the result and discussion in chapter 3-5 and investigate the effect of the viscosity of polymer matrix, the size of VGCF, dispersion of VGCF, the shape of VGCF, the content of VGCF and electric irradiation on the mechanical properties and thermal conductivity

of polymer/VGCF composites was investigated in terms of the properties of polymer/VGCF and conclusion in chapter 6.

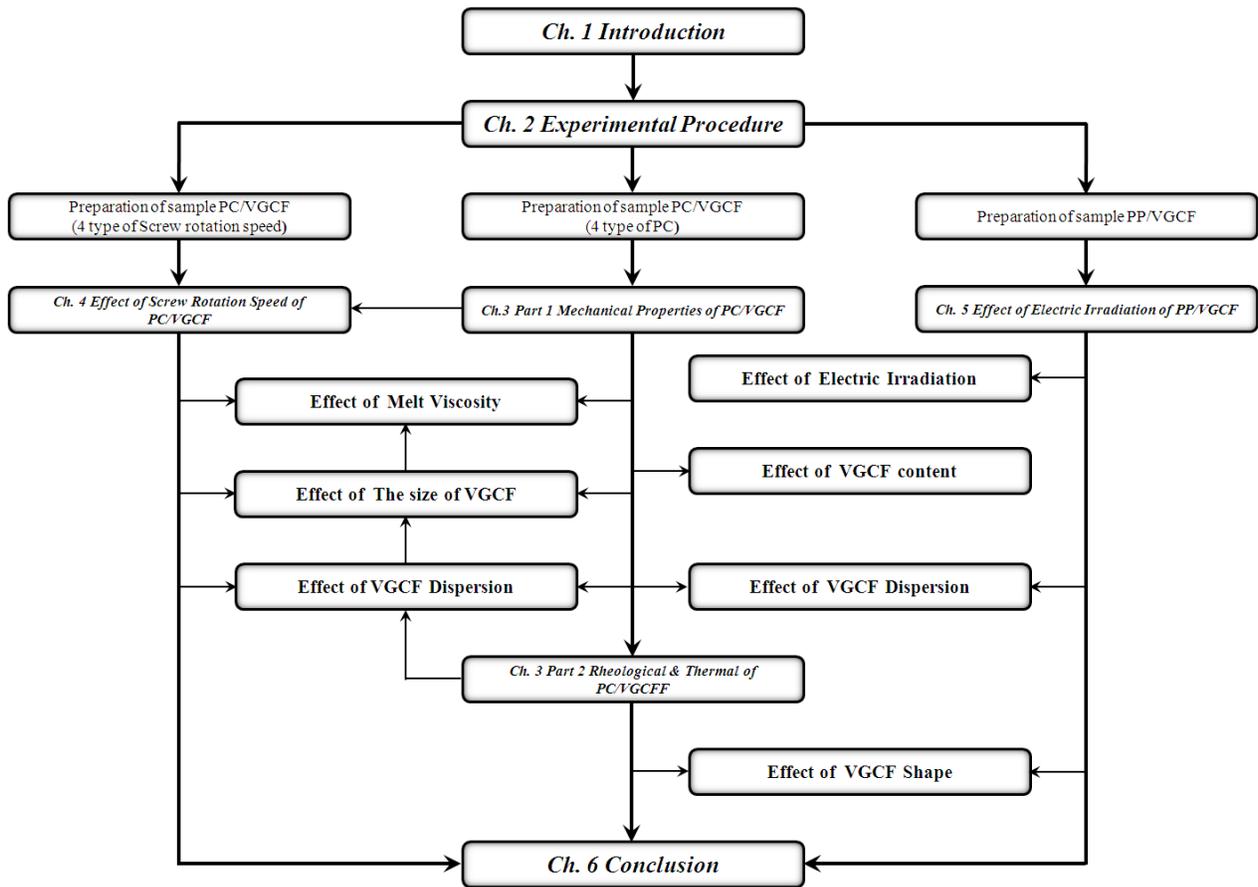


Figure 1.1 The relation ship of research study

1.8 Conclusion

In chapter 1 presents a general introduction for produce polymer/VGCF composites. This thesis we study the mechanical properties and thermal conductivity of polymer/VGCF composites from the view point of the characteristic of polymer. We will focus on producing PC/VGCF and PP/VGCF composites. Our laboratory has been working on various kinds of polymer composite for a long time and the expertise developed helps considerably the identification and interpretation of these processes. The main motive of the thesis is the study of preparation of polymer/VGCF composites by melt compounding using a twin-screw extruder and the factors influencing them, but the measurements were done on a wide variety of polymer related to various projects. At beginning of the research we wanted to obtain more knowledge about and experience in the use of melt compounding technique, thus selected the polymer for study such as polycarbonate and polypropylene modified with VGCF. The knowledge gained in these studies allowed us to progress towards more complex problems and we could develop a unique technique for the determination of interfacial adhesion in strongly bonded composites as described in the next chapter.

References

- [1] Iijima S (1991) Helical microtubules of graphitic carbon, *Nature*, **354**, 56-58
- [2] Darmstadt H, Roy C, Kaliaguine S, Ting JM, Alig RL (1998) Surface spectroscopic analysis of vapour grown carbon fibers prepared under various conditions, *Carbon*, **36**, 1183-1190
- [3] Kumar S, Doshi H, Srinivasrao M, Park JO, Schiraldi DA (2002) Fibers from polypropylene/nano carbon fiber composites, *Polymer*, **43**, 1701-1703
- [4] Tibbetts GG, Gorkiewicz DW, Hammond JrDC (1991) Apparatus for forming carbon fibers
US
- [5] Gordeyev SA, Ferreira JA, Bernardo CA, Ward IM (2001) A promising conductive material: highly oriented polypropylene filled with short vapour grown carbon fibers, *Materials Letters*, **51**, 32-36
- [6] Koyama T, Tanoue S, Iemoto Y (2009) Preparation and properties of polypropylene/vapor grown carbon fiber, *Journal of Textile Engineering*, **55**, 73-78
- [7] Cooper CA, Ravich D, Lips D, Mayer J, Wagner HD (2002) Distribution and Alignment of carbon nanotubes and nanofibrils in a polymer matrix, *Composites Science and Technology*, **62**, 1105-1112
- [8] Koyama T, Tanoue S, Iemoto Y (2010) Effect of processing conditions on the dispersion of vapor grow carbon fiber in a polyamide6 and the crystalline structure of their composites by melt compounding, *International Polymer Processing*, **25**, 181-187

- [9] Takase H, Mikata Y, Matsuda S, Murakami A (2002) Dispersion of carbon-nanotubes in a polymer matrix by a twin-screw extruder, *Seikei Kakou* (in Japanese), **14**, 126-131
- [10] Takase H, Furukawa M, Kishi H, Murakami A (2005) Dispersion of carbon-nanotubes in a polymer matrix by a twin-screw extruder II, *Seikei Kakou* (in Japanese), **17**, 50-54
- [11] Jin ZX, Pramoda KP, Goh SH, Xu GQ (2002) Poly(vinylidene fluoride)-assisted melt-blending of multi-walled carbon nanotube/poly(methyl methacrylate) composites, *Materials Research Bulletin*, **37**, 271-278
- [12] Adrews R, Jacques D, Minot M, Rantell T (2002) Fabrication of carbon multiwall nanotube/polymer composites by shear mixing, *Macromolecular Materials and Engineering* **287**, 395-403
- [13] Haggemuller R, Gonmas HH, Rinzler AG, Fischer JE, Winey KI (2000) Aligned single-wall carbon nanotubes in composites by melt processing methods, *Chemical Physics Letters*, **330**, 219-225
- [14] Safadi B, Andrews R, Grulke E. (2002) Multiwalled carbon nanotube polymer composites: Synthesis and characterization of thin films, *Journal of Applied Polymer Science*, **84** 2660-2669
- [15] Jia ZJ, Wang ZY, Xu CL, Liang J, Wei BA, Wu DH (1999) Study on poly(methyl methacrylate):carbon nanotube composites, *Materials Science and Engineering : A*, **271**, 395-400
- [16] Zeng H, Gao C, Wang Y, Watts PCP, Kong H, Cui X (2006) In situ polymerization approach to multiwalled carbon nanotubes-reinforced nylon 1010 composites: Mechanical properties and crystallization behavior, *Polymer*, **47** 113-122

- [17] Grossiord N, Miltner HE, Loos J, Meuldijk J, Mele BV, Koning CE (2007) On the crucial role of wetting in the preparation of conductive polystyrene-carbon nanotube composites, *Chemistry of Materials*, **19**, 3787-3792
- [18] Ha MLP, Grady BP, Lolli G, Resasco DE, Ford WT (2007) Composites of single-walled carbon nanotubes and styrene-isoprene copolymer lattices, *Macromolecular Chemistry and Physics*, **208**, 446-456
- [19] Kuriger RJ, Alam MK, Anderson DP, Jacobsen RL (2001) Processing and Characterization of aligned vapor grown carbon fiber reinforced polypropylene, *Composites Part A: Applied Science and Manufacturing*, **33**, 53-62
- [20] Boris L, Tatiana L, Hannah H, Gad M (2011) Flow induced orientated morphology and properties of nanocomposites of polypropylene/vapor grow carbon fibers, *Composites Science and Technology*, **71**, 177-182
- [21] Yang S, Taha-Tijerina J, Serrato-Diaz V, Hernandez K, Lozano K (2007) Dynamic mechanical and thermal analysis of aligned vapor grown carbon nanofiber reinforced polyethylene, *Composites Part B: Engineering*, **38**, 228-235
- [22] Shofnera ML, Rodríguez-Macías FJ, Vaidyanathan R, Barrera EV (2003) Single wall nanotube and vapor grown carbon fiber reinforced polymers processed by extrusion freeform fabrication, *Composites Part A: Applied Science and Manufacturing*, **34**, 1207-1217
- [23] Bin Z, Ruowen F, Mingqiu Z, Xianming D, Bin Z, Lichang W, Charles UP Jr. (2006) Studies of the vapor-induced sensitivity of hybrid composites fabricated by filling polystyrene with carbon black and carbon nanofibers, *Composites Part A: Applied Science and Manufacturing*, **37**, 1884-1889

- [24] Shibuya M, Sakurai M, Takahashi T (2007) Preparation and characteristics of a vapor-grown carbon fiber/ceramic composite using a methylsilicone precursor, *Composites Science and Technology*, **67**, 3338-3344
- [25] Wu G, Asai S, Sumita M (1999) A self-assembled electric conductive network in short carbon fiber filled poly(methyl methacrylate) composites with selective adsorption of polyethylene, *Macromolecules*, **32**, 3534-3536
- [26] Bernadette AH, William JB (2005) Polycarbonate carbon nanofiber composites, *European Polymer Journal*, **41**, 889-893
- [27] Brunelle JD, Korn RM (2005) Advances in polycarbonates, *American Chemical Society*, 1-5
- [28] Potschke P, Fornes TD, Paul DR, (2002) Rheological behavior of multiwalled carbon nanotube/polycarbonate composites, *Polymer*, **43**, 3247-3255
- [29] Dvir H, Gottlieb M, Daren S, Tartakovsky E (1865) Optimization of a flame-retarded polypropylene composite, *Composites Science and Technology*, **63**, 1865-1875
- [30] Rana AK, Mandal A, Bandyopadhyay S (2003) Short jute fiber reinforced polypropylene composites: effect of compatibiliser, impact modifier and fiber loading. *Composites Science and Technology*, **63**, 801-806
- [31] Arroyo M, Zitzumbo R, Avalos F (2000) Composites based on PP/EPDM blends and aramid short fibres morphology/behaviour relationship, *Polymer*, **41**, 6351-6359
- [32] Zhang H, Zhang Z (2007) Impact behaviour of polypropylene filled with multi-walled carbon nanotubes, *European Polymer Journal*, **43**, 3197-3207

- [33] Seo M, Lee J, Park S (2005) Crystallization kinetics and interfacial behaviors of polypropylene composites reinforced with multi-walled carbon nanotubes, *Materials Science and Engineering: A*, **404** (2005) 79–84
- [34] Brandl W, Marginean G, Chirila V, Warschewski W (2004) Production and characterisation of vapour grown carbon fiber/polypropylene composites. *Carbon*, **42**,5–9
- [35] Park SJ, Seo MK, Shim HB (2003) Effect of fiber shapes on physical characteristics of non-circular carbon fibers-reinforced composites, *Materials Science and Engineering: A*, **352**, 34-39
- [36] Park SJ, Kim HC, Kim HY (2002) Roles of work of adhesion between carbon blacks and thermoplastic polymers on electrical properties of composites, *Journal of Colloid and Interface Science*, **255** 145-149
- [37] Wang Y, Xiao Y, Zhang Q, Gao XL, Fu Q (2003) The morphology and mechanical properties of dynamic packing injection molded PP/PS blends, *Polymer*, **44**, 1469-1480
- [38] Wong ACY, Lam F (2002) Study of selected thermal characteristics of polypropylene/polyethylene binary blends using DSC and TGA, *Polymer Testing*, **21**, 691-696
- [39] Park SJ, Cho KS (2003) Filler–elastomer interactions: influence of silane coupling agent on crosslink density and thermal stability of silica/rubber composites, *Journal of Colloid and Interface Science*, **267**, 86-91
- [40] Park SJ, Seo DI, Lee JR (2002) Surface modification of montmorillonite on surface acid–base characteristics of clay and thermal stability of epoxy/clay nanocomposites, *Journal of Colloid and Interface Science*, **251**, 160-165

- [41] Da Silva ALN, Rocha MCG Moraes MAR, Valente CAR, Coutinh FMB (2002) Mechanical and rheological properties of composites based on polyolefin and mineral additives, *Polymer Testing*, **21**, 57-60
- [42] Halpin JC, Kardos JL (1976) The halpin-tsai equations a review, *Polymer Engineering and Science*, **16**, 344-352
- [43] Termonia Y (1993) Dependence of fibre critical length on modulus in single-fibre composites, *Journal of Materials Science Letters*, **12** 732-733
- [44] Nielsen LE (1970) Generalized equation for the elastic moduli of composite materials, *Journal of Applied Physics*, **41**, 4626-427
- [45] Tandon GP, Weng GJ (1984) The effect of aspect ratio of inclusions on the elastic properties of unidirectionally aligned composites, *Polymer Composites*, **5**, 327-333
- [46] Dunn ML, Taya M (1994) Elastic-plastic thermal stresses and deformation of short-fiber composites, *Journal of Materials Science*, **29**, 2053-2062
- [47] Reddy JN, Cheng Z (2001) Three-dimensional thermomechanical deformations of functionally graded rectangular plates, *European Journal of Mechanics - A/Solids*, **20**, 841-855
- [48] Halpin JC (1969) Stiffness and expansion estimates for oriented short fiber composites, *Journal of Composite Materials*, **3**, 732-734
- [49] Doshi SR, Charrier JM (1989) A simple illustration of structure-properties relationships for short fiber-reinforced thermoplastics, *Polymer Composites*, **10**, 28-38

- [50] Paiva MC, Bernardo CA, Edie DD (2001) A comparative analysis of alternative models to predict the tensile strength of untreated and surface oxidised carbon fibers, *Carbon*, **39**, 1091–1101
- [51] Padgett WJ, Durham SD, Mason AM (1995) Weibull analysis of the strength of carbon fibers using linear and power law models for the length effect, *Journal of Composite Materials*, **29**, 1873-1884
- [52] Advani SG, Tucker CL (1987) The use of tensors to describe and predict fiber orientation in short fiber composites, *Journal of Rheology*, **31**, 751-784
- [53] Qian D, Dickey EC, Andrews R, Rantell T (2000) Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites, *Applied Physics Letters*, **76**, 2868-2770
- [54] Camacho CW, Tucker III CL, Yalvaç S, McGee RL (1990) Stiffness and thermal expansion predictions for hybrid short fiber composites, *Polymer Composites*, **11**, 229-239
- [55] Fukuda H, Chou TW (1982) A probabilistic theory of the strength of short-fibre composites with variable fibre length and orientation, *Journal of Materials Science*, **17**, 1003-1011
- [56] Templeton PA (1990) Strength predictions of injection molding compounds, *Journal of Reinforced Plastics and Composites*, **9**, 210-225
- [57] Choi YK, Sugimoto KI, Song SM, Endo M (2006) Production and characterization of polycarbonate composite sheet reinforced with vapor grown carbon fiber, *Composites Part A: Applied Science and Manufacturing*, **37**, 1941-1951

- [58] Le QT, Schouler MC, Garden J, Gadelle P (1999) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}_3(\text{CO})_{12}$ as catalyst precursors for the elaboration of VGCF: SEM and TEM study—improvement of the process, *Carbon*, **37**, 505-514
- [59] Wu Q, Gub S, Gong J, Pan D (2006) SEM/STM studies on the surface structure of a novel carbon fiber from lyocell, *Synthetic Metals*, **156**, 792–795
- [60] Coi YK, Sugimoto KI, Song SM, Endo M (2005) Mechanical and thermal properties of vapor-grown carbon nanofiber and polycarbonate composite sheets, *Materials Letters*, **59**, 3514-3520
- [61] Sanchez-Soto M, Schiraldi DA, Hiescas S (2009) Study of morphology and properties of melt mixed polycarbonate-POSS nanocomposites, *European Polymer Journal*, **45**, 341-352
- [62] Abdel-Goad M, Potschke P (2005) Rheological characterization of melt processed polycarbonate-multiwalled carbon nanotube composites, *Journal Non-Newtonian Fluid Mechanics*, **128**, 2-6

Chapter 2

Experimental Procedure

2.1 Introduction

In chapter 2, the whole experimental procedures will be introduced. These composites can be prepared by melt compounding. After that, the samples are measured by variety ways. Tensile testing shows information on the mechanical properties of a material. The thermal conductivity is required for most applications. It can be explained the dispersion state of the VGCF and network structure of VGCF in polymer matrix. The structure of a composite is established using X-ray diffraction (XRD), SEM observation and length analyzed. Differential scanning calorimetry (DSC) was employed to investigate the effect of the VGCF on the glass transition temperature (T_g) of the composites. The rheological was measurement for investigation of the storage modulus (G') and loss modulus (G'') on rheological properties in polymer/VGCF composite. Therefore some additives are needed for improvement of mechanical properties of polymer by the electric irradiation.

2.2 Preparation of composites

The polymer/VGCF composites were prepared with different kind of VGCF loadings and difference screw rotation speed in a twin screw extruder. The PC, PP and VGCF were dried under vacuum at 80 °C for at least 24 h. before compounding and using a feeder for feeding into hopper of the twin screw extruder. Compounding was carried out at a constant barrel temperature of 200 °C (in neat PP and PP/VGCF) and 260 °C (in neat PC and PC/VGCF), a screw speed of 150 rpm for chapter 3 and 5. In chapter 4, we selected four kinds of screw rotation speed, 100, 125, 150 and 175 rpm. After that each polymer/VGCF composites was feed rate 1 kg/h for all extrusion cases. The sample were dried in and oven at 80 °C for at least 24 h under vacuum.

2.3 Tensile testing

The mechanical properties and the factors influencing them are of almost importance of us. Tensile test is often the preferred property to study. Tensile test was conducted in dumbbell specimens according to JIS K7162. Tensile test was performed by using the Shimazu Autograph AGS-J [1] with digital data acquisition. The cross head speeds were set at 1 mm/min for Young's modulus measurement and 10 mm/min for tensile strength and elongation at break measurements for chapter 3 and 4. In chapter 5, yield stress and yield strain were set at 50 mm/min for measurement. An extension rate was measured by using a strain gauge for the measurement of

Young's modulus. Typically, data from five specimens were averaged and standard deviation to determine mechanical properties.

2.4 SEM observation

SEM observation allows a qualitative understanding of the internal structure, spatial distribution and dispersion of the particles within the polymer matrix. In chapter 4, the surface of the sample PC/VGCF was fractured in liquid nitrogen. On the other hand, chapter 3 part 1 and chapter 5, the surface morphology of polymer/VGCF sample that was fractured after tensile testing was observed with a Hitachi S-2600H at an acceleration voltage of 15-20 kV. All samples were coated with gold (Au). We will discuss the dispersion state of VGCF in the composites from these SEM photographs. SEM analysis of each specimen found an average length of VGCF in polymer matrix.

2.5 Glass transition temperature measurement

We have focused the effect of VGCF on PC matrix under various annealing temperatures with DSC (differential scanning calorimeter). DSC was employed to investigate the effect of the VGCF on the glass transition temperature (T_g) of the composites. The glass transition temperature was measured with a DSC model 6220 (Seiko Instruments Inc.). Samples weighing

about 10 mg were sealed in aluminum pans [2]. The temperature range was conducted from 50 to 300 °C under nitrogen atmosphere. The heating and cooling rates were set at 10 °C /min. All samples were first heated to 300 °C and held isothermal for 3 min to remove thermal history. The samples were cooled to 50 °C using air cooling and reheated again to 300 °C. T_g was recorded during the second heating to avoid interaction from the sample pre-treatment. Detailed and results will be found in chapter 3.

2.6 Rheological measurements

With the aim of finding a correlation between the rheological of the PC/VGCF composites in chapter 3 part 2 and chapter 4, the rheological properties often give the useful information about the dispersion state of VGCF in PC matrix. It is investigated the effect of the viscosity of PC matrix and the size of VGCF on PC/VGCF composites. The sample was prepared by hot pressing at temperature of 260 °C under a constant pressure of 19.6 MPa. The sample was pre-heat for 5 minutes prior to applying a pressure for 2 minutes. The compression mold sample was subsequently rapid cooled under constant pressure for 5 minutes.

Dynamic rheological measurements of PC/VGCF composites were carried out at 260°C with a strain-controlled rheometer (ARES, TA Instruments) using parallel plates for fixture. Parallel plates with 25 mm in diameter were used for the frequency ω sweeps. The ω dependencies of the storage and loss moduli, G' and G'' , were measured in the frequency range

from 0.1 to 100 rad/s. The strain ranged from 0.01 to 0.2 in the linear viscoelastic criterion for PC/VGCF systems.

2.7 Thermal conductivity measurement

The thermal conductivity is required for most applications. It can be explained the dispersion state of the VGCF and network structure of VGCF in polymer matrix. The sample was prepared by hot pressing at temperature of 200 °C in chapter 5 (PP/VGCF) and 270 °C for the chapter 3 and 4 (PC/VGCF) under a constant pressure of 19.6 MPa. The sample was pre-heat for 5 minutes prior to applying a pressure for 2 minutes. The compression mold sample was subsequently rapid cooled under constant pressure for 2 minutes. Sample size required is 130W_150 L_1mm.

Thermal conductivity of PC/VGCF composite was measured with QTM-500 (Kyoto Electronics, Japan) at room temperature. The thermal conductivity of samples was quickly evaluated by employing a hot wire method according to the following equation [3].

$$\lambda = \frac{q \ln(t_2/t_1)}{4\pi(T_2 - T_1)} \quad (2-1)$$

Where λ refers to the thermal conductivity of the sample and q is the generated heat flux per unit length. T_1 and T_2 are the temperature at time of t_1 and t_2 , respectively.

Thermal conductivity of each sample was measured in the flat surface without the effect of irregularity of sample thickness on the thermal conductivity. In addition, we used the reference plates and the software for measuring the thermal conductivity of sheet type samples.

2.8 Evaluation of length of VGCF

The length analyzed of VGCF was investigated by evaluating the disaggregated VGCF according to previous reports [4, 5]. After stirring the dilute PC/VGCF solution dissolved in tetrahydrofuran (THF), the thin film of PC/VGCF was prepared by using a rotational coater at various rotating speed. PC component in PC/VGCF film was carbonized at 500 °C for 20 minute in order to capture the clear image. The length of VGCF was analyzed from the SEM pictures except the inter-tangling VGCF by the software (Nireco CORPORATION, LUZEX AP). Two hundreds of VGCF were analyzed since the average length of VGCF did not depend on the number of VGCF above two hundreds pieces.

2.9 Electric Irradiation

In this thesis, in chapter 5, we investigated the effect of effect of electric irradiation on the properties of PP/VGCF composites prepared by melt compounding using a twin screw extruder. Before doing the electric irradiation, the PP/VGCF was 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.

2.10 X-Ray diffraction (XRD)

XRD is widely used to qualitatively measure the crystalline structure of PP in this study. It is also generally used to ascertain the degree of orientation. The orientation of the crystalline phase is well detected by using the XRD method [6]. In addition, wide-angle X-ray spectra of the injection molded specimens were recorded with a Rigaku SWXD-FK X-ray diffractometer (Cu K α radiation with $\lambda = 1.5406 \text{ \AA}$; Tokyo, Japan). XRD measurements were carried out in a 2θ scan range of $10 \sim 25^\circ$ at a scanning rate of $0.5 \text{ }^\circ/\text{min}$ and at room temperature. This details and results were showed in chapter 5.

2.11 Conclusion

In chapter 2, we explained the experimental procedures carried out in this study. The relationship of experimental procedure in the chapter 1-6 is created by Figure 2.1. The Figure 2.1 shows the step of the experimental of study first chapter 1 introduction. Next chapter 2 experimental procedure is measurement of research concerned. After that, we separate the measurement in chapter 3-5 and the tensile testing SEM observation, glass transition temperature, rheological properties, thermal conductivity, length analyzed, XRD and electric irradiation. The polymer/VGCF composites were investigated in terms of the mechanical properties and thermal conductivity of polymer/VGCF and conclusion in chapter 6.

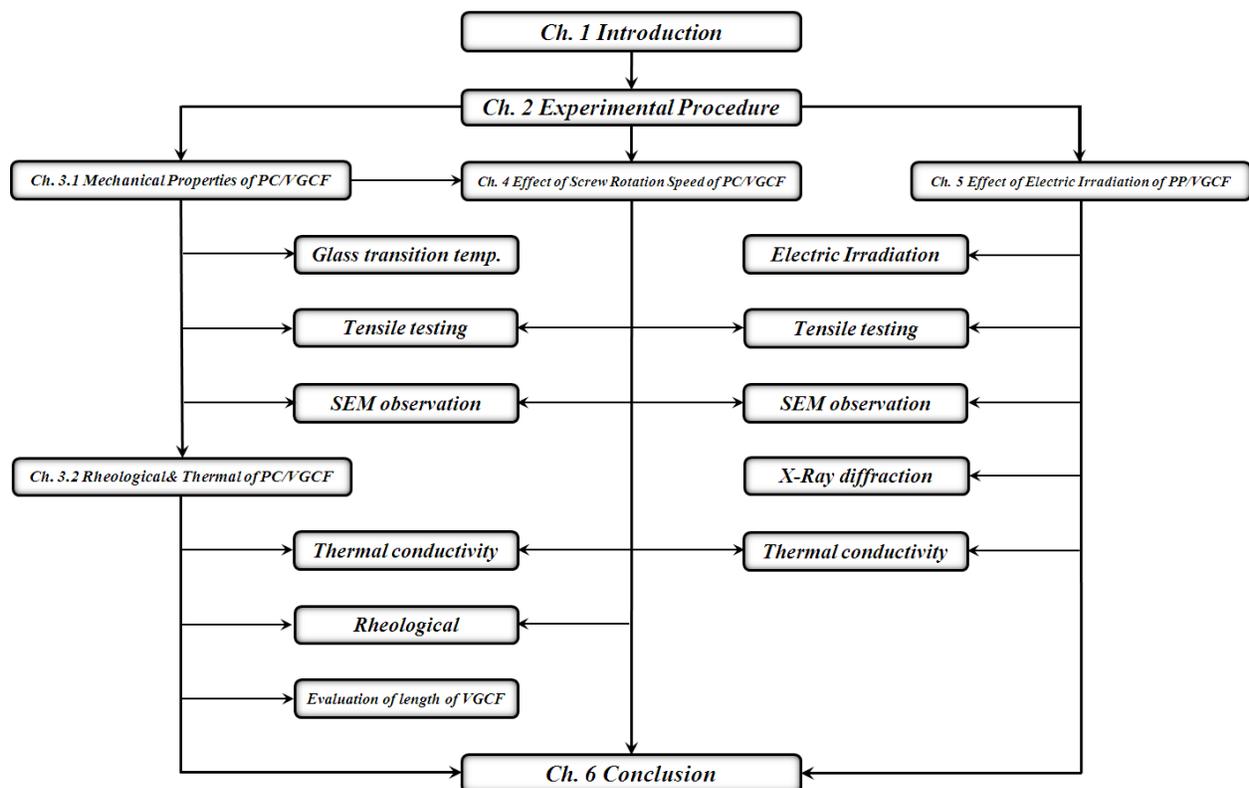


Figure 2.1 The relationship of experimental procedure of research study

The experiments will be conducted on PC/VGCF and PP/VGCF composites with a small amount of an additive in order to explore the effect on properties of the materials prepared by melt compounding using twin screw extruder. The tensile properties of a material are measured to provide information on the mechanical strength of a material. This method has wide application in determining thermal conductivity of polymer/VGCF. This work has been done on the effect of VGCF on the thermal conductivity. The structure of composites is established using XRD because this allows the distance between VGCF to be estimated by peak positions. Scanning electron microscopy (SEM) observation and length of VGCF analyzed can identify the dispersion state of the VGCF in the polymer/VGCF composites, example whether the dispersed VGCF, the size of VGCF and shape of VGCF in polymer matrix. Glass transition temperature measurement for achieve higher degradation temperature for the dispersion state of carbon fiber. The rheological measurement is for investigation the storage modulus (G') and loss modulus (G'') on rheological properties in polymer/VGCF composite. Therefore, an experimental investigation related to effects of VGCF and polymer on properties of polymer/VGCF was carried out by us and results of which have been reported chapter 3-5.

References

[1] Hasook A, Muramatsu H, Tanoue S, Iemoto Y, Unryu T (2008) Preparation of nanocomposites by melt compounding polylactic acid/polyamide 12/organoclay at different screw rotating speeds using a twin screw extruder, *Polymer. Composites*, **29**, 1-8

- [2] Koyama T, Tanoue S, Iemoto Y (2010) Effect of processing conditions on the dispersion of vapor grown carbon fiber in a polyamide 6 and the crystalline structure of their composites by melt compounding, *International Polymer Processing*, **25**, 181-187
- [3] Jinho H, Jeongwoo L, Dongsoo J, Sang ES (2010) Thermal and electrical conduction behavior of alumina and multiwalled carbon nanotube incorporated poly(dimethyl siloxane). *Thermochimica Acta*, **512**, 34-39
- [4] Sato E, Takahashi T, Natsume T, Koyama K (2003) Development of dispersion and length-evaluation method of vapor-grown carbon fiber, *TANSO* (in Jananese), **209**, 159-164
- [5] Sato E, Takahashi T, Natsume T, Koyama K (2004) Comparison of the length of vapor-grown carbon fiber before and after mixing process, *Kobunshi Ronbunshu* (in Jananese), **61**, 144-148
- [6] Abbasi S, Carreau JP, Derdouri A (2010) Flow induced orientation of multiwalled carbon nanotubes in polycarbonate nanocomposites: Rheology, conductivity and mechanical properties, *Polymer*, **51** 922-935

Chapter 3

Properties of Poly(Carbonate)/Vapor Grown Carbon Fiber Composites Prepared by Melt compounding

3.1 Introduction

Carbon fiber is widely used as reinforcements for polymeric matrices in many high technology applications, due to their high specific mechanical properties and excellent thermal conductivity. Carbon fiber, especially carbon nanotube (CNT), has been considered as one of the good fillers for polymer composites due to control of mechanical, electrical and thermal properties [1]. It is interesting to note that good CNT dispersion at relatively low contents is effective in enhancing properties of polymer composites [2, 3]. Vapor grown carbon fiber (VGCF) is a new class of carbon fiber that is distinct from other types of carbon fibers in its production method [4]. VGCF is a highly crystalline carbon nanofiber synthesized by the gas-phase method. Nowadays VGCF's size is smaller than traditional carbon fibers because VGCF's diameters are about 20-200 nm and their lengths below 100 μm . There is a difference in fiber structure between VGCF and CNT, the VGCF has relatively linear fiber structure and higher diameter, than CNT with mostly curve tubes [5]. Thus, the dispersion of VGCF in polymer composites is easier than that of CNT. VGCF structure exhibits excellent electrical conductivity, thermal conductivity, strength, lubricity and resiliency for a high graphitization degree of fiber [6, 7]. Furthermore, VGCF is chemically stable with small surface area. It therefore absorbs only trace quantities of

water. Polymer composites containing VGCF have been attracted because of their high mechanical properties and conductivity. The advantage of VGCF compared to conventional carbon fiber is higher aspect ratio, which is important to improve properties of the composites [8]. According to the utilization of VGCF as reinforcement, fibers must possess a good functionalization of the outer surface (smaller size but higher contact area) in order to be compatible with the matrix as well as promote dispersion and distribution in polymer matrix [9]. Therefore, VGCF reinforced polymer composites have potential application as conducting polymeric materials especially promoting stiffness and thermal properties, which are classified as a new generation of polymer composites and alternative composite materials for aerospace, automotive and structural applications. One of the most important challenges towards improving the properties of composites based on VGCF is obtaining a uniform dispersion of VGCF within the polymer matrix [10].

Polymer is designed for specific applications based on their structure and properties. The most polymer requires modification for a greater range of applications that may require different structural or physical properties [11]. One modification method is the addition of a mixer to create a composite where the polymer may exhibit improvements in mechanical properties and thermal properties. VGCF has been used to modify several polymer compounds. For example, Koyama et al. [12] prepared the polypropylene (PP) /VGCF composite monofilament by melt compounding. The tensile properties of PP/VGCF composite monofilament were improved by melt compounding using a twin screw extruder and fiber spinning operation even if the VGCF content is very small (1wt% in this study). There are some research examples of the effect of melt viscosity of matrix polymers on the tensile properties of the carbon fiber/polymer composites. For example, Koyama et al. [13] studied the effect of the matrix viscosity and the

screw rotation speed on the properties of polyamide 6 (PA6)/VGCF composites by melt compounding. They found that the matrix viscosity influences on the tensile properties of PA6/VGCF composites using VGCF with high aspect ratio and does not influence on the tensile properties of PA6/VGCF composites using VGCF with low value of aspect ratio. In addition, the screw rotation speed has very few influences on the tensile properties of PA6/VGCF composites using low value aspect ratio. However, it may not clear the net relationship between the tensile properties and the melt viscosity of matrix polymer in this paper because PA6 is crystalline polymer. One possibility to solve this problem is to use an amorphous polymer, e.g. Polystyrene (PS), Polycarbonate (PC), Polymethyl methacrylate (PMMA). Takase et al. [14, 15] studied the dispersion state of VGCF in PC matrix by melt compounding. However, they did not focus the melt viscosity of polymer matrix on the dispersion state of VGCF in the composites. Then, there is little study example focused to PC/VGCF systems although there are some research examples of the effect of melt viscosity of matrix polymers on the tensile properties of the carbon fiber/polymer composites. On the other hand, there are some researches about tensile testing, SEM observations and thermal analysis. For example, Shofner et al. [16] compounded poly(acrylonitrile-co-butadieneco-styrene) (ABS) with single wall carbon nanotube (SWNTs) and vapor grown carbon fibers (VGCFs) to create composite materials for use with Extrusion Freeform Fabrication (EFF). The materials containing oriented VGCFs and SWNTs showed modulus improvements of 44 and 93 %, respectively. Bin et al. [17] demonstrated that the addition of VGCF in PS can effectively improve the conductivity of a composite at a relatively small filler content for PS/VGCF/CB(Carbon black) composite. Yang et al. [18] performed the dynamic mechanical and thermal analysis of aligned vapor grown carbon-nanofibers (VGCNFs)-reinforced HDPE by preparing the composite tapes on the drawing process. By differential

scanning calorimetry, they showed that the inclusion of nanofibers hindered the structure evolution of PE upon drawing. However, there are a little research example that the mechanical properties are discussed from the point of view of the melt compounding conditions, e.g. melt viscosity, filler size.

However, fiber suspension generally has remarkably higher viscosity and elasticity than spherical particle suspensions at the same volume concentration. Potschke et al. [2] investigated the rheological properties of PC/CNT composites. The increase in viscosity associated with the addition of CNT is much higher than that of carbon black. The rheological behavior for CNT dispersed suspension was studied by Kinloch et al. [19]. He has discussed the network structure of CNT from the elasticity components measured in oscillatory shear. Mason proposed the equation for the critical concentration in terms of forming the network structure of pulp fiber [20]. Same researchers have also obtained the equation between the modulus and concentration in pulp fiber suspension system [21-25]. Tatsumi et al. particularly have reported that the power law expresses the relationship between the elastic modulus and the concentration of the pulp fiber [26]. They have also reported that a power law in micro fiber suspension system could be theoretically expressed based on the polymer gel solution system [27]. In other words, it is suggested that the dispersion state of fiber can be indirectly estimated with melt rheological properties.

This study is intended to develop vapor grow carbon fiber (VGCF) reinforced polymer (polymer/VGCF) composites. This chapter presents the processing of PC/VGCF composites and mechanical properties, rheological behavior and thermal conductivity. PC/VGCF composites will be produced in the form of a continuous strand by a polymer extrusion process. Composites

strands containing VGCF are obtained by using twin screw extruder. The composite filler have 0 wt% to 6.54 wt% VGCF by volume and investigated for their mechanical properties, such as tensile strength and the Young's modulus. Scanning electron microscopy (SEM) is performed to examine the dispersion state of VGCF in the composites.

In part 1, traditional polymer processing of twin screw extrusion has been widely used in melt compounding process, which provided uniform fiber dispersion by the large shear forces during processing [28]. Hence it can be expected that this process may be able to overcome for compounding VGCF with polymer matrix in order to achieve good dispersion of fiber. This paper focuses on the preparation of polycarbonate(PC)/VGCF composites by a melt compounding using a twin screw extruder using various PC matrices which have different melt viscosity each other in order to discuss the effect of matrix melt viscosity on VGCF dispersion state and the properties of composites. In addition, we discuss the effects of the size and content of VGCF on the mechanical and thermal properties of the PC.

In part 2, the relationship between the rheological properties and the thermal properties is scarcely investigated. Especially, the effect of the viscosity of matrix polymer on the dispersion of VGCF has been hardly investigated. We investigated the effect of the viscosity of matrix polymer on the thermal conductivity of VGCF composite from the view point of rheological properties of PC/VGCF.

Part 1

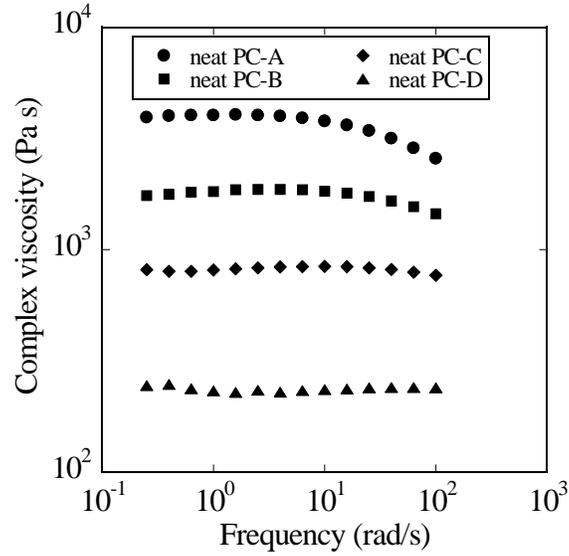
3.2 Mechanical Properties of Poly(Carbonate)/Vapor Grown Carbon Fiber Composites Prepared by Melt Compounding

3.2.1 Material

Commercial grade polycarbonate was kindly supplied by Teijin Chemicals Ltd., Japan. Four different types of melt volume flow rate (MVR) of PC are listed in Table 3.1, which will be referred to PC-A, PC-B, PC-C, and PC-D. Figure 3.1 shows the complex viscosity as a function of angular frequency of PC melts at temperature of 260 °C, and this temperature is as same as the barrel temperature on melt compounding part explained in the next section. The MVR is similar to MFR (Melt flow rate). Obviously, the complex viscosity of PC melt decreases with an increase of MVR. For example, the complex viscosity of PC-A melt at frequency of 100 rad/s is about 10 times larger than that of PC-D one at same frequency. In addition, the vapor grown carbon fibers with two different sizes, namely VGCF-S and VGCF-H provided by Showa Denko K. K., Japan, were used as a nano-filler in this study. The characteristics of the VGCF are listed in Table 3.2

Table 3.1 Properties of polycarbonate

Polycarbonate		Specification		
Type	Commercial code	M_n (g/mol)	M_w (g/mol)	MVR (cm ³ /10 min)
PC-A	K-1300	22,100	57,800	2.5
PC-B	L-1250	16,300	44,800	8
PC-C	L-1225L	16,200	36,400	18
PC-D	AD-5503	12,800	27,600	54

**Figure 3.1** Complex viscosity of neat PC as a function of frequency**Table 3.2** Characteristics of VGCF

Type	Diameter (nm)	Length (μm)	Aspect ratio	Thermal Conductivity (W/(m·K))	Electrical Conductivity ($\Omega\cdot\text{m}$)
VGCF-S	100	10	100	1200	1×10^{-4}
VGCF-H	150	6	40	1200	1×10^{-4}

3.2.2 Sample preparation

The composition of PC/VGCF composites is shown in Table 3.3. PC was compounded with VGCF of 1, 2, 4 and 7 phr (phr is the parts per hundred resins by weight) using a co-rotating twin screw extruder (TSE) (S1 KRC kneader by Kurimoto, Ltd., Japan, its screw diameter of 25 mm, screw length/diameter ratio (L/D) of 10.2). Melt compounding system is shown in Figure 3.2. PC and VGCF were dried in an oven at 80 °C for at least 24 h. The compounding was carried out at a uniform barrel temperature of 260 °C at a screw rotation speed of 150 rpm. The feed rate was set at 1 kg/h for all extrusion cases. After compounding, the composites were then pelletized. Pelletized PC/VGCF composites were molded by the injection molding into tensile testing using the injection molding machine (NP7 Real Mini, Nissel Plastic Industrial Co., Ltd., Japan). Test specimens (dumbbell specimens) were prepared using a barrel temperature of 300-320°C, molded temperature of 80°C, injection pressure of 73-153 MPa and a injection speed of 20-48 cm³/s. Before injection molding, the pelletized PC/VGCF composites were dried in an oven at 80°C for at least 24 h.

Table 3.3 Compounding ratios for various kinds of PC/VGCF composites

Case number of materials	PC	VGCF-S (phr)	VGCF-H (phr)
1	100	0	0
2	100	1	0
3	100	2	0
4	100	4	0
5	100	7	0
6	100	0	1
7	100	0	2
8	100	0	4
9	100	0	7

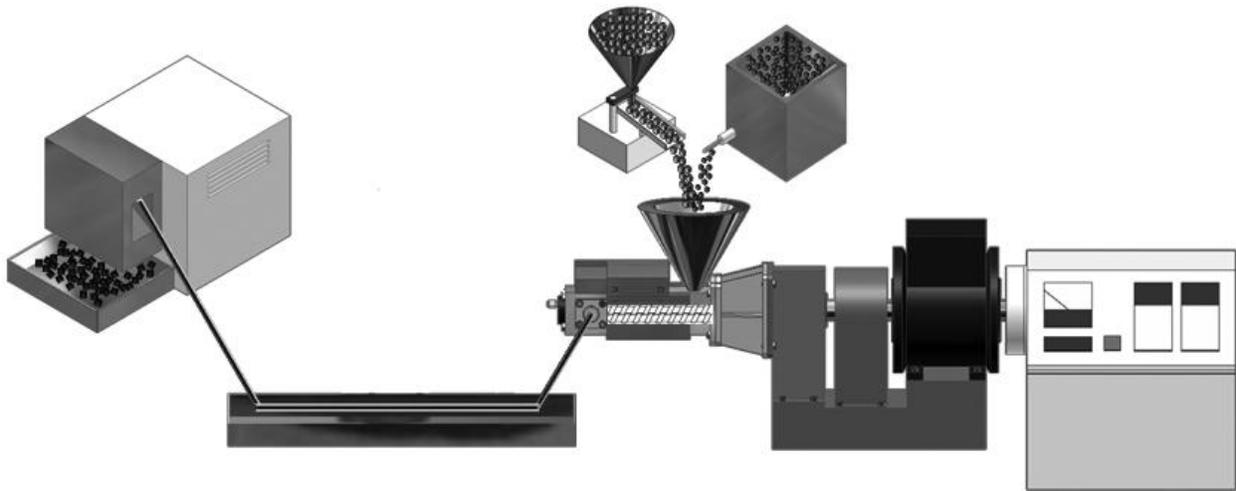
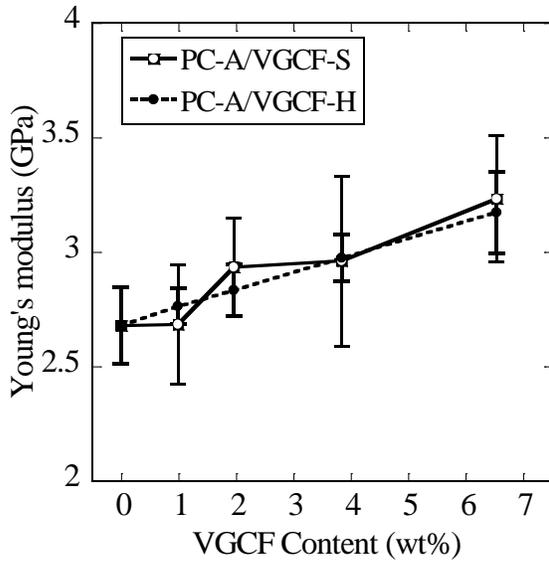


Figure 3.2 Illustration of equipment used for the preparation of composites

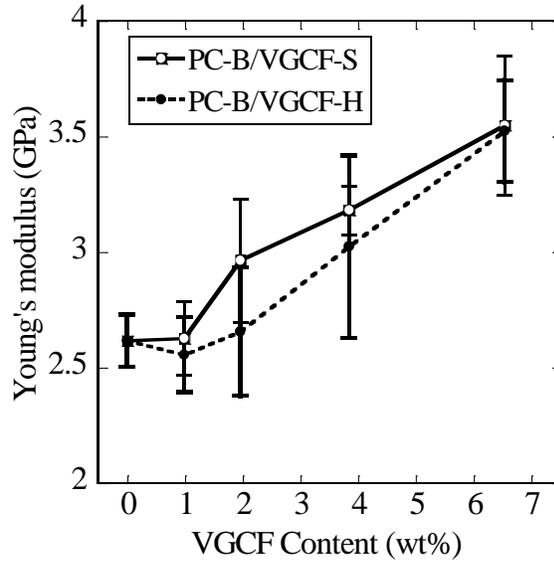
3.2.3 Results and Discussion

3.2.3.1 Tensile testing

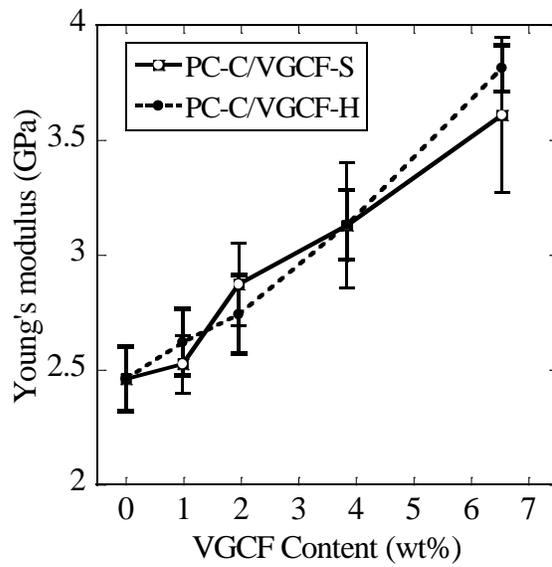
Firstly, we will discuss the effect of VGCF content on the tensile properties of the composites having various PC matrices. Figure 3.3 shows the Young's modulus as a function of VGCF content for various PC/VGCF composites. The width of error bars in the results show the region of standard deviation. The Young's modulus of each PC/VGCF composite increased with blending of VGCF-S and VGCF-H. An increment of Young's modulus of PC/VGCF composites depended on the PC type. PC-C/VGCF composite presents the highest degree of increment in Young's modulus as shown in Figure 3.3 (c). On the other hand, the Young's modulus of PC-D/VGCF composites increased up to VGCF content of 3.85 wt% with no further increment of



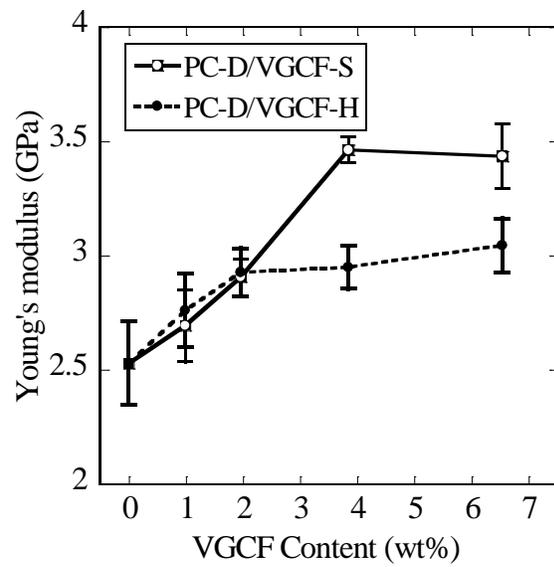
(a) PC-A/VGCF composite



(b) PC-B/VGCF composite



(c) PC-C/VGCF composite



(d) PC-D/VGCF composite

Figure 3.3 Young's modulus as a function of VGCF content for various PC/VGCF composites prepared by melt compounding

Young's modulus at higher VGCF content shown in Figure 3.3 (d). It will be probably due to the lowest melt viscosity of PC-D resulting in an agglomeration of VGCF in PC-D matrix. During compounding, the shear stress imposed on PC-D/VGCF composites becomes small along mixing process.

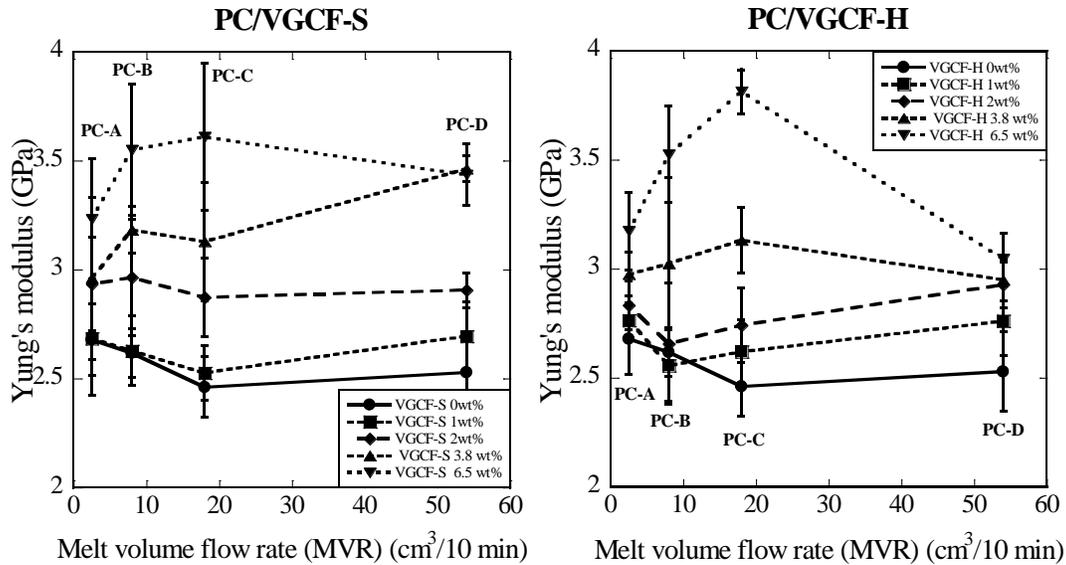


Figure 3.4 Young's modulus as a function of melt volume flow rate (MVR) of neat PC for various PC/VGCF composites prepared by melt compounding

Figure 3.4 shows the Young's modulus of PC/VGCF composites as a function of melt volume flow of neat PC. This Figure was created from the base of Figure 3.3. The VGCF may be not easy to achieve the dispersive mixing in PC-D composites. This may be one reason that the Young's modulus of PC-D/VGCF composites is independent of VGCF content at higher VGCF content. In addition, the increment in Young's modulus of PC-A/VGCF composites per VGCF content becomes also smaller than that of PC-C/VGCF composites. The melt viscosity of PC-A is the largest of all four PC matrixes. Then, the VGCF will be easy to be broken by the strong

shear stress during melt compounding. This may be one of the reasons of low increasing rate of Young's modulus with VGCF content in case using PC-A matrix.

Figure 3.5 shows the tensile strength as a function of VGCF content for various PC/VGCF composites and neat PC. The width of error bars in the results show the region of standard deviation. Tensile strength of PC-C/VGCF and PC-D/VGCF composites with low melt viscosity slightly increased with both VGCF-S and VGCF-H contents while tensile strength of PC-B/VGCF composites almost unchanged as exhibited in Figures 3.5 (a)-(d). On the other hand, tensile strength of the PC-A/VGCF composite with high melt viscosity decreased with an increase of VGCF content. It can be noted that melt viscosity influences on tensile strength of the composites. The degradation of fiber length would occur during melt compounding using the polymer matrix with high melt viscosity because the higher shear stress could be imposed on the fiber in the composites. Thus, the reinforcing capabilities and load transferred between fiber and polymer matrix would be reduced [29]. The shear stress imposed on PC/VGCF composites with high melt viscosity such as PC-A matrix becomes large during mixing process. If the broken VGCF aggregated in PC-A in compounding, the PC-A/VGCF specimen would be nonuniformly deformed before reaching maximum tensile stress because the agglomeration of VGCF became the defection point. This seemed to be reasonable, and may result in the effect of VGCF content on tensile properties of composites based on PC-A matrix. On the whole of Young's modulus and tensile strength, the optimized PC (PC-C in this study) would be existed in the region from PC-A to PC-D.

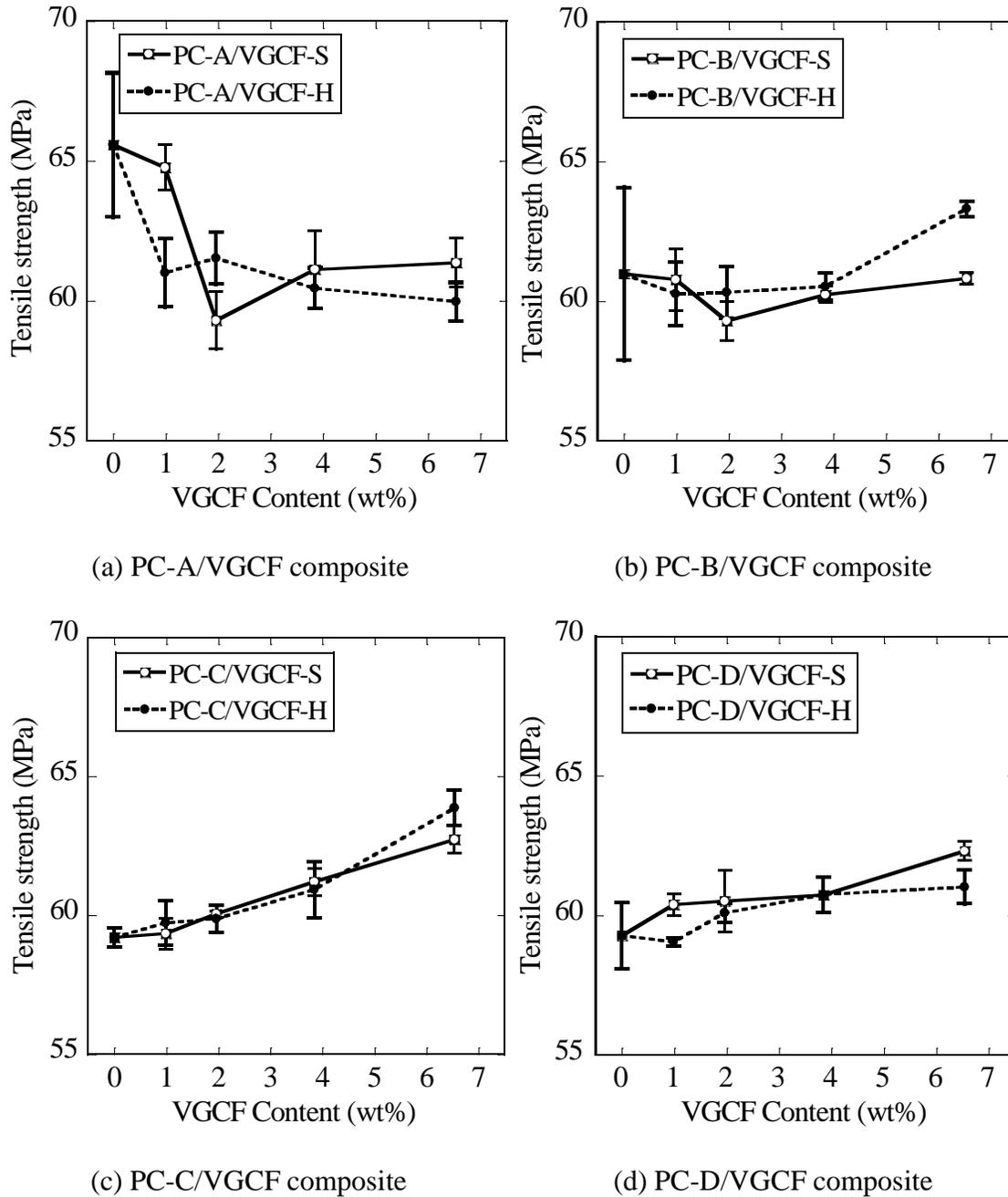


Figure 3.5 Tensile strength as a function of VGCF content for various PC/VGCF composites prepared by melt compounding

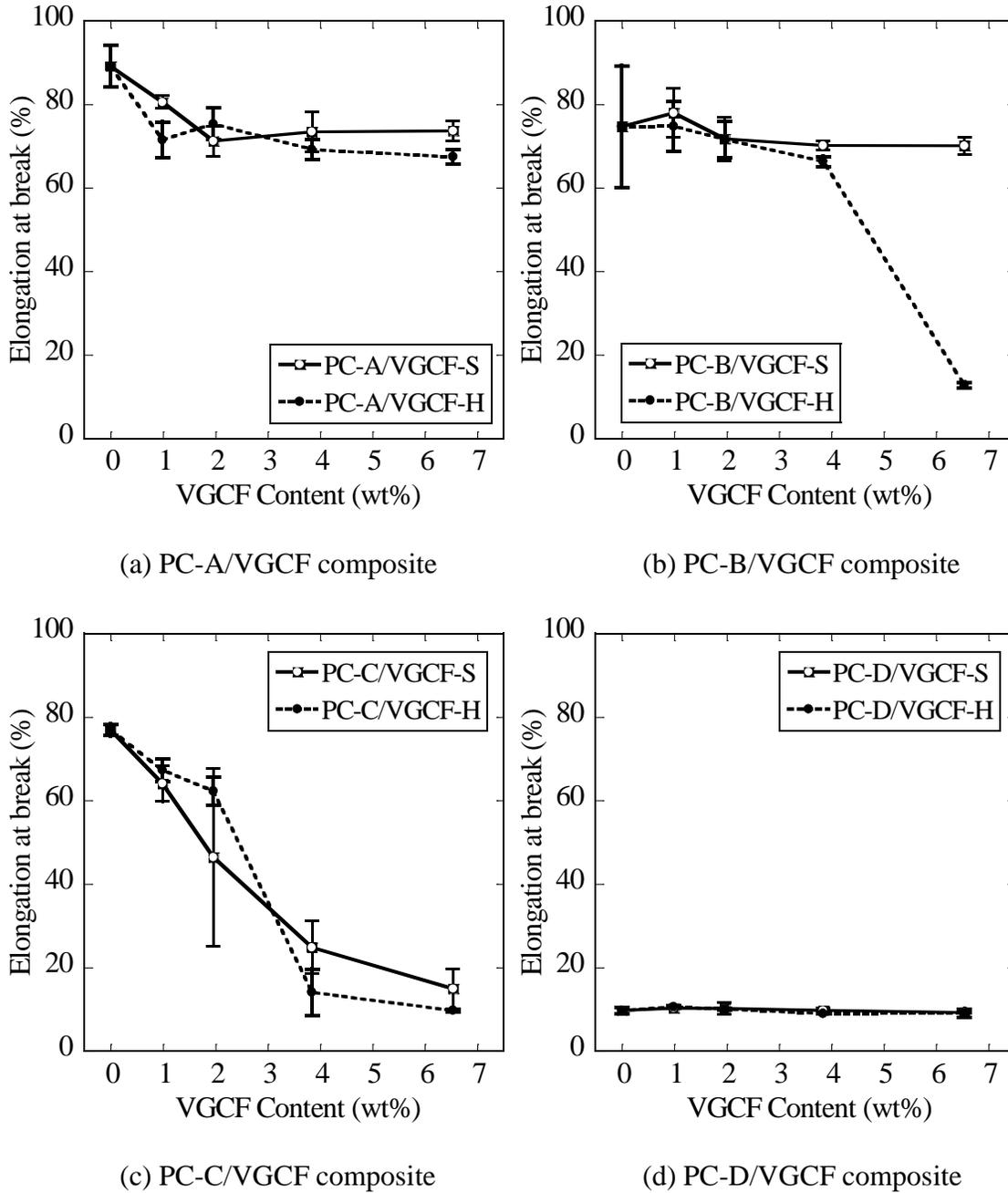


Figure 3.6 Elongation at break as a function of VGCF content for various PC/VGCF composites prepared by melt compounding

Figure 3.6 shows the elongation at break as a function of VGCF content for various PC/VGCF composites and neat PC. The width of error bars in the results show the region of standard deviation. Elongation at break of PC-A/VGCF and PC-B/VGCF composites with restively high melt viscosity slightly decreased with VGCF content except for PC-B/VGCF-H composites at VGCF content of 6.54 wt%. On the contrary, elongation at break of PC-D/VGCF composites almost unchanged. Conversely, elongation at break of the PC-C/VGCF composite with relatively low melt viscosity decreased with an increase of VGCF content in cases using VGCF-S and VGCF-H. At least, these results imply that the elongation at break of PC/VGCF composite as a function of VGCF content mainly depends on the property of matrix polymer, melt viscosity in this study.

Next, we will discuss the effect of VGCF size as well as aspect ratio on the tensile properties of PC/VGCF composite. Fiber diameter of VGCF-S is smaller than that of VGCF-H, however the aspect ratio of VGCF-S is larger than that of VGCF-H. We could obtain the different relativity to the magnitude correlation of Young's modulus and tensile strength of PC/VGCF composites with difference in size as well as the aspect ratio of VGCF. The tensile properties of the composite using VGCF-S with high aspect ratio seem to be slightly larger than those of the composite using VGCF-H with low aspect ratio. The volume per unit fiber of VGCF-S is 0.75 times of that of VGCF-H. Therefore, the number of VGCF-S in the composites would be greater than that of VGCF-H at same VGCF content. Furthermore, the surface area per unit fiber of VGCF-S is about 10% larger than that of VGCF-H. Therefore, the total contact area between VGCF-S and PC matrix is larger than that between VGCF-H and PC one. This may cause the difference of tensile properties of the composites. We expected that the tensile strength and Young's modulus of PC/VGCF-S composites are larger than those of PC/VGCF-H one.

However the relationship between the tensile properties (the Young's modulus and the tensile strength of the composites in this study) and the VGCF size would not orderly depend on the matrix viscosity. Taking into consideration standard deviations, the tensile properties of PC/VGCF composite would be independent of VGCF size. This result implied that VGCF-S was easily fractured by shear flow as compared with VGCF-H because the shape of VGCF-S is slim and long.

3.2.3.2 SEM observation

Figure 3.7 shows SEM photographs of fractured surface of PC/VGCF composites with 6.54 wt% VGCF content after tensile testing. The dark regions and white bands represent the matrix polymer and VGCF, respectively. The photographs revealed brittle fractured surface on the sample with some ductile deformation as melt volume flow rate of the PC matrix became high. This tendency seems to be independent of VGCF size. VGCF appears in the fracture surface in both cases (using VGCF-S and VGCF-H). Some of VGCF protrudes from the fracture surface in case using VGCF-S. However, there is no protruded VGCF on the fracture surface in case using VGCF-H. On the whole, it could be seen that both VGCF-S and VGCF-H were well dispersing in the PC matrix. However, there are some aggregations of the VGCF in the PC matrix (indicated by the circle in Figure 3.7) regardless of melt flow rate of the PC matrix. Moreover, the aggregation size of VGCF-S system was slightly larger than that of VGCF-H one. From the result of SEM observation, it is suggested that the VGCF-S could be easily flocculated as compared with VGCF-H. In addition, the increase of stiffness and strength of the composite in case using VGCF-H is larger than that is case using VGCF-S when PC-C is used as the matrix polymer.

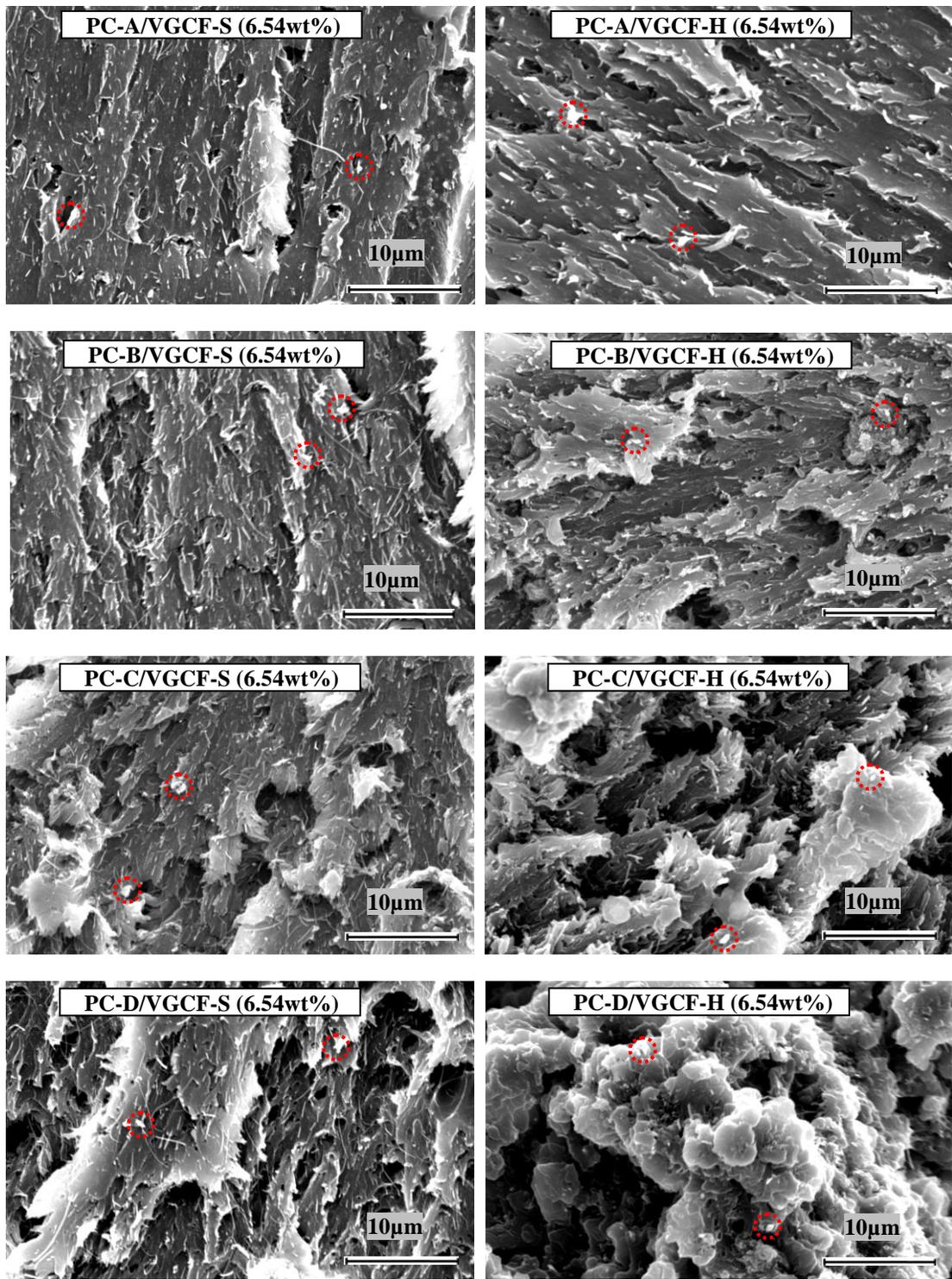


Figure 3.7 SEM photographs of the fracture surface for PC/VGCF composite

3.2.3.3 Glass transition temperature

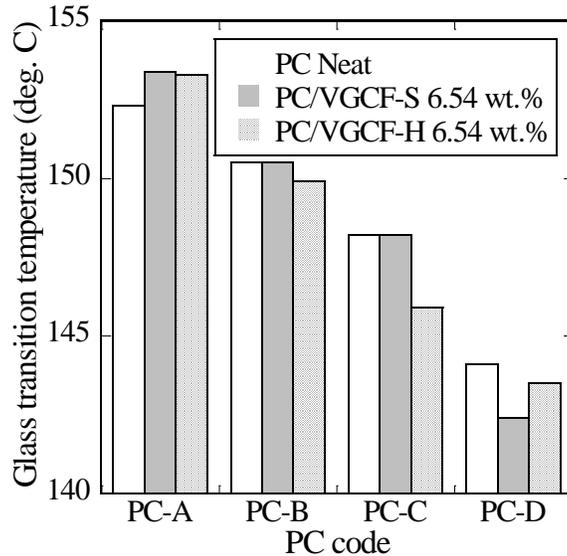


Figure 3.8 Glass transition temperatures of neat PC and PC/VGCF composites at VGCF content of 6.54 wt%

Figure 3.8 shows the effect of VGCF on glass transition temperature (T_g) of neat PC and PC/VGCF composites at VGCF content of 6.54 wt%. T_g of PC-A/VGCF composites increased when PC is incorporated both VGCF-S and VGCF-H. The melt viscosity of PC-A is the largest of all four matrices used in this study, and in general, high viscosity of the composites restricts chain mobility of PC molecule hence T_g of the composites based on PC-A matrix becomes large. Furthermore, an increment of T_g of these composites may indicate a large interaction between VGCF and PC-A matrix. On the other hand, T_g of PC/VGCF-H composites based on PC-B, PC-C and PC-D are smaller than those of neat PC. It could be due to intrinsic low viscosity of these PC matrices. The region of the molecular motion in PC/VGCF composite near the glass

transition temperature would not be restricted by the existence of VGCF-H, which has lower aspect ratio than VGCF-S, in PC/VGCF-H composites. On the whole, the VGCF size has little influence on the glass transition temperature of PC/VGCF composites at VGCF content of 6.54 wt%. This result implies that the VGCF size has a little influence on tensile properties shown in Figures 3.3 and 3.5. As a result, the addition of VGCF would not cause the structure change of PC composites. In addition, the glass transition temperature of these PC/VGCF composites depends on the melt volume rate of PC matrix. In this study, we did not carry out any surface treatment of VGCF because of the reduction of the operation step on melt compounding process. The glass transition temperature of PC composite may increase by adding VGCF with surface treatment. The important part of this argument is that the mobility of polymer chain does not reflect on the mechanical properties because the tensile testing was carried out below T_g of PC. Therefore, what is significant in this argument is that the effect of the dispersion and/or agglomeration of VGCF on the deformation behavior of PC during extension concern the Young's modulus and tensile strength.

3.2.3.4 Discussion of Young's modulus of PC/VGCF composite using the modified Halpin-Tsai equation

The Halpin-Tsai equation has been successful to predict the modulus of polymer/carbon nanotube composites [30]. Considering the random distribution of carbon nanotubes in the polymer matrix, the modified Halpin-Tsai equation [31] can be written as,

$$\frac{E_C}{E_P} = \frac{3}{8} \left(\frac{1 + 2(l_F / D_F) \eta_L V_F}{1 - \eta_L V_F} \right) + \frac{5}{8} \left(\frac{1 + 2\eta_T V_F}{1 - \eta_T V_F} \right) \quad (3-1)$$

$$\eta_L = \frac{E_F / E_P - 1}{E_F / E_P + 2(l_F / D_F)} \quad (3-2)$$

$$\eta_T = \frac{E_F / E_P - 1}{E_F / E_P + 2} \quad (3-3)$$

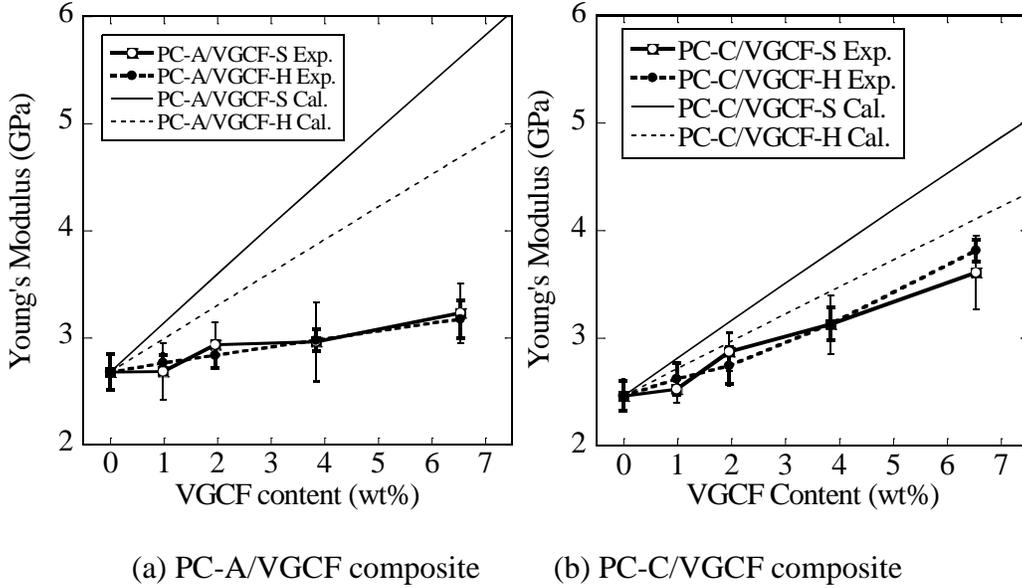


Figure 3.9 Comparison of Young's modulus as a function of VGCF content for PC-A and PC-C based VGCF composites between the calculated values and the experimental data.

Where E_C , E_F and E_P are the Young's modulus of the composite, carbon nanotube and polymer matrix, respectively, and l_F , D_F and V_F are the length, diameter and volume fraction of the nanotubes in the composite, respectively. The VGCF used in this study can be considered as a kind of the carbon nanotubes. Therefore, the Young's modulus of PC/VGCF composite would be estimated by using these equations when the conditions of PC/VGCF composite are assumed to be almost as same as the assumptions of these equations. Then we tried to estimate the Young's modulus of PC/VGCF composites using Eqs. (3-1)-(3-3) and compared the calculated

values to the experimental data. Figure 3.9 shows the comparison of Young's modulus as a function of VGCF content between the experimental data and prediction values calculated by Eqs. (3-1)-(3-3) for PC-A and PC-C based VGCF composites, which shows typical large or small Young's modulus at same VGCF content. In this estimation, we used the following material constants; the Young's modulus of VGCF is assumed as 300 GPa, the density of VGCF is 2.0 g/cm³, and the density of PC 1.2 g/cm³. The estimated Young's modulus is larger than experimental data in both cases even if the Young's modulus of VGCF was assumed as the typical low value in these calculations. According to the SEM photographs, the dispersion state of VGCF in the composite is almost well. The interaction between the surface of VGCF and matrix polymer would be weak, and the added VGCF in the composite would not contribute to the internal structure of the composite. This is clear from the DSC measurement results described in the last section. The difference in Young's modulus between the experimental data and predicted values at same VGCF content in case of PC-C/VGCF composite is smaller than that in case of PC-A/VGCF one. These observations may show that our PC/VGCF data deviated from predicted data because VGCF were broken during melt compounding. It is also indicated that VGCF could be broken easily in higher viscosity PC.

The length and diameter of VGCF before melt compounding was used as the values when we calculated the Young's modulus using the modified Halpin-Tsai equation, and the calculated Young's modulus of PC/VGCF-S composite was larger than that of PC-VGCF-H one. However, the experimental data of Young's modulus was almost independent of the kinds of VGCF. These imply that the aspect ratio of VGCF-S and VGCF-H in the composite after melt compounding may become almost the same each other because VGCF would break by melt compounding. To clarify these matters is one of the future works.

Part 2

3.3 The Rheological Behavior and Thermal Conductivity of Melt-Compounded Polycarbonate/Vapor-Grown Carbon Fiber Composites

3.3.1. Material

Two kinds of PC (K1300 and 1225L, which were provided from Teijin Chemical Co., Ltd., Japan) with different melt volume flow rate (MVR) were used as matrix polymers. Table 3.1 shows the characteristics properties of PC. We decided to call K1300 PC-A and to call 1225L PC-C, respectively. We selected the PC, which is a typical amorphous polymer, to discuss the dispersion of VGCF without the effect of crystalline component of polymer. Two types of the VGCF (VGCF-S and VGCF-H) made by Showa Denko K. K., Japan were added to PC. Table 3.2 shows the characteristic properties of VGCF. The content of VGCF was from 0 to 6.5 wt%. The characteristic properties of PC and VGCF are shown in Tables 3.1 and 3.2, respectively. PC and VGCF were dried at 80 °C in a decompression state for 24 h. The composite was prepared by using a twin screw extruder (KURIMOTO, LTD, KRC-S1 kneader) at 260 °C. Twin screw rotation speed was 150 rpm.

3.3.2 Results and Discussion

3.3.2.1 Rheological behavior

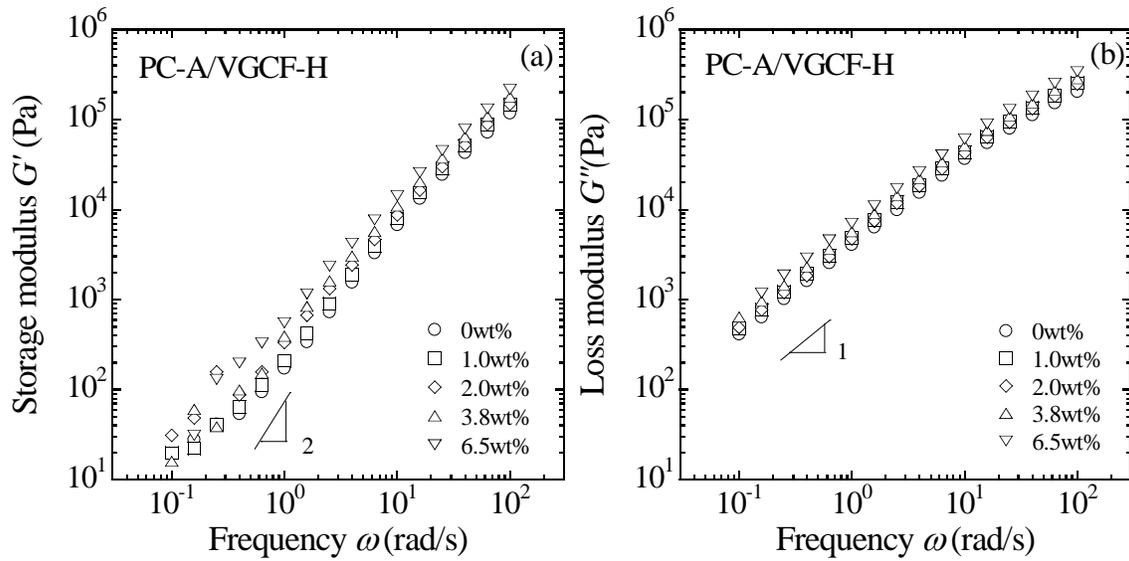


Figure 3.10 Frequency (ω) dependence of the linear viscoelastic moduli

(a) Storage modulus G' and (b) loss modulus G'' for PC-A/VGCF-H system at $T = 260^\circ\text{C}$

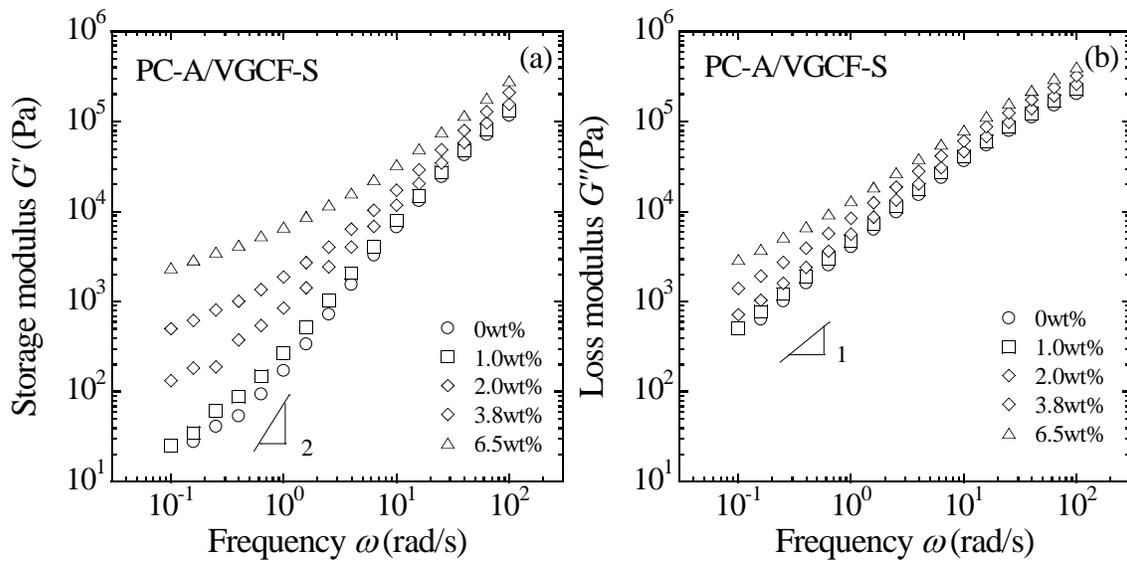


Figure 3.11 Frequency (ω) dependence of the linear viscoelastic moduli

(a) Storage modulus G' and (b) loss modulus G'' for PC-A/VGCF-S system at $T = 260^\circ\text{C}$

Figure 3.10 shows the frequency (ω) dependence of the storage modulus G' and loss modulus G'' of the PC-A/VGCF-H composite at 260°C. In the low- ω region (< 1.0 rad/s), the slope of G' and G'' for the PC-A matrix was 2 and 1, respectively. In other words, terminal relaxation behavior was observed. However, the G' and G'' values of PC-A monotonically increased with the content of VGCF-H. The slopes of G' and G'' for PC-A/VGCF-H were almost independent of the content of VGCF-H. We found that the effect of VGCF-H on rheological properties of PC-A was small. This result implies that VGCF-H may disperse well in PC-A. In Figure 3.11, G' and G'' are shown in the PC-A/VGCF-S system. The G' and G'' of PC-A increased monotonically in the high- ω region (> 10 rad/s) with increasing VGCF-S content. However, in the low- ω region (< 1.0 rad/s), the G' and G'' of PC-A rapidly increased and the slopes of G' and G'' gradually decreased with VGCF-S content above 2.0 wt%. In other words, the long-time relaxation behavior was observed and the relaxation component slightly increased in the region of more than 2.0 wt% in the PC-A/VGCF-S system. This result implies that the dispersion state of VGCF-S in PC-A would change in the region of more than 2.0 wt%. Figure 3.12 shows the G' and G'' values as a function of ω in the PC-C/VGCF-S system. As observed in Figure 3.12, terminal relaxation behavior was observed in the PC-C matrix, as in the PC-A matrix. The complex viscosity η^* ($\eta^* = [(G''/\omega)^2 + (G'/\omega)^2]^{1/2}$) of PC-A and PC-C was almost independent of the frequency ω in our measurement region. We found that the η^* of PC-A and PC-C were 4000 Pa s and 700 Pa s, respectively, and that the G' and G'' of PC-C/VGCF-S dramatically increased above 2.0 wt%. In the low- ω region (< 0.4 rad/s), the slope of G' for PC-C/VGCF-S was almost flat and the magnitude of G' was only slightly affected by the content of VGCF-S. In other

words, the second plateau region was observed above 2.0 wt% in PC-C/VGCF-S system. This result implies that the structure with low mobility would be formed in PC-C by adding VGCF-S.

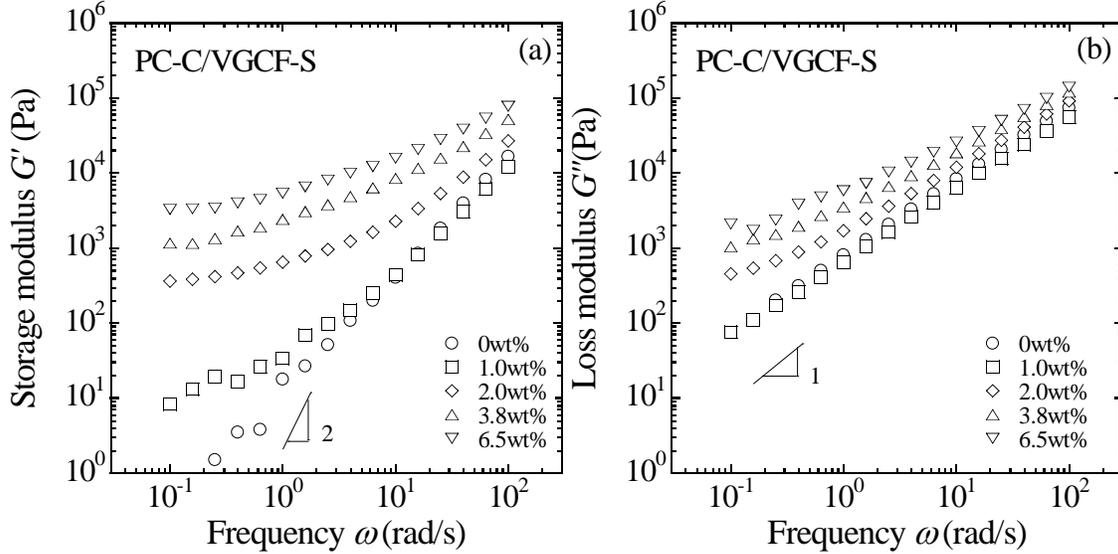


Figure 3.12 Frequency (ω) dependence of the linear viscoelastic moduli

(a) Storage modulus G' and (b) loss modulus G'' for PC-C/VGCF-S system at $T = 260^\circ\text{C}$

The elastic component of the polymer can be increased by adding rigid particles [32-35], and it is well known that the elasticity of fiber suspensions (e.g., PC/multiwall carbon nanotube composites [2] or aqueous multi-walled carbon nanotube dilute suspensions [19]) drastically increases with their concentration [2, 19]. These results correspond to our obtained results. In addition, some researchers have reported that the plateau modulus G' in low- ω region was reflected the properties of the fiber network structure [20-26]. According to these reports, a power law correlation was found between the plateau modulus G' and volume concentration c_v , namely, $G' = k c_v^a$, where k and a are parameters that are independent of c_v . Tatsumi et al. also have explained that the k is the index of fiber flexibility, which depends on the Young's modulus

and aspect ratio of the fiber [25, 26]. The result of investigation of the plateau modulus and the content of VGCF in Figure 3.12 was that $\log G'$ was proportional to $\log c_v$ of VGCF-S in PC-C/VGCF-S system. The result implies that the network structure of VGCF-S would be formed in PC-C matrix. Notably, our data indicate that the network structure of VGCF-S cannot be expressly formed in the PC-A matrix. This result leads to our presumption that the network structure of VGCF is locally formed or that the coarse network structure of VGCF is formed in the PC-A matrix. In other words, it is not easy to form a network structure of VGCF in a high-viscosity matrix.

3.3.2.2 Thermal conductivity

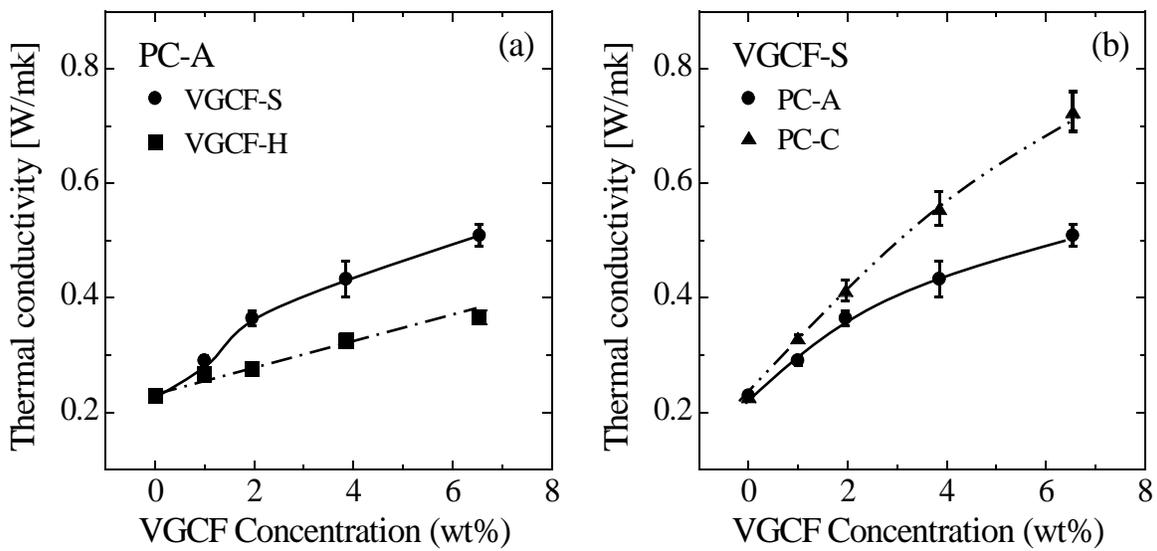


Figure 3.13 Thermal conductivity plotted against the content of VGCF for (a) PC-A/VGCF system and (b) PC/VGCF-S system at room temperature

Figure 3.13(a) shows the thermal conductivity as a function of VGCF content for the PC-A/VGCF system. The thermal conductivity of PC-A/VGCF-H slightly increased with increasing VGCF-H content and the thermal conductivity of PC-A was observed to strongly increase by adding VGCF-S above 2.0 wt% compared to that in the PC-A/VGCF-H system. In Figure 3.13(b), the thermal conductivities of PC-A and PC-C were plotted as a function of VGCF-S content. The thermal conductivity of each PC was almost the same below 2.0 wt%; however, the thermal conductivity of PC-C drastically increased above 2.0 wt% compared to that of PC-A.

It is predicted that the thermal conductivity of PC/VGCF composites depends on the degree of the connecting of VGCF connections because the thermal conductivity of VGCF is much higher than that of PC. From the result shown in Figure 3.12, we suggest that the thermal conductivity of PC-C drastically increased above 2 wt% because the network structure of VGCF-S would be formed in PC-C matrix. Because the network structure of VGCF-H would not be sufficiently formed in PC-A, the thermal conductivity of PC-A/VGCF-H was lower than that of PC-A/VGCF-S. These observations indicate that the effect of VGCF on the thermal conductivity of PC may be interpreted from the results of the rheological behavior of the composite. A further important point is that the thermal conductivity and rheological behavior depend on the viscosity of the PC matrix despite the fact that the same amount of VGCF is added to both samples. We investigated the morphology of PC-A/VGCF-S and PC-C/VGCF-S with SEM [36]. The flocculating of VGCF was only minimally observed in each composite. However, it is difficult to discuss the dispersion state of VGCF because a clear network structure of VGCF could not be observed. To investigate the effect of viscosity of the PC matrix on the formation of network of VGCF, we focused on the length of VGCF in various PCs.

3.3.2.3 Evaluation of length of VGCF

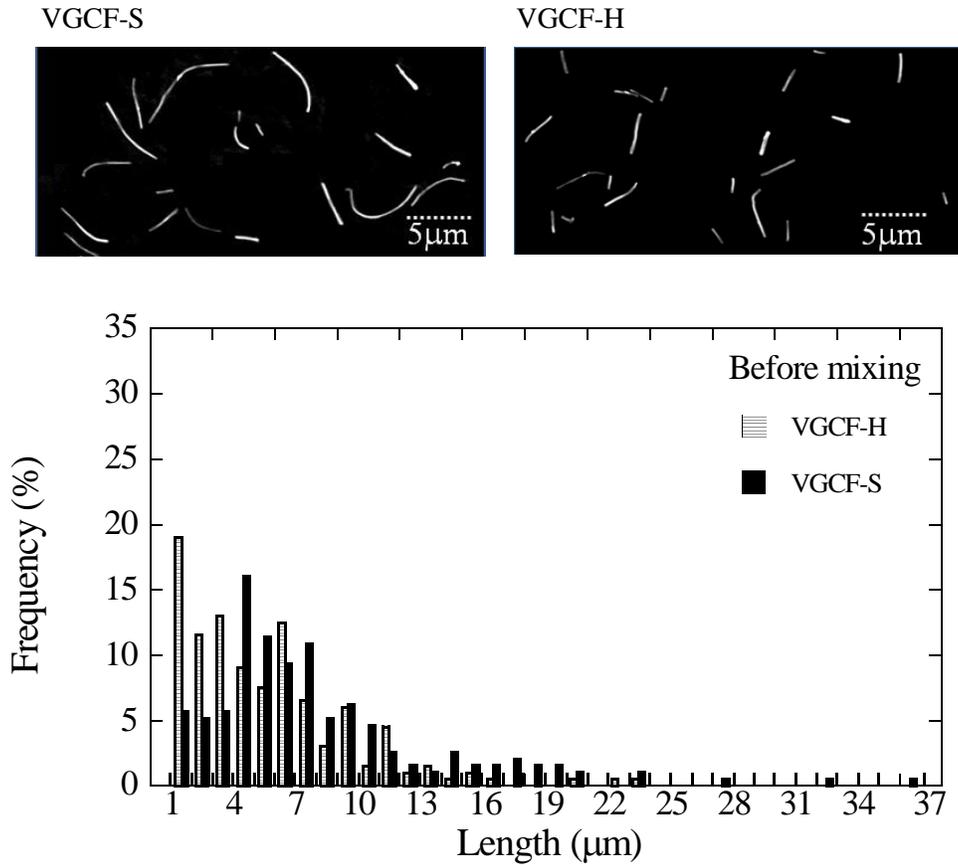


Figure 3.14 Length distribution and the picture for VGCF-S and VGCF-H before mixing

The length of VGCF was investigated by evaluating the disaggregated VGCF, with reference to previous reports [37,38]. After stirring neat VGCF-H and VGCF-S in dilute PC/THF solution, a very thin film cast by rotary coater was observed with SEM. The image and the length distribution of VGCF-H and VGCF-S before mixing are shown in Figure 3.14. The number of VGCF segments analyzed was approximately 200 because the average length of VGCF was independent of the number of VGCF segments analyzed above 150 in each case. The class

interval was 1 μm , and each class bar was plotted as 1 μm . As observed in the images and figure, a longer VGCF was confirmed in VGCF-S than in VGCF-H. The important point is the shape of the length distribution. The shapes of the VGCF-H and VGCF-S distributions resemble single and bimodal distributions, respectively, in Figure 3.14. The length distribution of VGCF-H and VGCF-S after mixing with PC-A at a VGCF content of 6.5 wt% is shown in Figure 3.15 (a). We found that the average length of VGCF-S and -H decreased by approximately 40% after mixing with PC-A. However, a broader distribution in the PC-A/VGCF-S system than in the PC-A/VGCF-H system was observed. The averages of VGCF-S and VGCF-H were 4.9 and 3.3 μm , respectively. The ratio of breaking for VGCF-S was more than that of VGCF-H. Figure 3.15 (b) shows the result of PC-C/VGCF-S and PC-A/VGCF-S at a VGCF content of 6.5 wt%. It was also found that the length of VGCF-S decreased with mixing. However, the shapes of the length distribution of VGCF-S in PC-A and PC-C resemble single and bimodal distributions, respectively. The average length of VGCF-S in PC-A and PC-C were 4.9 and 5.9 μm , respectively. This result implies that it is easy to break VGCF in the kneading process in a high viscosity matrix.

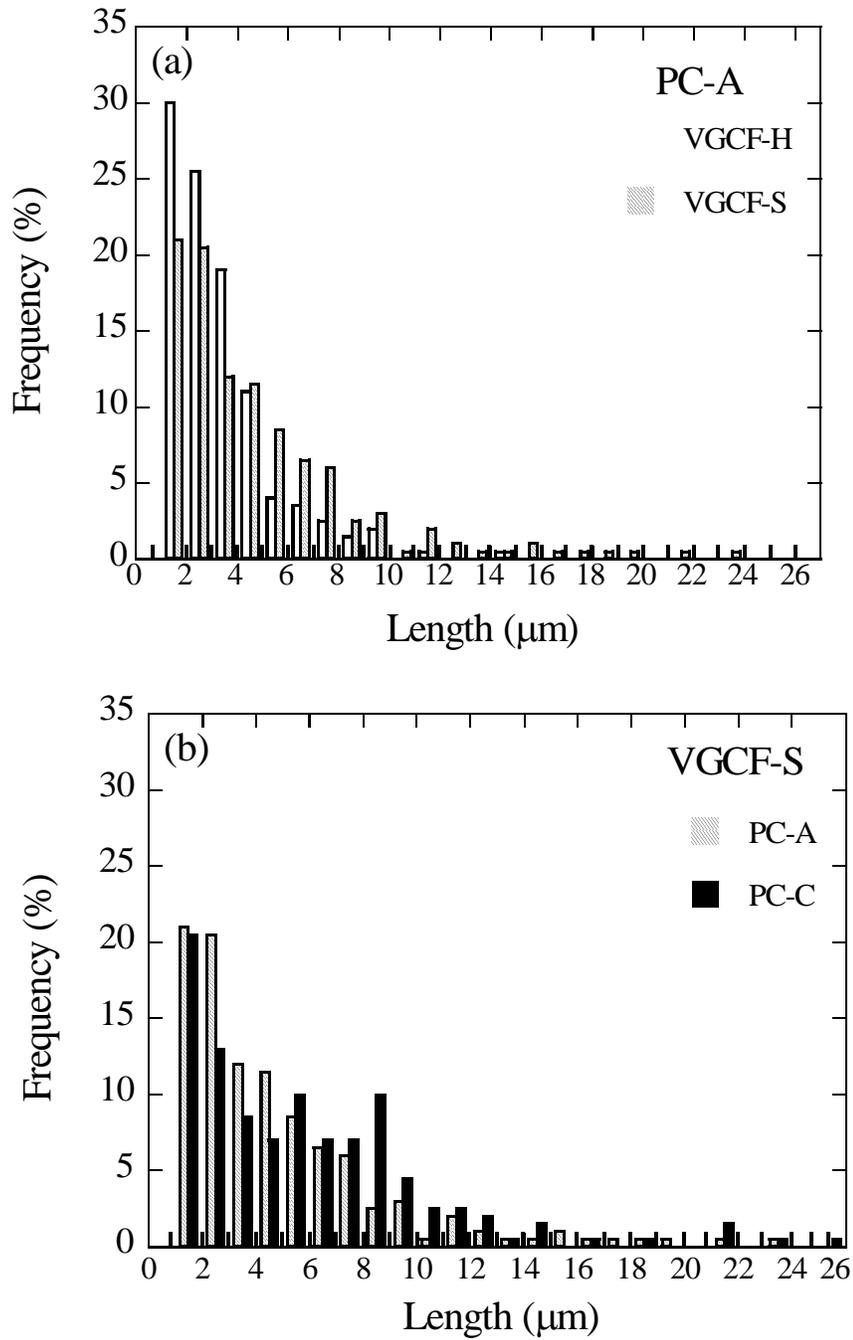


Figure 3.15 Length distribution of (a) VGCF-H and VGCF-S in PC-A and (b) VGCF-S in PC-A and PC-C after mixing

The diameter of VGCF-S was larger than that of VGCF-H at the same VGCF content because the volume per fiber of VGCF-S was 25% lower than that of VGCF-H, as shown in Table 3.2 before mixing. The surface area per fiber of VGCF-S was also approximately 10% larger than that of VGCF-H. However, the number of VGCF-S also increased with mixing because the ratio of breaking for VGCF-S was more than that for VGCF-H. The total contact point between VGCF-S was smaller than that of VGCF-H after mixing. Therefore, it is very interesting that the thermal conductivity of the PC-A/VGCF-S system is so different from that of the PC-C/VGCF-S system, although the average length of VGCF-S in the PC-A/VGCF-S system is a little larger (the difference is approximately 1 μm) compared to that in PC-C/VGCF-S. In this study, we clarified that the viscosity of the polymer matrix is an important factor to assure that the VGCF will have sufficient effects on the properties of the PC/VGCF composite. Therefore, these results suggest that the dispersion of VGCF may be able to be controlled with temperature because the viscosity of PC depends on the temperature. The effect of temperature on the dispersion of VGCF will be the subject of future work.

3.4 Conclusions

In part 1, this study, PC/VGCF composites were prepared by melt compounding using a co-rotating type twin screw extruder. We described the effect of the VGCF size, VGCF content and the melt viscosity of matrix polymer (PC in this study) on the properties of the PC/VGCF composites. This resulted in the following conclusions:

1) The Young's modulus of PC increased with VGCF content in each case, and these tendencies would be almost independent of VGCF size and melt viscosity of PC matrix, except for the case using PC with low melt viscosity at high VGCF content.

2) The tensile strength of PC slightly increased with VGCF content in case using PC with comparatively low melt viscosity. On the contrary, tensile strength of PC/VGCF composite decreased with an increase of VGCF content in case using PC with the largest melt viscosity. These tendencies would be almost independent of the VGCF size.

3) According to the SEM photographs of the fracture surface of the specimens after tensile testing, the state of the fracture surface would slightly depend on the VGCF size. The aggregation size of VGCF-S with high aspect ratio was slightly larger than that of VGCF-H one. On the whole, the good dispersion state of VGCF in PC/VGCF composites could be realized on the melt compounding even if there are some aggregations in the composites.

4) The glass transition temperature of PC/VGCF composites was almost independent of the VGCF size, and this depended on the melt viscosity of based PC.

5) The results of our experiment would show the possibility that the dispersion and aggregation of VGCF composite could be controlled by the viscosity of matrix. In the future works, the dispersion state of VGCF, e.g. length distribution or aggregation state of VGCF in the compounded composite is needed to investigate more detail in order to clear this possibility.

In part 2, we investigated the effect of the PC matrix viscosity on the thermal conductivity of a PC/VGCF composite from the viewpoint of the rheological properties. Two types of VGCF with aspect ratios of 40 and 100 were used in this study. The content of VGCF ranged from 0 to 6.5 wt%. The rheological behavior results from the network structure of VGCF were observed in the low viscosity PC system that contained VGCF with a high aspect ratio

because a power law correlation was found between the plateau modulus and the volume concentration. In the high-viscosity PC system, the rheological behavior originating from the network structure of VGCF was not shown. The thermal conductivity of low-viscosity PC drastically increased by adding VGCF with a high aspect ratio, in contrast to the result from high-viscosity PC. From the analysis of the VGCF length in each composite, it was clearly found that the VGCF length decreased with mixing. However, the degree of VGCF length decrease in the high-viscosity PC was higher. Therefore, we concluded that the thermal conductivity of polymer/VGCF composites could be controlled with the viscosity of the polymer because the length of the VGCF changed as a function of the viscosity of the matrix.

References

- [1] Ki HK, Won HJ (2009) A strategy for enhancement of mechanical and electrical properties of polycarbonate/multi-walled carbon nanotube composites, *Carbon*, **47**, 1126-1134
- [2] Pötschke P, Fornes TD, Paul DR (2002) Rheological behavior of multiwalled carbon nanotube/polycarbonate composites, *Polymer*, **43**, 3247-3255
- [3] Sandler J, Shaffer MSP, Prase T, Bauhofer W, Schulte K, Windle AH (1999) Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties, *Polymer*, **40**, 5967-5971

- [4] Choi YK, Sugimoto KI, Song SM, Endo M (2005) Mechanical and thermal properties of vapor-grown carbon nanofiber and polycarbonate composite sheets, *Materials Letters*, **59**, 3514-3520
- [5] Takahashi T, Yonetake K, Koyama K, Kikuchi T (2003) Polycarbonate crystallization by vapor-grown carbon fiber with and without magnetic field, *Macromolecular Rapid Communications*, **24**, 763-767
- [6] Endo M, Kim YA, Hayashi T, Nishimura K, Matusita T, Miyashita K (2001) Vapor-grown carbon fibers (VGCFs): Basic properties and their battery applications, *Carbon*, **39**, 1287-1297
- [7] Chung DDL (2001) Comparison of submicron-diameter carbon filaments and conventional carbon fibers as fillers in composite materials, *Carbon*, **39**, 1119-1125
- [8] Brandl W, Marginean G, Chirila V, Warschewski W (2004) Production and characterisation of vapour grown carbon fiber/polypropylene composites, *Carbon*, **42**, 5-9
- [9] Choi YK, Sugimoto KI, Song SM, Endo M (2006) Production and characterization of polycarbonate composite sheets reinforced with vapor grown carbon fiber, *Composites Part A: Applied Science and Manufacturing*, **37**, 1944-1951
- [10] Bernadette AH, William JB (2005) Polycarbonate carbon nanofiber composites, *European Polymer Journal*, **41**, 889-893
- [11] Jin ZX, Pramoda KP, Goh SH, Xu GQ (2002) Poly(vinylidene fluoride)-assisted melt-blending of multi-walled carbon nanotube/poly(methyl methacrylate) composites, *Materials Research Bulletin*, **37**, 271-278

- [12] Koyama T, Tanoue S, Iemoto Y (2009) Preparation and properties of polypropylene/vapor grown carbon fiber composite monofilaments by melt compounding, *Journal of Textile Engineering*, **55**, 73-78
- [13] Koyama T, Tanoue S, Iemoto Y (2010) Effect of processing conditions on the dispersion of vapor grown carbon fiber in a polyamide 6 and the crystalline structure of their composites by melt compounding, *International Polymer Processing*, **25**, 181-187
- [14] Takase H, Mikata Y, Matsuda S, Murakami A (2002) Dispersion of carbon-nanotubes in a polymer matrix by a twin-screw extruder, *Seikei Kakou (in Japanese)*, **14**, 126-131
- [15] Takase H, Furukawa M, Kishi H, Murakami A (2005) Dispersion of carbon-nanotubes in a polymer matrix by a twin-screw extruder II, *Seikei Kakou (in Japanese)*, **17**, 50-54
- [16] Shofner ML, Rodri'guez-Maci'asb FJ, Vaidyanathanc R, Barreraa EF (2003) Single wall nanotube and vapor grown carbon fiber reinforced polymer, composite processed by solid freeform fabrication, *Composites Part A: Applied Science and Manufacturing*, **34**, 1207-1217
- [17] Zhang B, Fu R, Zhang M, Dong X, Zhao B, Wang L, Pittman Jr. CU (2006) Studies of the vapor-induced sensitivity of hybrid composites fabricated by filling polystyrene with carbon black and carbon nanofibers, *Composites Part A: Applied Science and Manufacturing*, **37**, 1884-1889
- [18] Yang S, Taha-Tijerina J, Serrato-Diaz V, Hernandez K, Lozano K (2007) Dynamic mechanical and thermal analysis of aligned vapor grown carbon nanofiber reinforced polyethylene, *Composites Part B: Engineering*, **38**, 228-235

- [19] Kinloch IA, Roberts SA, Windle AH (2002) A rheological study of concentrated aqueous nanotube dispersions, *Polymer*, **43**, 7483-7491
- [20] Mason SG (1950) Some factors involved in the flocculation of pulp suspensions and the formation of paper, *Pulp and Paper Canada Magazine*, **51**, 94-98
- [21] Kurath SF (1959) The network and viscoelastic properties of wet pulp (I): Dynamic mechanical properties, *Tappi Journal* **42**, 953-959
- [22] Thalén N, Wahren D (1964) Shear modulus and ultimate shear strength of some paper pulp fibre networks, *Svensk Papperstidn*, **67**, 259-264
- [23] Damani R, Powell RL, Hagen N (1993) Viscoelastic characterization of medium consistency pulp suspensions, *Canada Journal of Chemical Engineering*, **71**, 676-684
- [24] Tatsumi D, Ishioka S, Matsumoto T (1999) Effect of particle and salt concentrations on the rheological properties of cellulose fibrous suspensions, *Nihon Reoroji Gakkaishi (The Society of Rheology in Japan)*, **27**, 243-248
- [25] Tatsumi D, Ishioka S, Matsumoto T (2002) Effect of fiber concentration and axial ratio on the rheological properties of cellulose fiber suspensions, *Nihon Reoroji Gakkaishi (The Society of Rheology in Japan)*, **30**, 27-32
- [26] Tatsumi D (2007) Rheology of Cellulose Fiber Disperse Systems and Cellulose Solutions, *Nihon Reoroji Gakkaishi (The Society of Rheology in Japan)*, **35**, 251-256
- [27] de Gennes PG (1979) *Scaling concepts in polymer physics*, Cornell University Press, Ithaca

- [28] Liming F, Yang L, Ping G (2006) Processing and mechanical properties of HA/UHMWPE nanocomposites, *Biomaterials*, **27**, 3701-3707
- [29] Carneiro OS, Maia JM (2000) Rheological behavior of (short) carbon fiber/thermoplastic composites, *Polymer Composites*, **21**, 970-977
- [30] Qian D, Dickey EC, Andrews R, Rantell T (2000) Load transfer and deformation mechanisms in carbon nanotube- polystyrene composites, *Applied Physics Letters*, **76**, 2868-2770
- [31] Mallick PK (1993) Fiber-reinforced composites, Marcel Dekker, New York
- [32] Leyland NS, Evans JR, Harrison DJ (2002) Lithographic printing of ceramics, *Journal of the European Ceramic Society*, **22**, 1-13
- [33] Lin JC, Wang CY (1996) Effects of surfactant treatment of silver powder on the rheology of its thick-film paste, *Materials Chemistry and Physics*, **45**, 136-144
- [34] Goto T, Otsubo Y (2001) Rheology control of ceramic slurries for sintering of thin films, *Nihon Reoroji Gakkaishi (The Society of Rheology in Japan)* **29**, 205-210
- [35] Ray SS, Yamada K, Okamoto M, Fujimoto Y, Ogami A, Ueda K (2003) New polylactide/layered silicate nanocomposites. 5. Designing of materials with desired properties, *Polymer*, **44**, 6633-6646
- [36] Nithikarnjanatharn J, Ueda H, Tanoue S, Uematsu H, Iemoto Y, (2011) Properties of poly(carbonate)/vapor-grown carbon fiber composites prepared by melt compounding, *Journal of Textile Engineering*, **57**, 97-106

[37] Sato E, Takahashi T, Natsume T, Koyama K (2003) Development of Dispersion and Length-evaluation Methods of Vapor-grown Carbon Fiber, *TANSO (in Japanese)*, 209, 159-164

[38] Sato E, Takahashi T, Natsume T, Koyama K (2004) Comparison of the length of vapor-grown carbon fiber before and after mixing process, *Kobunshi Ronbunshu (in Japanese)*, **61**, 144-148

Chapter 4

Effect of Screw Rotation Speed of a Twin Screw Extruder on the Mechanical Properties and Thermal Conductivity of Polycarbonate/Vapor Grown Carbon Fiber Composites

4.1 Introduction

The use of carbon fibers is growing in a variety of applications due to its functional properties. Composites reinforced by carbon fiber would be stronger as compare to metal while it is lighter. Carbon fiber, especially carbon nanotube (CNT), has been considered as one of the good fillers for polymer composites due to control of mechanical, electrical and thermal conductivity [1]. It is interesting to note that good CNT dispersion at relatively low contents is effective in enhancing properties of polymer composites. CNT reinforced polymer composites would obtain superior mechanical properties for various applications. Furthermore, CNT have been known for high thermal conductivity. Therefore carbon fiber composites is an excellent choice for high performance applications.

Carbon nanotube were discovered while studying in evaporation synthesis of fullerenes [2]. These are large macromolecules that are distinctive for their size and possess extraordinary physical properties. They can be depicted as a sheet of graphite rolled up like a cylinder. These

network structures have formed much enthusiasm in the recent year and a large amount of research has been devoted to their understanding. It has been found that nanotubes have a very wide range of thermal and mechanical property depending on their structures, such as diameter and length. VGCF is a variation of multi wall nanotube (MWNT), which is assembly of concentric single well nanotube (SWNTs).

Vapor grown carbon fiber (VGCF) is a new class of highly graphitic carbon nanofiber and offers advantages of economy and simple processing over continuous fiber composites [3]. VGCF has received increasing attention as a lower cost alternative for conventional carbon fibers. The typical of VGCF diameter becomes 20 to 200 nm, and the length is about 100 μm while general carbon fiber have diameter of 5 to 10 μm and are continuous [4, 5]. It has to consider on properties of VGCF reinforced polymer composite, which is significantly depend on good dispersion and interfacial adhesion of VGCF on polymer matrix as well as the alignment of VGCF in a specific direction.

Polycarbonate (PC) has been widely used in the engineering applications. PC presents the excellent properties on good toughness, high impact performance and good thermal stability [6]. PC is nonpolar polymer. Therefore it is difficult to obtain the fully exfoliated of carbon fiber on its polymer matrix of carbon fiber composites. Potechk et al. [7] studied the process conditions for preparation of PC/MWNT composites with a twin-screw extruder. 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. Nithikarnjanatharn et al. [8] studied properties of PC/VGCF prepared by melt compounding. That is condition on melt viscosity of PC, VGCF size and VGCF content and investigate in tensile testing, SEM and DSC. They focus

mechanical property and dispersion of VGCF in different melt viscosity of PC. However, they did not focus the screw rotation speed of melt compounding using a twin screw extruder.

Polymer/VGCF composites possess good thermal conductivity and excellent mechanical properties. In addition, twin screw extrusion was widely used in melt compounding processing polymer composites. It produced uniform particle dispersion by the large shear forces [9]. Different screw rotation speeds and additives polymer improved mechanical properties and thermal conductivity. L. Incarnato et al. [10] studied the melt compounding using a commercial polyamide 6-based copolymer, with a partially aromatic structure, as thermoplastic matrix prepared by a twin-screw extruder at different extrusion rates. Koyama et al. [11] studied the melt compounding process of polyamid(PA-6)/VGCF composites using various twin-screw extruders and mixers. The difference viscosity and screw rotation speed were found to influence the mechanical properties of PA6/VGCF composites. Tanoue et al. [12] studied the effect of screw rotation speed on the mechanical and rheological properties and clay dispersion state of PS/clay composites prepared by melt compounding with a twin-screw extruder. Hasook et al. [13] studied analyzes the effect of different screw rotating speeds on the clay dispersion and mechanical properties of nanocomposites prepared by melt compounding polylactic acid (PLA) with an organoclay in a co-rotating twin screw extruder. Polyamide 12 (PA12) was used as an additive. The higher screw rotation speed resulted in materials with better performance than that of the lower screw rotation speed in twin screw extruder. However, they did not focus the melt viscosity of polymer matrix on the adding of VGCF in the composites.

Hence this process overcomes for compounding VGCF with polymer matrix in order to achieve good dispersion of filler and good functionalization of the outer surface (smaller size but higher contact area) in the composites of polymer/VGCF. Other studies of melt compounding

process for preparation of polymer/VGCF composites were carried out by other researchers using other polymer e.g. poly(propylene) [14-15], poly(ethylene) [16], poly(acrylonitrile-co-butadiene-co-styrene) [17], poly(styrene)[18] and poly(methyl methacrylate) [19-20]. Polymer composites containing VGCF have been attracted because of their high mechanical properties and thermal conductivity. The advantage of VGCF compared to conventional carbon fiber is higher aspect ratio, which is important to improve properties of the composites [21]. However, there are little research that interesting in the effect of screw rotation speed on the mechanical properties and thermal conductivity.

The aim of this study to investigate the effect of screw rotation speed on PC/VGCF composites by melt compounding from the view point of mechanical properties and thermal conductivity. The rheological behavior and thermal conductivity are reported for composites based on different aspect ratios of VGCF, melt viscosity of PC and screw rotations speed. We selected a range of screw rotation speeds from several functions of melt compounding with a twin-screw extruder.

4.2 Experimental

4.2.1 Material

The polycarbonate (PC) was PC-H (L1225-L) and PC-L (AD5503) supplied by Teijin co., LTD., Japan. The melt volume rate (MVR) indices of two materials are 18 and 54 cm³/10min respectively. The physical form and specification of two materials are described in Table 4.1 The selected VGCF, coded as VGCF, are VGCF-S and VGCF-H, which have the different size that was kindly supplied from Showa Denko K.K Japan Company. The dimensions of this VGCF are

average diameter 100, 150 nm and length of 10, 6 μm respectively. The characteristics VGCF used in this study are listed in Table 4.2.

Table 4.1 Characteristics of PC used in this study

Polycarbonate		Specification		
Type	Commercial code	M_n (g/mol)	M_w (g/mol)	MVR ($\text{cm}^3/10 \text{ min}$)
PC-H	L-1225L	16,200	36,400	18
PC-L	AD-5503	12,800	27,600	54

Table 4.2 Characteristics of VGCF used in this study

Type	Diameter (nm)	Length (μm)	Aspect ratio	Thermal Conductivity (W/(m·K))	Electrical Conductivity ($\Omega\cdot\text{m}$)
VGCF-S	100	10	100	1200	1×10^{-4}
VGCF-H	150	6	40	1200	1×10^{-4}

4.2.2 Melt Compounding

The material was dried for a minimum of 24 h. at 80 °C in a vacuum oven. The composition of PC/VGCF composites is shown in Table 4.3. PC was compounded with VGCF of 4 phr (phr is the parts per hundred resins by weight) using a co-rotating twin screw extruder (TSE) (S1 KRC kneader by Kurimoto, Ltd., Japan, its screw diameter of 25 mm, screw length/diameter ratio (L/D) of 10.2). The compounding was carried out at a uniform barrel temperature of 260 °C and a feed rate of 1,000 g/h for each sample. We selected four kinds of screw rotation speed, 100, 125, 150 and 175 rpm for each PC/VGCF composite.

Table 4.3 Compounding ratios for various kinds of PC/VGCF composites

Case	PC contents	VGCF	VGCF contents	SRS (rpm)
1	100	-	0	100
2	100	-	0	125
3	100	-	0	150
4	100	-	0	175
5	100	VGCF-S	4	100
6	100	VGCF-S	4	125
7	100	VGCF-S	4	150
8	100	VGCF-S	4	175
9	100	VGCF-H	4	100
10	100	VGCF-H	4	125
11	100	VGCF-H	4	150
12	100	VGCF-H	4	175

4.2.3 Sample preparation

The composites were then pelletized. The pellets were dried in an oven at 80 °C for at least 24 hours. The composites were molded by injection molding machine (NP7 Real Mini, Nissel Plastic Industrial Co., Ltd., Japan) into dumbbell specimens according to JIS K7162, Type 1BA. The barrel temperature was set at 300-320 °C with injection pressure of 73-153 MPa and injection speed of 20-48 cm³/s. The mold temperature was set at 80 °C.

The pellets were prepared to form 1 mm-thick sheet by compression molded for thermal conductivity measurement. The size of the sheet was 150 mm long ×130 mm wide ×1 mm thick. The compression molded was set at 270 °C. The compound was pre-heated for 5 minutes prior to applying a pressure of 19.6 MPa for another 2 minutes. The mold was subsequently rapid cooled by flowing water while the specimens were kept under constant pressure for 2 minutes.

4.3 Results and Discussion

4.3.1 Tensile testing

Figure 4.1 shows the Young's modulus results of composites at various screw rotation speeds. The Young's modulus of neat PC was independent of screw rotation speed exceptional PC-L at screw rotation speed 175 rpm increased small amount. On the other hand, Young's modulus increased with screw rotation speed. The dispersion state of VGCF was improved in high screw rotation speed. The highest Young's modulus was found in VGCF-H filled PC-H at screw rotation speed of 175 rpm while Young's modulus of VGCF-S filled PC-H was improved up to screw rotation speed of 150 rpm. On the other hand, Young's modulus of VGCF-H filled PC-L composites trended to increase with screw rotation speed while Young's modulus of PC/VGCF-S composites unchanged at screw speed of 100-150 rpm. Declination of Young's modulus of PC/VGCF-S composites at screw rotation speed of 175 rpm was probably due to change network structure of VGCF particle size at high speed of screw rotation.

Therefore, the effect of screw rotation speed on the Young's modulus of the composites will be small. The important point to note is that the Young's modulus of PC-H/VGCF increased by VGCF, however the increase of Young's modulus of PC-L/VGCF to screw rotation speed were smaller than those of PC-H. In other words, the network structure of VGCF could be formed with PC. The increment amount of Young's modulus for PC-H and PC-L by adding of VGCF-H almost agreed except for the screw rotation speed at 175 rpm. This result implies that the effect of screw rotation speed is extremely low. Therefore, The increase of Young's modulus

of PC-H/VGCF and PC-L/VGCF means that the polymer chain could not be reacted by screw rotation speed.

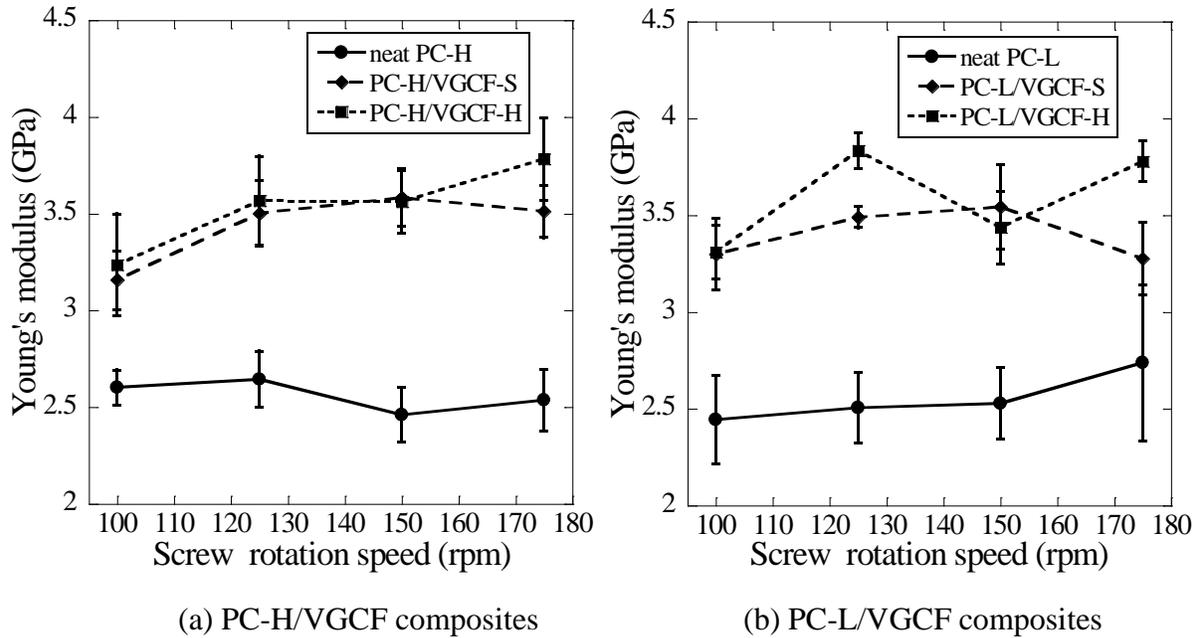


Figure 4.1 Young's modulus for various PC/VGCF composites with difference in MVR and screw rotation speed

Figure 4.2 shows the tensile strength as a function of screw rotation speed for various PC/VGCF composites and neat PC. Tensile strength of PC increased by adding VGCF on PC matrix. The screw rotation speed affected on improving tensile strength of PC and PC/VGCF composites. However, tensile strength of PC and PC-H/VGCF-S composite decreased at screw rotation speed of 175 rpm. PC-L/VGCF-S becomes almost constant with an increase of screw rotation speed. Neat PC-L and PC-L/VGCF-H in screw rotation speed 125-150 rpm are tendency but in screw rotation speed 175 rpm are independent.

However, this is a reasonable result because tensile strength of neat PC and PC/VGCF composites increase with screw rotation speed. In case of screw rotation speed 100 -150 rpm, the tensile strength increased by adding VGCF. Same tendency can be seen in the case of screw rotation speed 125 and 150 rpm. On the contrary, the tensile strength decreased with an increase of screw rotation speed in case screw rotation speed 175 rpm. Obviously, the size of VGCF in the composite would be decreased by melt compounding in case of PC-H/VGCF-S. Then the broken VGCF-S creates the aggregation in PC-H matrix during high screw rotation speed. The result implies that the tensile strength would be almost dependent on the VGCF size.

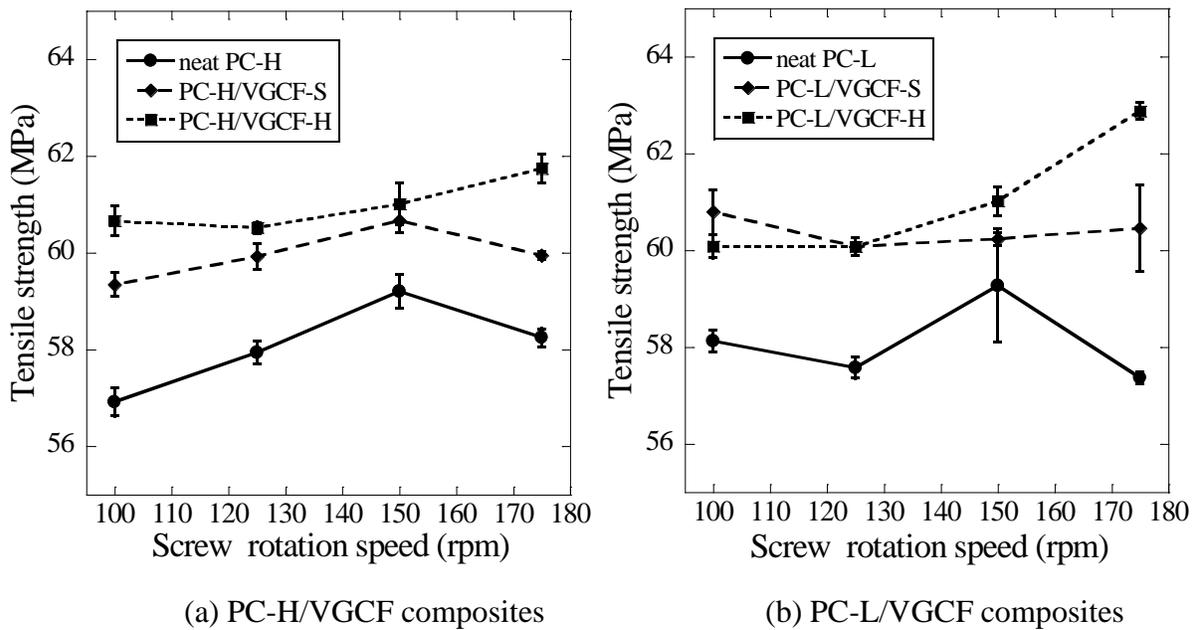


Figure 4.2 Tensile strength for various PC/VGCF composites with difference in MVR and screw rotation speed

Therefore, we found that this result was the same as Figure 4.1. This result is reasonable due to increasing of Young's modulus. It is an important point that the increment of tensile

strength and the Young's modulus by adding VGCF. We predict the dispersion state of VGCF was improved in high screw rotation speed. The result of tensile properties, it is difficult to discuss effect of VGCF in PC matrix because the value of tensile properties of PC/VGCF cannot be observed. To investigate the effect of screw rotation speed of PC/VGCF on the formation of network of VGCF, we discuss the result with the rheological behavior.

4.3.2 Rheological behavior

Figure 4.3 and 4.4 respectively shows the frequency ω dependence of the storage modulus G' and loss modulus G'' of the PC/VGCF at screw rotation speed 100 and 175 rpm respectively composite at 260 °C. The increase in G' and G'' with VGCF composite is primarily caused by a monotonically increase in the G' , as may be seen in Figure 4.3 (a),(c) and 4.4 (a),(c). The corresponding increase in G'' is much lower as seen in Figure 4.3 (b),(d) and 4.4 (b),(d). Both moduli increased with frequency however, the rate of increase becomes less in higher the PC/VGCF-S. Thus, the effect of VGCF size on PC-H and PC-L is much higher at low frequencies than at high frequencies. The neat PC and PC/VGCF-H the values of G' and G'' , the slopes of the modulus curves change significantly. However, in case PC/VGCF-S the values of G' and G'' are nearly independent of frequency. The result implies that the network structure of VGCF in PC matrix would be formed in the region of PC/VGCF-S.

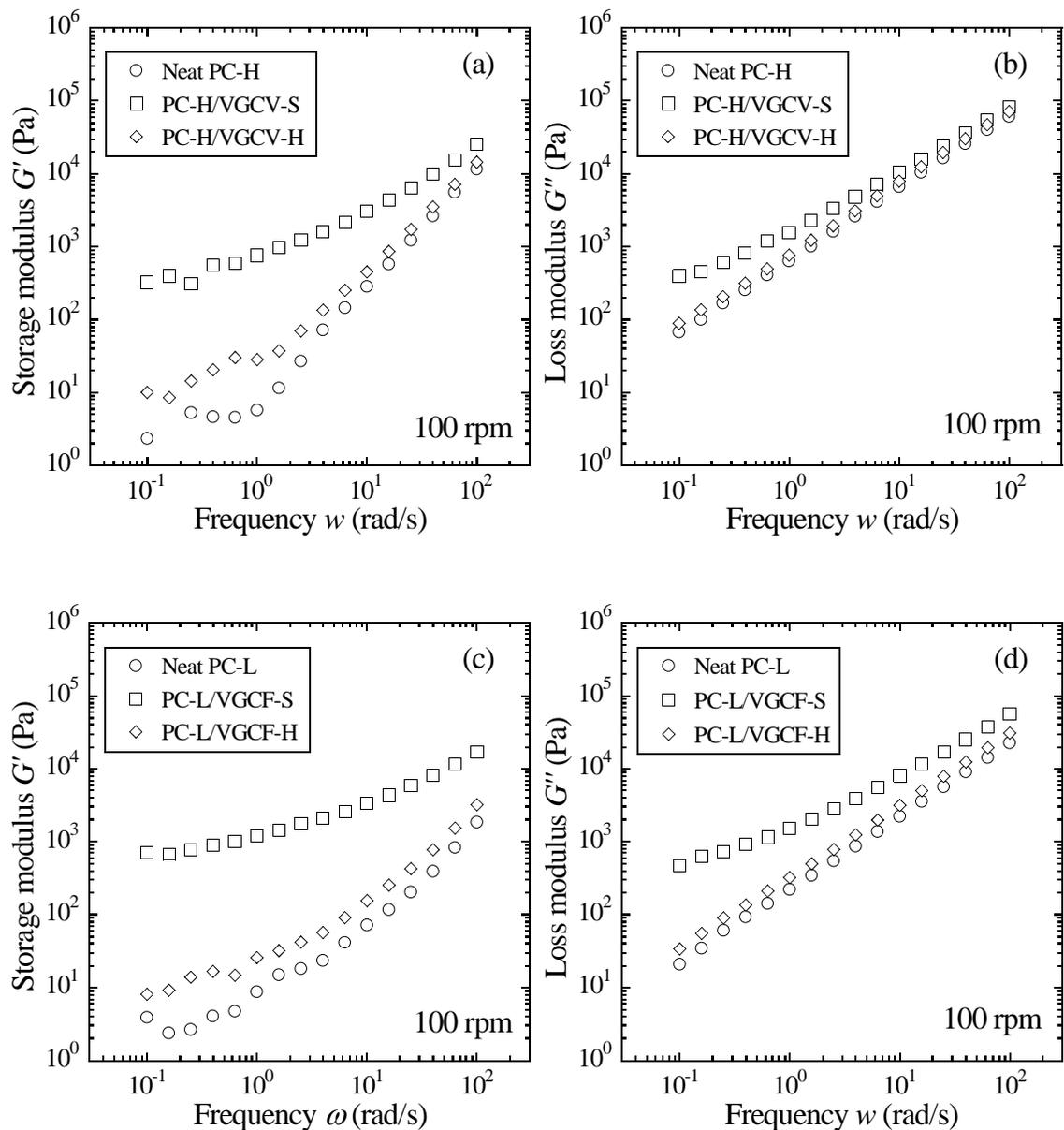


Figure 4.3 Frequency (ω) dependence of the linear viscoelastic moduli (a) Storage modulus G' of PC-H/VGCF, (b) loss modulus G'' of PC-H/VGCF, (c) Storage modulus G' of PC-L/VGCF and (d) loss modulus G'' of PC-L/VGCF at $T=260$ °C, VGCF content = 3.84 wt%, screw rotation speed = 100 rpm

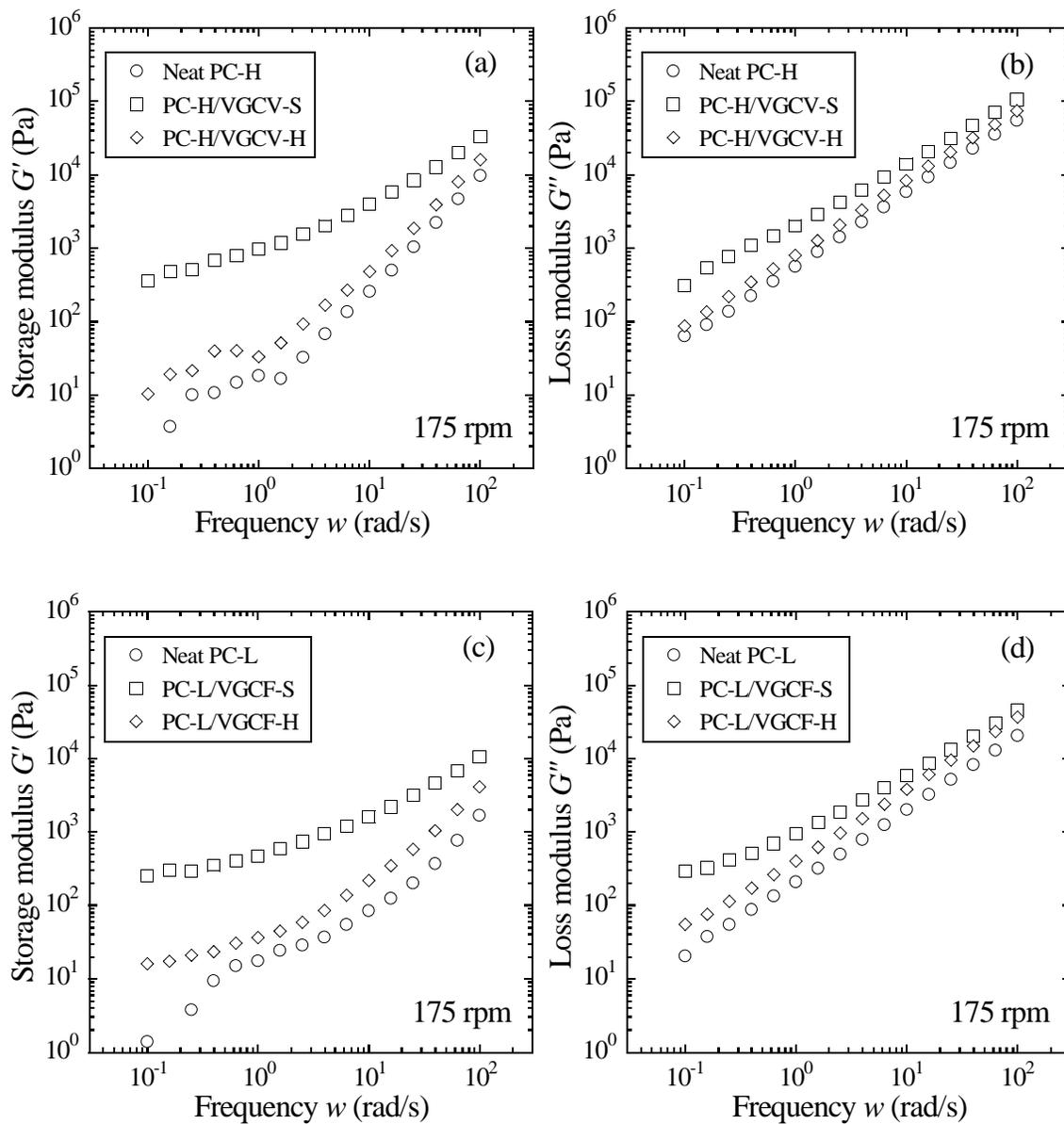
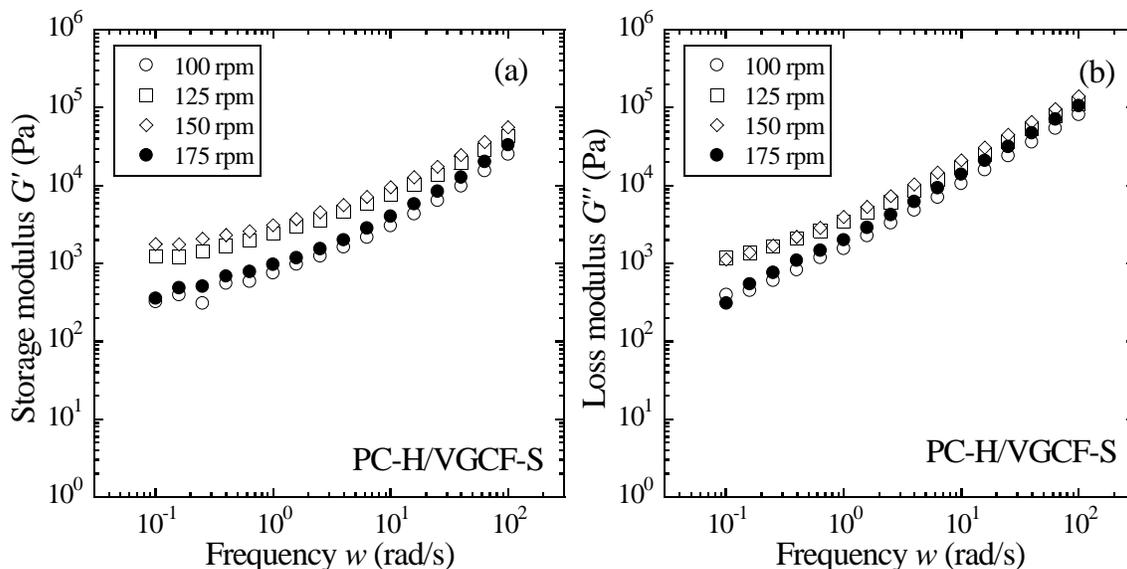
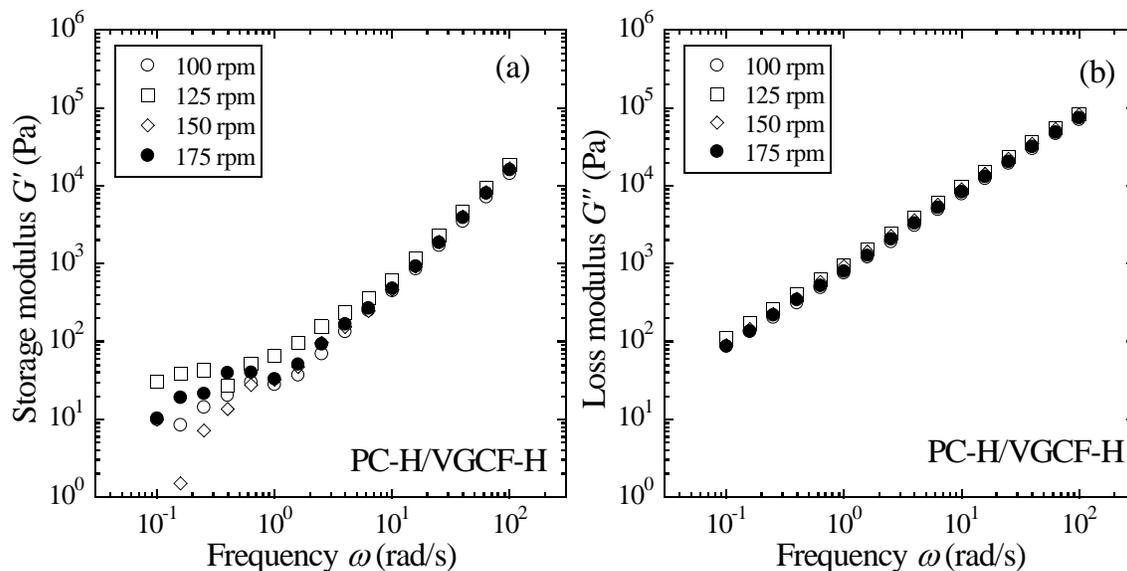


Figure 4.4 Frequency (ω) dependence of the linear viscoelastic moduli (a) Storage modulus G' of PC-H/VGCF, (b) loss modulus G'' of PC-H/VGCF, (c) Storage modulus G' of PC-L/VGCF and (d) loss modulus G'' of PC-L/VGCF at $T=260$ °C, VGCF content = 3.84 wt%, screw rotation speed = 175 rpm



Figures 4.5 Frequency (ω) dependence of the linear viscoelastic moduli (a) Storage modulus G' and (b) loss modulus G'' for PC-H/VGCF-S system at $T=260$ °C, VGCF content = 3.84 wt%

It is known from structures of an isometric fillers result in an apparent tensile strength which is visible in dynamic measurements by a plateau of G' or G'' at low frequencies. This effect is more pronounced in G' than G'' . As the size of VGCF in this composites system, VGCF interactions begin to dominate, eventually lead to percolation and the formation of an interconnected structure of VGCF. Starting at about VGCF-S, G' seems to reach such a plateau at low frequencies. Therefore, the dense network structure is assumed to form. This critical composite is regarded as a rheological behavior composite. This result implied that the rheological properties originated in the network structure of VGCF were observed using VGCF of high aspect ratio. Therefore, we are interested in the matter of screw rotation speed, we will consider in Figure 4.5-4.6.



Figures 4.6 Frequency (ω) dependence of the linear viscoelastic moduli (a) Storage modulus G' and (b) loss modulus G'' for PC-H/VGCF-H system at $T=260$ °C, VGCF content = 3.84 wt%

Figures 4.5 shows the storage and loss moduli recorded at 260 °C for the four samples. Both G' and G'' exhibit a monotonic increase with increasing VGCF loading at all frequencies. There are four samples of PC-H/VGCF-S composites in various screw rotation speed. This result further suggests that the inconsistency observed in the PC composites with the screw rotation speed 125 and 150 rpm samples showing a higher G' and G'' value than that for the 100 rpm and 175 rpm samples may be caused by the different in screw rotation speed. On the other hand, in Figure 4.6 shows, the slope of G' and G'' of PC-H/VGCF-H was almost independent of the screw rotation speed. We found that the effect of VGCF-H on rheological properties of PC-H is little, which is considered well dispersed at about 100 rpm.

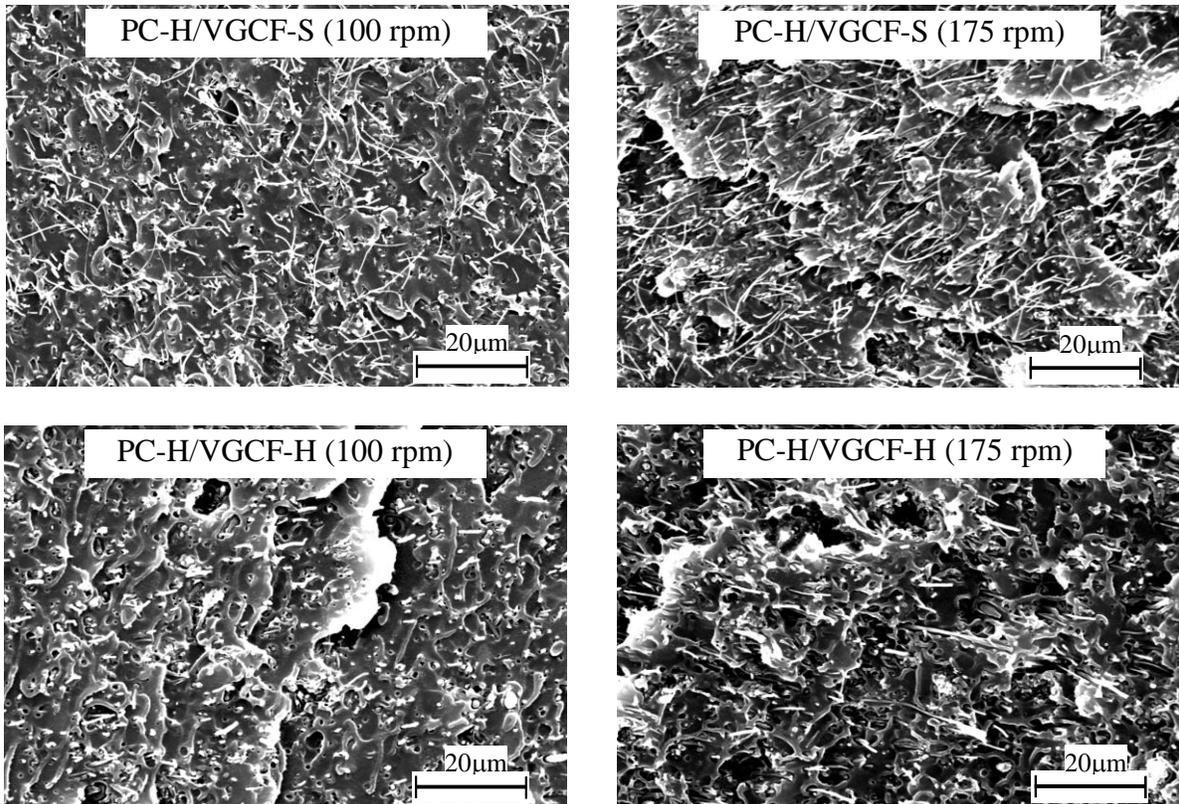
It is predicted that the rheological behavior of PC-H/VGCF-S composites depends on the screw rotation speed because the rheological behavior of PC/VGCF-S at 125 and 150 rpm are

much higher than that of PC/VGCF-S at 100 and 175 rpm. From the result of Figure 4.5 (a) in low ω region, the slope of G' of PC-H/VGCF-S was almost flat and absolute value of G' was depended in screw rotation speed at 125 and 150 rpm. In the other word, the second plateau region was observed in the region of screw rotation speed 125 and 150 rpm in PC-H/VGCF-S. The result implied that the structure would be formed in PC-H/VGCF-S in screw rotation speed 125 and 150 rpm. Since the network structure of PC-H/VGCF-S would be hardly formed in PC-H/VGCF-S at 100 and 175 rpm. Form the effect of screw rotation speed and VGCF size of PC matrix on the formation of dispersion state of VGCF, we focus on SEM of VGCF in various PC matrix and screw rotation speed.

4.3.3 SEM observations

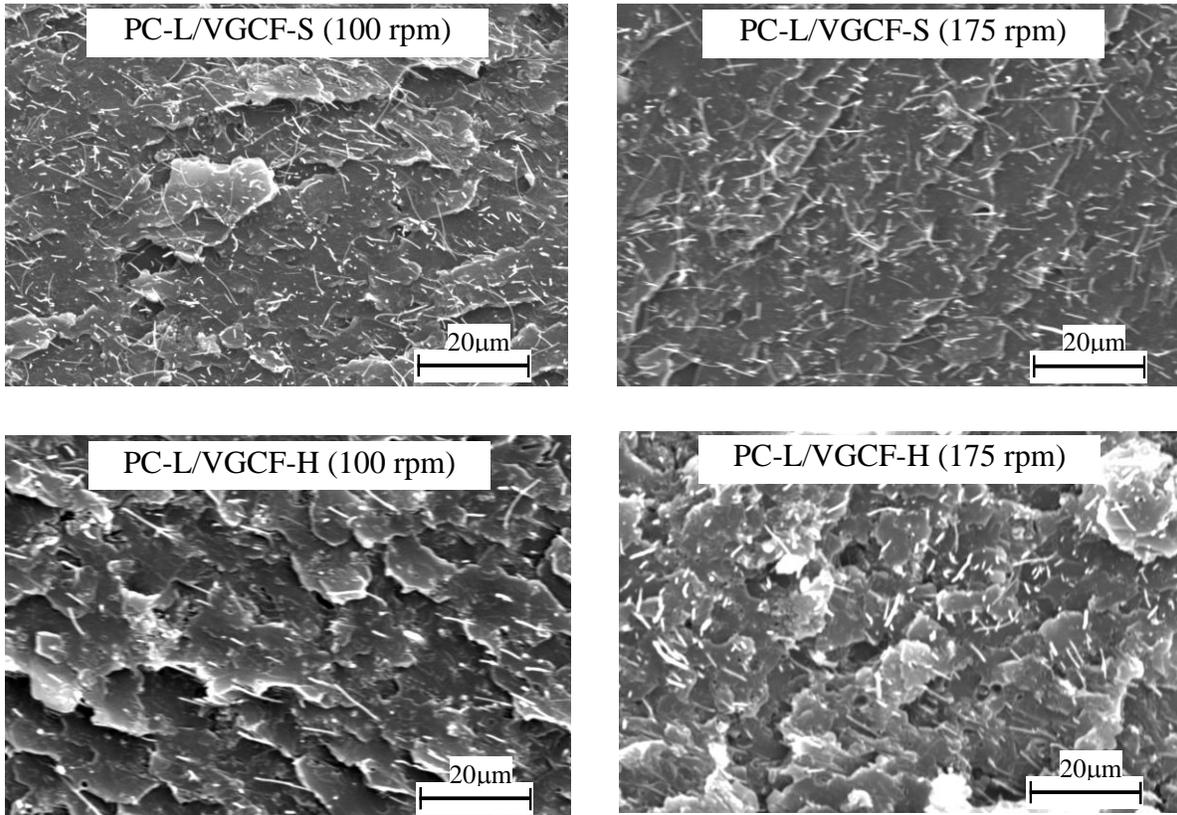
We check the VGCF dispersion state of our prepared mixtures by taking SEM photographs. SEM photographs of the surface were fractured in liquid nitrogen with PC-H/VGCF and PC-L/VGCF composites. It seems that these photographs are almost the same. We investigate the different of tensile testing by choosing PC/VGCF at screw rotation speed 100 and 175 rpm. The surface of specimens used in SEM photographs of VGCF size for each screw rotation speed is shown in Figures 4.7-4.8. The SEM photograph of VGCF is the white color PC/VGCF also showed no aggregation of VGCF. They were good dispersed state. Although, it has difference in melt viscosity of PC, VGCF size and screw rotation speeds had an influence of the dispersion state of VGCF. From Table 4.2, in case of VGCF-S with high aspect ratio, VGCF dispersed with an increase of screw rotation speed. On the other hand, case of VGCF-H with low aspect ratio, the dispersion of VGCF was independent on the screw rotation speed. Therefore, the total contact area between VGCF-S and PC matrix is larger than that between VGCF-H and PC one.

The SEM photographs of PC-H/VGCF-S composites at various screw rotation speed. In the case of screw rotation speed at 175 rpm there is some large VGCF shape and the dispersion of VGCF-S would be easy for PC-H. However, some VGCF-S was seen to be smaller of the case of screw rotation speeds at 100 rpm. This result implies that VGCF-S would be easy to create the dispersion of VGCF in PC/VGCF composites as compared with VGCF-H. And the dispersion state of VGCF was depended on the size of VGCF. According to SEM photographs, the aggregate of VGCF was hardly observed in each PC/VGCF-H composite. The size of VGCF and the viscosity of polymer matrix are important to make enough the effect of the VGCF on the properties of PC/VGCF composite at various screw rotation speed.



Figures 4.7 SEM photo PC-H/VGCF composites at various screw rotation speed

(VGCF content = 3.84 wt%)



Figures 4.8 SEM photo PC-L/VGCF composites at various screw rotation speed
(VGCF content = 3.84 wt%)

4.3.4 Thermal conductivity

Figure 4.9 shows the thermal conductivity results of the composites at various screw rotation speeds. The thermal conductivity of neat PC was almost independent of the screw rotation speed. The thermal conductivity of PC/VGCF shows the dispersion of VGCF in the PC matrix then VGCF-S has a better thermal conductivity than VGCF-H. In Figure 4.9 (a) the thermal conductivity of the PC-H/VGCF-H composites is stable with screw rotation speed, and was larger than that of neat PC-H. Then, the thermal conductivity was independent on screw rotation speed of PC-H/VGCF-H. However, the thermal conductivity of PC-H/VGCF-S composite

increased at screw rotation speed of 100-150 rpm. This thermal conductivity shows maximum value at screw rotation speed 150 rpm. On the other hand, the thermal conductivity was decreased at screw rotation speed 175 rpm. These observations may appear that the effect of VGCF-S on thermal conductivity of PC-H could be related from the result of tensile strength. In Figure 4.9-(b) the thermal conductivity of each composite is almost independent of screw rotation speed. The thermal conductivity of PC-L/VGCF-H and PC-L/VGCF-S composites was larger than that neat PC. In PC-L/VGCF, the thermal conductivity was constant in screw rotation speed at 100 rpm – 150 rpm. But the thermal conductivity of screw rotation speed at 175 rpm decreased in PC-L/VGCF-S and increased in PC-L/VGCF-H. From the Young's modulus result, at screw rotation speed 175 rpm, PC-L/VGCF-H was increased and PC-L/VGCF-S was decreased. It was similar with thermal conductivity. By the way, the thermal conductivity of PC-H/VGCF-H and PC-L/VGCF-H composite were independent on the screw rotation speeds system by melt compounding although this addition made an influence on the PC-H/VGCF-S at high value of screw rotation speeds. This result implied that the thermal conductivity was depended on the different size of VGCF and a further important point is that the thermal conductivity depended on high melt viscosity of PC matrix in spite of adding VGCF-S in various screw rotation speed.

Next we discuss the thermal conductivity of neat PC was independent from screw rotation speeds. On the other hand, the thermal conductivity depended on adding VGCF. Therefore, the thermal conductivity of PC/VGCF composites was affected from the size of VGCF. The surface area per fiber of VGCF-S is larger than that of VGCF-H. The total contact point of VGCF-S in PC matrix is larger than that of VGCF-H [8]. Therefore, a lot of conduction

channel is formed in PC of VGCF-S. This may cause the difference of thermal conductivity of composites.

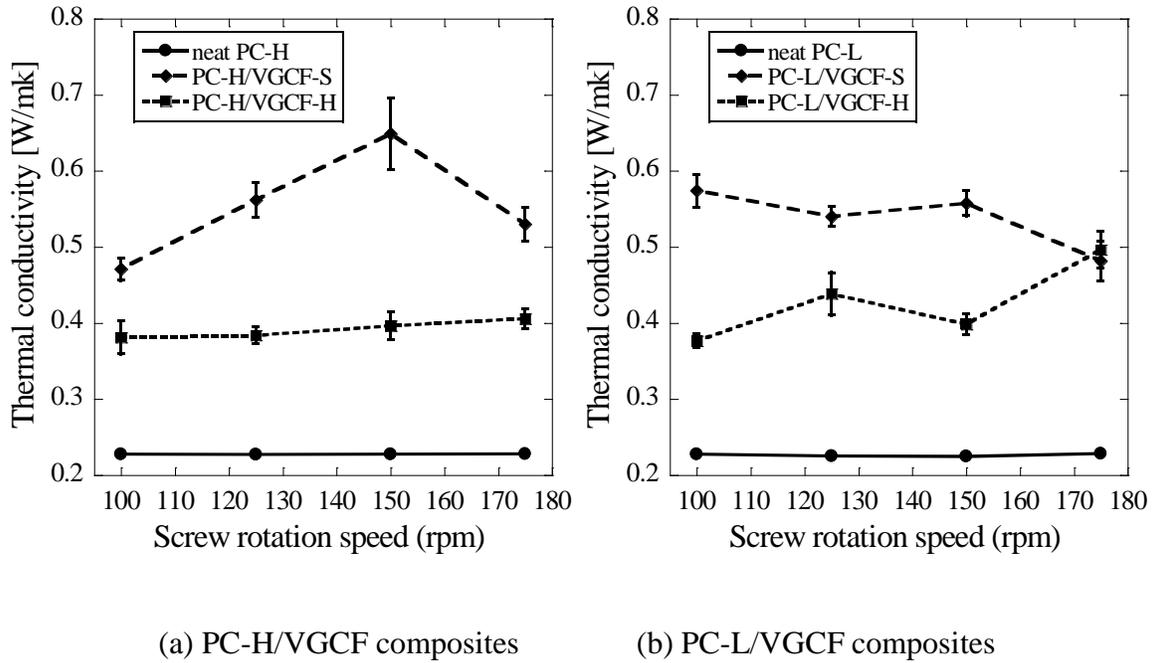


Figure 4.9 Thermal conductivity for various PC/VGCF composites with difference in MVR and screw rotation speed

4.4 Conclusions

We discussed the effect of screw rotation speed and PC type and VGCF size on mechanical, thermal conductivity, rheological behavior and the dispersion state of PC/VGCF composites by melt compounding with a twin screw extruder. The following results were obtained.

1) The mechanical properties were independent of screw rotation speed. Higher and lower screw rotation speeds were not provided better dispersion in mechanical properties of PC/VGCF composite. On the other hand, the size of VGCF was influenced to the mechanical properties.

2) Storage modulus G' and loss modulus G'' of PC were monotonically increased by adding VGCF-H. On the other hands, the second plateau modulus in the PC/VGCF-S. It is indicated that the network structure of VGCF-S was formed in PC matrix since a power law correlation was found between the plateau modulus and adding VGCF.

3) The VGCF-S would be easy to create the dispersion of VGCF in PC/VGCF composites as compared with VGCF-H. And the dispersion state of VGCF was depended on the size of VGCF. According to SEM photographs, the aggregate of VGCF was hardly observed in each PC/VGCF-H composite.

4) The thermal conductivity was depended on the different size of VGCF and a further important point is that the thermal conductivity depended on high melt viscosity of PC matrix in spite of adding VGCF-S in various screw rotation speed.

References

- [1] Ki HK, Won HJ (2009) A strategy for enhancement of mechanical and electrical properties of polycarbonate/multi-walled carbon nanotube composites, *Carbon*, **47**, 1126-1134
- [2] Iijima S (1991) Helical microtubules of graphitic carbon, *Letters to Nature*, **54**, 56-58
- [3] Choi YK, Sugimoto KI, Song SM, Endo M (2005) Mechanical and thermal properties of vapor-grown carbon nanofiber and polycarbonate composite sheets, *Materials Letters*, **59**, 3514-3520
- [4] Darmstadt H, Roy C, Kaliaguine S, Ting JM, Alig RL (1998) Surface spectroscopic analysis of vapour grown carbon fibres prepared under various conditions, *Carbon*, **36**, 1183-1190

- [5] Kumar S, Doshi H, Srinivasrao M, Park JO, Schiraldi DA (2002) Fibers from polypropylene/nano carbon fiber composites, *Polymer*, **43**, 1701-1703
- [6] Sánchez-Soto M, Shiraldi DA, Illescas S (2009) Study of the morphology and properties of melt-mixed polycarbonate-POSS nanocomposites, *European Polymer Journal*, **45**, 341-352
- [7] Potschke P, Fornes TD, Paul DR (2002) Rheological behavior of multiwalled carbon nanotube/polycarbonate composites, *Polymer*, **43**, 3247-3255
- [8] Nithikarnjanatharn J, Ueda H, Tanoue S, Uematsu H, Iemoto Y, (2011) Properties of poly(carbonate)/vapor-grown carbon fiber composites prepared by melt compounding, *Journal of Textile Engineering*, **57**, 97-106
- [9] Liming F, Yang L, Ping G (2006) Processing and mechanical properties of HA/UHMWPE nanocomposites, *Biomaterials*, **27**, 3701-3707
- [10] Incarnato L, Scarfato P, Russo GM, Dimaio L, Iannelli P, Acierno D (2003) Preparation and characterization of new melt compounded copolyamide nanocomposites, *Polymer*, **44** 4625-4634
- [11] Koyama T, Tanoue S, Iemoto Y (2010) Effect of processing conditions on the dispersion of vapor grown carbon fiber in a polyamide 6 and the crystalline structure of their composites by melt compounding, *International Polymer Processing*, **25**, 181-187
- [12] Tanoue S, Hasook A, Itoh T, Yanou M, Iemoto Y, Unryu T (2005) Effect of screw rotation speed on the properties of polystyrene/organoclay nanocomposites prepared by a twin-screw extruder, *Journal of Applied Polymer Science*, **101**, 1165-1173
- [13] Hasook A, Muramatsu H, Tanoue S, Iemoto Y, Unryu T (2008) Preparation of nanocomposites by melt compounding polylactic acid/polyamide 12/organoclay at different screw rotating speeds using a twin screw extruder, *Polymer Composites*, **29**, 1-8

- [14] Tanoue S, Nithikarnjanatharn J, Suzuki T, Uematsu H, Iemoto Y, (2011) Effect of Electric Irradiation on the Mechanical Properties of Polypropylene/Vapor Grown Carbon Fiber Composites Prepared by Melt Compounding, *Journal of Textile Engineering*, in press
- [15] Koyama T, Tanoue S, Iemoto Y (2009) Preparation and properties of polypropylene/vapor grown carbon fiber composite monofilaments by melt compounding, *Journal of Textile Engineering*, **55**, 73-78
- [16] Yang S, Taha-Tijerina J, Serrato-Diaz V, Hernandez K, Lozano K (2007) Dynamic mechanical and thermal analysis of aligned vapor grown carbon nanofiber reinforced polyethylene, *Composites Part B: Engineering*, **38**, 228-235
- [17] Shofner ML, Rodri'guez-Maci'asb FJ, Vaidyanathanc R, Barreraa EF (2003) Single wall nanotube and vapor grown carbon fiber reinforced polymer, composite processed by solid freeform fabrication, *Composites Part A: Applied Science and Manufacturing*, **34**, 1207-1217
- [18] Bin Z, Ruowen F, Mingqiu Z, Xianming D, Bin Z, Lichang W, Charles UPJr. (2006) Studies of the vapor-induced sensitivity of hybrid composites fabricated by filling polystyrene with carbon black and carbon nanofibers, *Composites Part A: Applied Science and Manufacturing*, **37**, 1884-1889
- [19] Shibuya M, Sakurai M, Takahashi T (2007) Preparation and characteristics of a vapor-grown carbon fiber/ceramic composite using a methylsilicone precursor, *Composites Science and Technology*, **67**, 3338-3344
- [20] Wu G, Asai S, Sumita M (1999) A self-assembled electric conductive network in short carbon fiber filled poly(methyl methacrylate) composites with selective adsorption of polyethylene, *Macromolecules*, **32**, 3534-3536

[21] Bernadette AH, William JB (2005) Polycarbonate carbon nanofiber composites, *European Polymer Journal*, **41**, 889-893

Chapter 5

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

5.1 Introduction

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 [1, 2]. In addition, the moldability of the polymer for film molding process is improved by the electric irradiation operation. [3]

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 [4]. One example of the

polymer/nano-order composite systems with high performance is the polymer/clay nanocomposite using layered montmorillonate. Kojima et al. [5] 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 [6-9].

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. [10] 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. [11] 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. [12] studied the melt 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. [13] 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. [14] 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. [15] 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. [16] 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.

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.

5.2 Experimental

5.2.1 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 μm , 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 5.1.

Table 5.1 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.

5.2.2 Melt Compounding

Table 5.2 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 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.

Table 5.2 Compounding ratio

Case	Matrix polymer		VGCF	VGCF contents (wt%)
	PP	MA-PP		
1	100	0	0	0
2	90	10	0	0
3	100	0	2	1.96
4	90	10	2	1.96

5.2.3 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 X 130 mm X 1 mm in each case.

5.3. Results and Discussions

5.3.1 Tensile testing

First, we discuss the relationship between the tensile properties and the irradiation dose for various PP/VGCF composites. Figure 5.1 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 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 $65 \text{ }^\circ\text{C}$ [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.

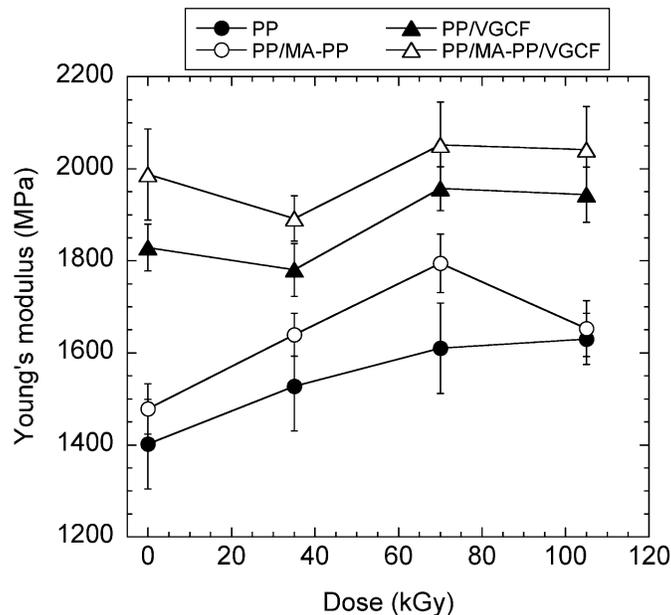


Figure 5.1 Young's modulus as a function of irradiation dose for various PP or PP/VGCF composites.

Figure 5.2 shows the yield stress as a function of the dose for various composites. The width of error bars in the results show the region of standard deviation. In case of PP/MA-PP/VGCF composite at 105 kGy, we show the maximum stress in Figure 5.2. 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 Figure 5.1. 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 Figure 5.3. 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 Figures 5.1 and 5.2, 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. This clarification is one of the future works.

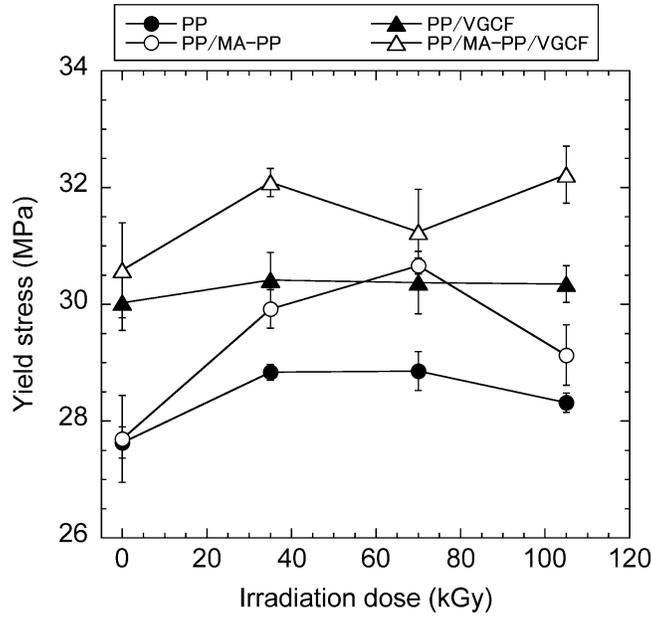


Figure 5.2 Yield stress as a function of irradiation dose for various PP or PP/VGCF composites.

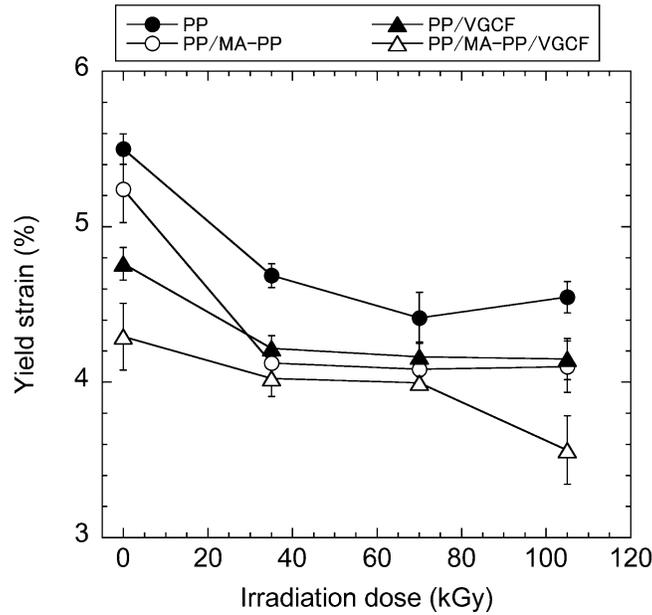


Figure 5.3 Yield strain as a function of irradiation dose for various PP or PP/VGCF composites.

5.3.2 X-ray diffraction

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 5.4 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 [15], 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 $-50\text{ }^\circ\text{C}$. It should be also explained that the amorphous MA-PP chain, of which T_g is about $-10\text{ }^\circ\text{C}$, 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 Figures 5.1 and 5.2, 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.

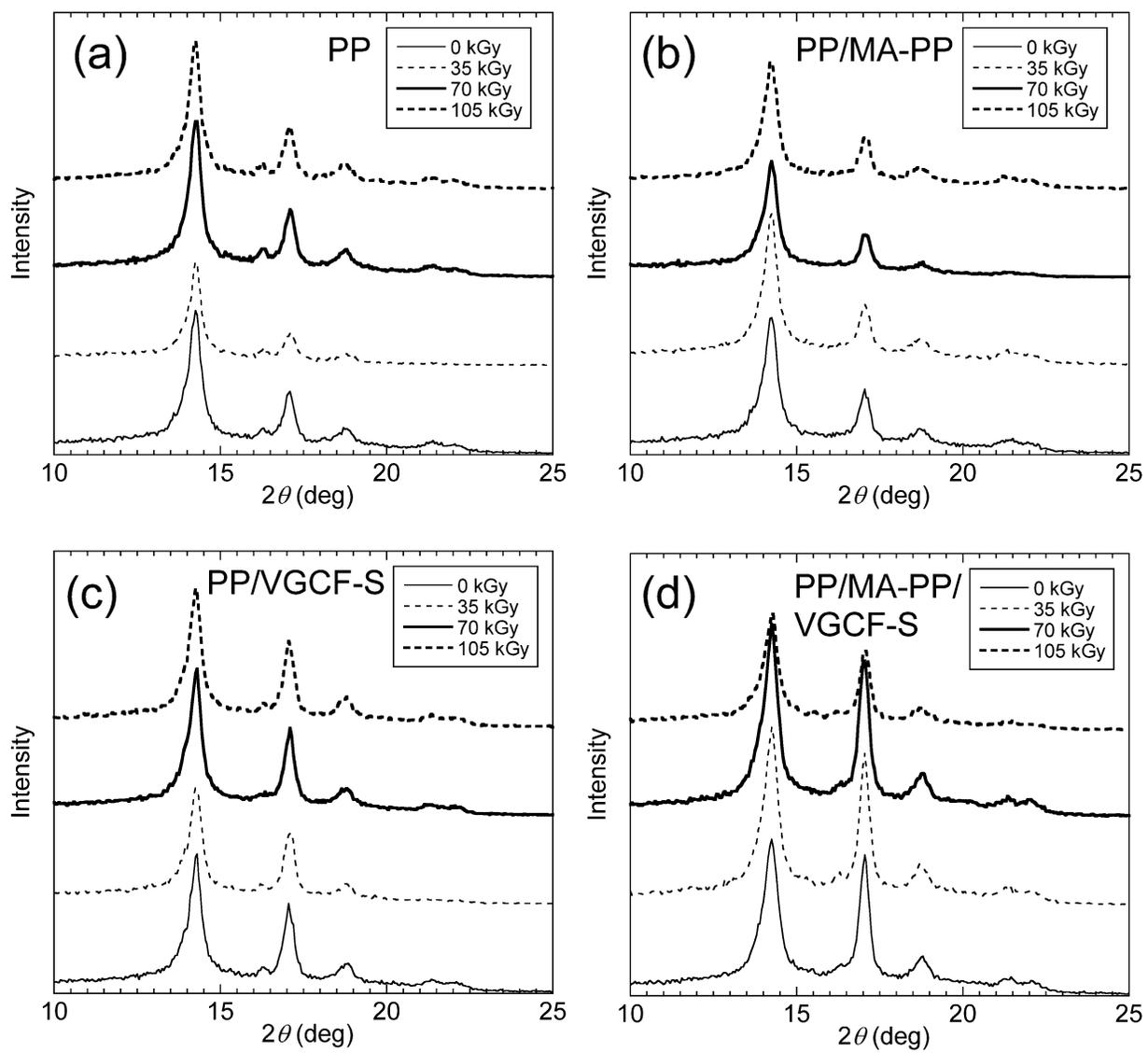
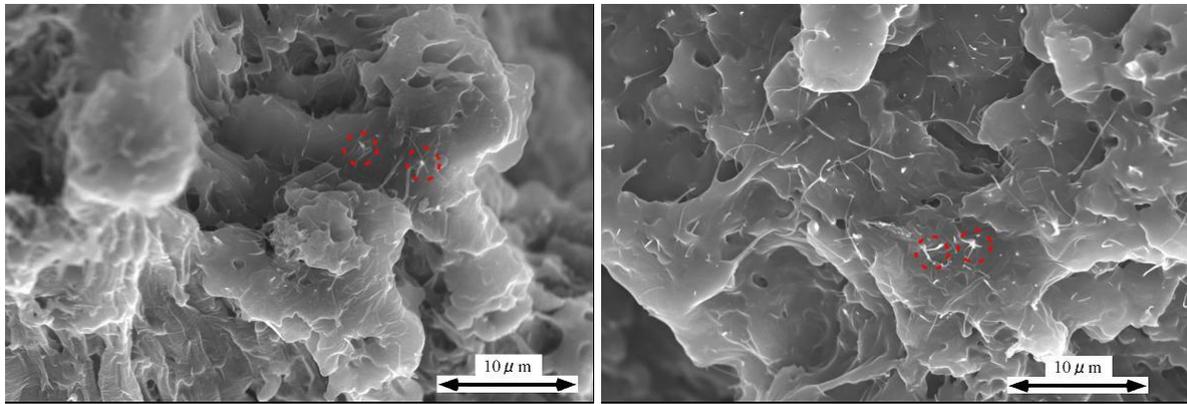


Figure 5.4 XRD diffraction results for the injection molded specimen of each PP or PP/VGCF composites. (a) neat PP, (b) PP/MA-PP composites, (c) PP/VGCF-S composites, (d) PP/MA-PP/VGCF-S composites.

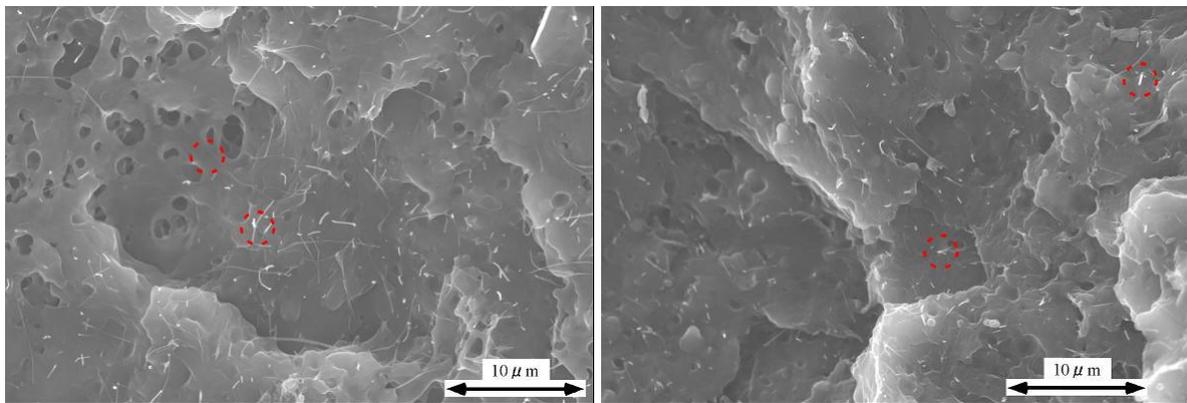
5.3.3 SEM observations

Figure 5.5 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 5.6 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 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].



(a) 0 kGy

(b) 35 kGy



(c) 70 kGy

(d) 105 kGy

Figure 5.5 SEM photos of the fracture cross-section of the injection molded specimens after tensile testing for PP/VGCF-S composites at various irradiation dose.

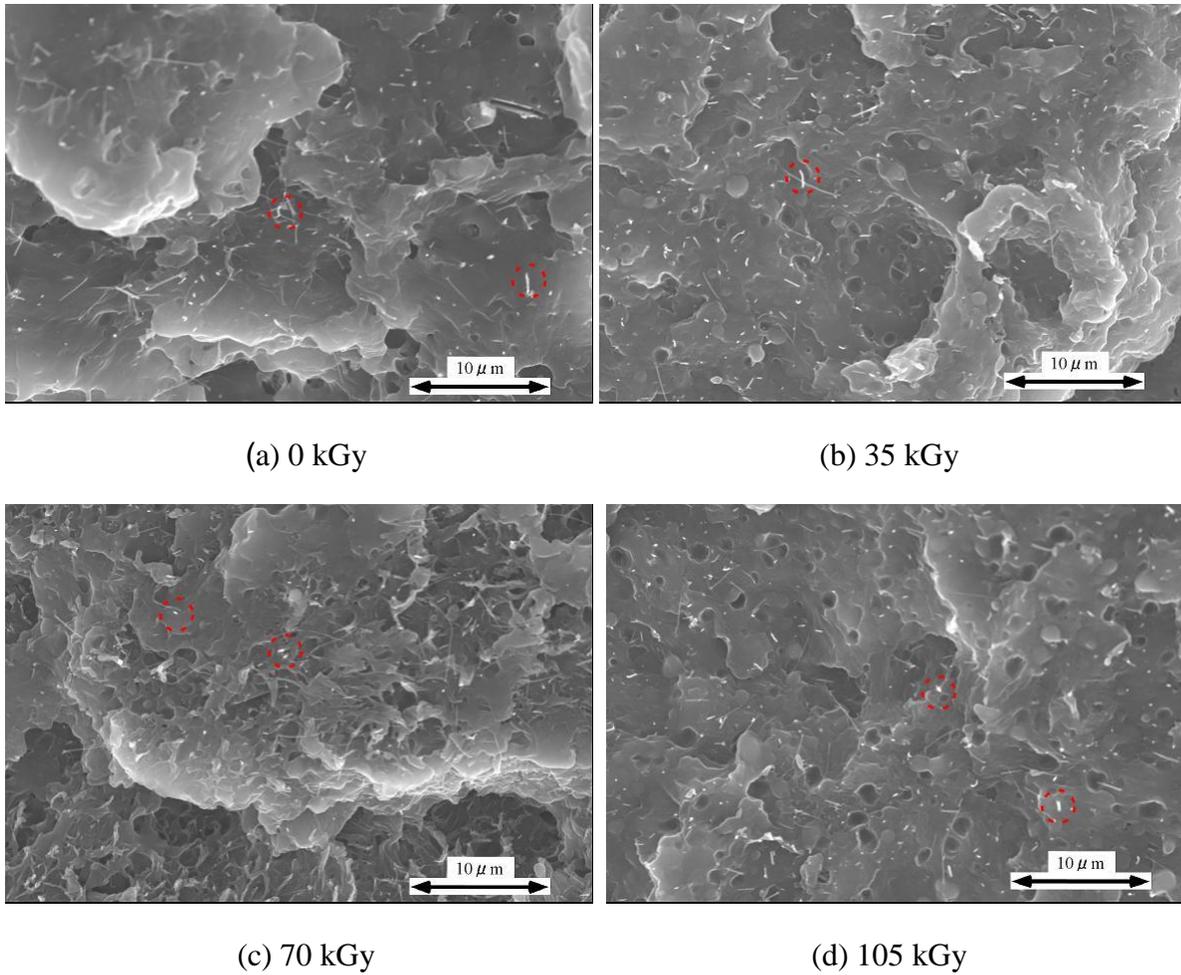


Figure 5.6 SEM photos of the fracture cross-section of the injection molded specimens after tensile testing for PP/MA-PP/VGCF-S composites at various irradiation dose.

5.3.4 Thermal conductivity

Figure 5.7 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.

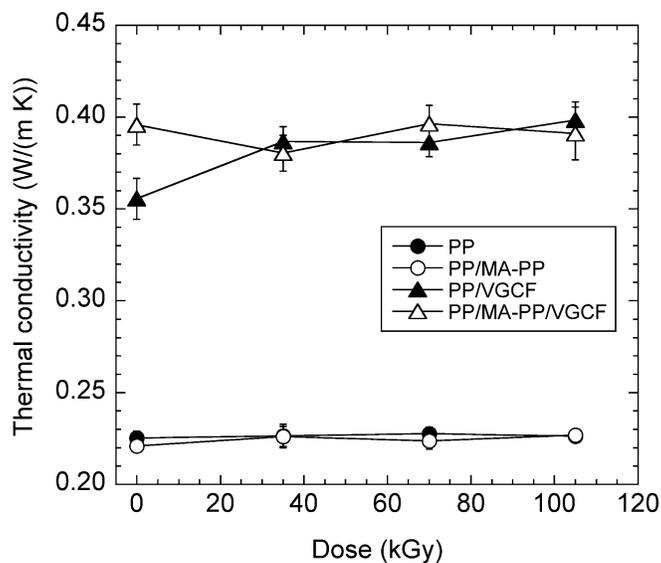


Figure 5.7 Thermal conductivity of the compression molded specimens as a function of irradiation dose for various PP or PP/VGCF composites.

5.4 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.

References

- [1] Yoshii F, Makuuchi K, Kikukawa S, Tanaka T, Saitoh J, Koyama K (1996) High-Melt-Strength Polypropylene with Electron-Beam Irradiation in the Presence of Polyfunctional Monomers, *Journal of Applied Polymer Science*, **60**, 617-623

- [2] Shukushima S, Hayami H, Ito T, Nishimoto S (2001) Terpolymeric membranes obtained by radiation grafting of styrene-acrylonitrile mixtures onto polyethylene films, *Radiation Physics and Chemistry*, **60**, 489-493

- [3] Darwis D, Nishimura K, Mitomo H, Yoshii F (1999) Improvement of processability of poly(epsilon-caprolactone) by radiation techniques, *Journal of Applied Polymer Science*, **74**, 1815-1820
- [4] Utracki LA (2004) "Clay-Containing Polymeric Nanocomposites", RAPRA Technology, Shrewsbury, Shropshire, UK
- [5] Kojima Y, Usuki A, Kawasumi K, Okada A, Fukushima Y, Karauchi T, Kamigaito O (1993) Mechanical properties of nylon 6-clay hybrid, *Journal of Materials Research*, **6**, 1185-1189
- [6] Dennis HR, Hunter DL, Chang D, Kim S, White JL, Cho JW, Paul DR (2001) Effect of melt processing conditions on the extent of exfoliation in organoclay-based nanocomposites, *Polymer*, **42**, 9513-9522
- [7] Tanoue S, Utracki LA, Garcia-Rejon A, Tatibouët J, Cole KC, Kamal MR (2004) Melt compounding of different grades of polystyrene with organoclay: Part 1. Compounding and characterization, *Polymer Engineering and Science*, **44**, 1046-1060
- [8] Tanoue S, Utracki LA, Garcia-Rejon A, Tatibouët J, Kamai MR (2005) Melt compounding of different grades of polystyrene with organoclay: Part 3. Mechanical properties, *Polymer Engineering and Science*, **45**, 827-837
- [9] Tanoue S, Hasook A, Itoh T, Yanou M, Iemoto Y, Unryu T (2006) Effect of screw rotation speed on the properties of polystyrene/organoclay nanocomposites prepared by a twin screw extruder, *Journal of Applied Polymer Science*, **102**, 1165-1173

- [10] Isayev AI, Kumar R, Lewis TM (2009) Ultrasound assisted twin screw extrusion of polymer–nanocomposites containing carbon nanotubes, *Polymer*, **50**, 250-260
- [11] Meincke O, Kaempfer D, Weickmann H, Friedrich C, Vathauer M, Warth H (2004) Mechanical properties and electrical conductivity of carbon-nanotube filled polyamide-6 and its blends with acrylonitrile/butadiene/styrene, *Polymer*, **45**, 739-748
- [12] Potschke P, Fornes TD, Paul DR (2002) Rheological behavior of multiwalled carbon nanotube/polycarbonate composites, *Polymer*, **43**, 3247-3255
- [13] Villmow T, Pötschke P, Pegel S, Häussler L, Kretschmar B (2008) Influence of twin-screw extrusion conditions on the dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix, *Polymer*, **49**, 3500-3509
- [14] Koyama T, Tanoue S, Iemoto Y (2009) Preparation and properties of polypropylene/vapor grown carbon fiber composite monofilaments by melt compounding, *Journal of Textile Engineering*, **55**, 73-78
- [15] Koyama T, Tanoue S, Iemoto Y (2010) Effect of processing conditions on the dispersion of vapor grown carbon fiber in a polyamide 6 and the crystalline structure of their composites by melt compounding, *International Polymer Processing*, **25**, 181-187
- [16] Yang S, Taha-Tijerina J, Serrato-Diaz V, Hernandez K, Lozano K (2007) Dynamic mechanical and thermal analysis of aligned vapor grown carbon nanofiber reinforced polyethylene, *Composites Part B: Engineering*, **38**, 228-235
- [17] Diyakon LV, Dmytrenko OP, Kulish NP, Prylutskyi YI, Grabovskiy YE, Belyy NM, Alekseev SA, Alekseev AN, Sementsov YI, Gavrylyuk NA, Shlapatskaya VV, Valkunas L,

Ritter U, Scharff P (2008) Radiation damage of isotactic polypropylene composites with multi-walled carbon nanotubes, *Functional Materials*, **15**, 169-174

[18] Ziabicki A (1976) "Fundamentals of Fibre Formation", John Wiley & Sons

[19] Shiromoto S, Koyama K (2004) Study on viscoelastic behavior and extrusion blow molding processability of PP/PE blends, *International Polymer Processing*, **19**, 287-295

Chapter 6

Conclusions and Future Work

6.1 Conclusions

Vapor grown carbon fiber (VGCF) are the new class of discontinuous nano size carbon fibers. These fibers are 20 to 200 nm in diameter with a length longer than several 100 μm . They are different from other common carbon fibers in their way of manufacture, their mechanical properties and thermal conductivity. The work performed in this thesis includes polymer/VGCF composites and investigating characteristics of polymer. Investigation of polymer/VGCF composite on mechanical properties and thermal conductivity is an important issue with the trial investigator.

6.1.1 Properties of poly(carbonate)/vapor grown carbon fiber composite prepared by melt compounding

In chapter 3, we discussed the mechanical properties, thermal properties and rheological properties of composite and also the effect of adding vapor grown carbon fiber (VGCF) size and VGCF contents and different melt viscosity of PC composites prepared by using a twin screw extruder.

In part 1, we discuss the effect of poly(carbonate) (PC) type and VGCF size on the mechanical properties of PC/VGCF composites prepared by melt compounding using a twin screw extruder. Four kinds of PC which have different melt volume flow rate, and two kinds of VGCF which have different aspect ratio (VGCF-S which is the aspect ratio of 100, and VGCF-H which is the aspect ratio of 40.) were used in this study. In addition, the several VGCF contents were set up in each PC/VGCF composite. The Young's modulus of PC/VGCF composite overall increased with VGCF content in each case. However, the enhancement of Young's modulus in PC with low and high melt viscosity is little. Tensile strength, which is maximum stress during tensile testing, of PC/VGCF composite increases a little with VGCF content except for the case using PC with high melt viscosity. Though VGCF-S is the smaller surface area and higher aspect ratio as compared with VGCF-H, the effect of each VGCF on the mechanical properties of PC is almost same. The dispersion, agglomeration and breaking of VGCF could be interpreted from the investigation of the morphology, thermal properties and Halpin-Tsai model, which predicts the Young's modulus of the polymer/fiber composites. We concluded that the VGCF could be easily broken in high viscosity matrix.

In part 2, the effect of the PC matrix viscosity on the thermal conductivity of a PC/VGCF composite was investigated in this study in terms of the rheological properties of the PC/VGCF using two types of VGCF. Two types of VGCF, which have different aspect ratios, were added to two types of PC with different viscosities. The storage modulus (G') and loss modulus (G'') of the PC slightly increased and the thermal conductivity gradually increased with the content of VGCF-H. By adding VGCF-S to low-viscosity PC, rheological properties originating in the network structure were observed. The thermal conductivity of low viscosity PC drastically increased with the content of VGCF-S. By analyzing the length of the VGCF in

each composite, we found that the length of VGCF decreased with mixing. It was also easy to shorten the VGCF in high-viscosity PC. We clarified that the thermal conductivity of PC/VGCF could be controlled with the viscosity of the polymer matrix because the spread of the network structure of VGCF and/or the breaking of the VGCF depended on the viscosity of the polymer matrix.

6.1.2 Effect of screw rotation speed of a twin screw extruder on the mechanical properties and thermal conductivity of polycarbonate/vapor grown carbon fiber composites

In chapter 4, we discussed the effect of screw rotation speed and polycarbonate (PC) type and vapor grown carbon fiber (VGCF) size on mechanical, thermal conductivity and the dispersion state of PC/VGCF composites by melt compounding with a twin screw extruder. The following results were obtained.

We discuss the effect of screw rotation speed on mechanical properties and thermal conductivity of composites prepared from PC/VGCF by melt compounding using a twin screw extruder. The screw rotation speeds was 100, 125, 150 and 175 rpm. The melt viscosity of the PC extruder 2 types which have different melt viscosity (PC-H and PC-L) and VGCF 2 types of VGCF-H (aspect ratio 40) and VGCF-S (aspect ratio 100) were used in this study. The Young's modulus of PC/VGCF composite is extremely low in screw rotation speed. Tensile strength of PC/VGCF composite depended on high melt viscosity and increase screw rotation speed. The effect of dispersion resulting from adding VGCF to PC matrix at various screw rotation speed, depends on the size of VGCF in PC matrix. The thermal conductivity of high viscosity PC increased with adding of VGCF-S in various screw rotation speed. The storage modulus (G') and

loss modulus (G'') of PC slightly increased with the adding VGCF-H. By adding VGCF-S in PC matrix, the rheological properties originate in the network structure was observed. By the analysis of dispersion state of VGCF in each composite, it was clearly found that the dispersion of VGCF was depended on the size of VGCF. It was easy to create the network structure of VGCF-S in PC matrix. We concluded the screw rotation speed depended on the size of VGCF because VGCF-S with high aspect ratio, VGCF dispersed with an increase of screw rotation speed. Contrary VGCF-H with low aspect ratio, the dispersion of VGCF was independent on the screw rotation speed.

6.1.3 Effect of electric irradiation on the mechanical properties of polypropylene/vapor grown carbon fiber composites prepared by melt compounding

In chapter 5, in this study, we investigated the effect of the electric irradiation on the mechanical properties of polypropylene (PP)/vapor grown carbon fiber (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.

We discussed the effect of the electric irradiation on the properties of PP/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.

6.2 Future work

In this thesis, the filler VGCF to polymer composite have shown improvement in the properties from the point of view mechanical properties and thermal conductivity. This study leaves wide scope for future investigations. It can be extended to newer composites using other reinforcing phases and the resulting experimental findings can be similarly analyzed.

There is a very wide scope for future researcher to explore this area of research. Many other aspects of this problem like effect of carbon fiber orientation on wear response of such composites require further investigation. From the results of the research present in this thesis and results and discussion presented in chapter 3-5 and conclusions 6.1, the following future work can be recommended:

- 1) To study the electrical conductivity of VGCF and relate these to the morphologies.
- 2) To continue the study of the application of VGCFs in polymer composites using different weight-average molecular.
- 3) To study the electrical conductivity of polymer/VGCF composites.
- 4) To study the properties of polymer/VGCF composites, comparatively to those of other carbon fiber reinforced composites.
- 5) To extend the use of the polymer/VGCF composites to a wider range of composites having different fiber aspect ratio.
- 6) To apply the models prediction in structural analysis of short fiber composites.

Publications

Journal Papers

- [1] Nithikarnjanatharn Jittiwat, Ueda Hisai, Tanoue Shuichi, Uematsu Hideyuki, Iemoto Yoshiyuki. Properties of Poly(Carbonate)/Vapor-Grown Carbon Fiber Composite Prepared by Melt Compounding. *Journal of Textile Engineering*, Vol. 57, No.4, 2011, pages 97-106
- [2] Tanoue Shuichi, Nithikarnjanatharn Jittiwat, Suzuki Takeo, Uematsu Hideyuki, Iemoto Yoshiyuki. Effect of Electric Irradiation on the Mechanical Properties of Polypropylene/Vapor Grown Carbon Fiber Composites Prepared by Melt Compounding. *Journal of Textile Engineering*, Vol. 58, No.1, 2012, pages 1-7
- [3] Nithikarnjanatharn Jittiwat, Ueda Hisai, Tanoue Shuichi, Uematsu Hideyuki, Iemoto Yoshiyuki. The Rheological Behavior and Thermal Conductivity of Melt-Compounded Polycarbonate/Vapor-Grown Carbon Fiber Composites. *Polymer Journal*, 2012 (in press)
- [4] Nithikarnjanatharn Jittiwat, Hiroki Okuzono, Tanoue Shuichi, Uematsu Hideyuki, Iemoto Yoshiyuki. Effect of Screw Rotation Speed of a Twin Screw Extruder on the Mechanical Properties and Thermal Conductivity of Polycarbonate/Vapor Grown Carbon Fiber Composites. 2012 (in preparing)

International Conferences Papers

[1] Nithikarnjanatharn Jittiwat, Ueda Hisai, Tanoue Shuichi, Uematsu Hideyuki, Iemoto Yoshiyuki. Mechanical Properties of Poly(Carbonate)/Vapor-Grown Carbon Fiber Composites Prepared by Melt Compounding. *Proceedings of the 26th Annual Meeting of the Polymer Processing Society*, July 4-8, 2010, Banff CANADA.

[2] Nithikarnjanatharn Jittiwat, Kurome Yuki, Ueda Hisai, Tanoue Shuichi, Uematsu Hideyuki, Iemoto Yoshiyuki. Rheological Properties and Thermal Conductivity of Poly(Carbonate)/Vapor Grown Carbon Fiber Composites Prepared by Melt Compounding. *Proceeding of the 40th Textile Research Symposium*, August 25-27, 2011 Kyoto, JAPAN.

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