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Rheological Properties of Surface Treated Glass Fiber Reinforced Polypropylenes in Molten State

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1. Introduction

Fiber reinforced thermoplastics (FRTP) are widely used to industrial applications such as automobiles and electric devices in recent years (Thomason & Vlug, 1996; Kitano et al., 2000; Nishitani et al., 1999, 2001; Hausnerova et al., 2006). Since the machine and the electric devices became small and lightweight, the good balance of the physical properties and processability of FRTP is desired strongly. Polyolefines represent a group of the most common used polymers as matrix for FRTP, because they are inexpensive, easily processed and recycled (Nishitani et al., 1998a, 1998b, 2007). On the other hand, glass fiber (GF) is the most used as reinforcement for FRTP so as to modify the mechanical properties such as stiffness, strength, toughness, heat resistance and so on, and the other properties. Hence, glass fiber reinforced polypropylene composites (GF/PP) are of particular interest in these fields. However, it is difficult to form a strong bond between filler (fiber) and polymer due to poor wettability of the filler (fiber) especially in nonpolar polymer (Shenoy, 1999). The interfacial bond can be enhanced and the mechanical properties of the composites will be improved by suitable surface treatment. Most of fillers (fibers) are pretreated before they are used as secondary phases in composite materials. As typical surface treatment for polymer matrix composites, we often use the coupling agent as follows: silanes, azidosilanes, titanates and organopolysiloxanes, and so on (Shenoy, 1999). In particular, the most effective methods for controlling of the interface and interphase adhesion between GF and PP in GF/PP composites in industrial fields are considered to use silane coupling agents (Mader, 1996; Nishitani et al. 1998b). Many authors have investigated the effect of surface treatment on the various physical and chemical properties of GF/PP composites (Yue & Quek, 1994; Thomason & Schoolenberg, 1994; Mader, 1996, 2001; Lee & Jang, 1997; Kikuchi et al., 1997; Van Den Oever & Peijs, 1998; Hamada et al., 2000). However, their properties will be able to still be improved more by the suitable control of the interphase adhesion between GF and PP.

In order to achieve higher performance in FRTP such as GF/PP, there is a key issue that the rheological properties in molten state is very critical for these materials to understand

processability, internal microstructures, their change and structure property relationship (Hausnerova, 2006, 2008a, 2008b; Nishitani, 2010a, 2010b, 2010c). In particular, although FRTPs undergo various flows during processing by flow molding such as injection, extrusion and compression, generally, the effect of surface treatment on processing properties has not been studied enough (Boaira & Chaffey, 1977; Han et al., 1981; Bigg 1982; Luo et al., 1983; Sani et al., 1985; Khan & Prud'Homme, 1987; Nishitani et al. 1998b, 2007; Shenoy 1999). Therefore, we need a proper rheological study on the effect of surface treatment taking into account the various factors such as type of fiber, its size and size distribution, and degree of agglomeration. However, since these factors are interrelated, the determination of the effect of surface treatment on the interphase adhesion is thought to be necessarily a complicated task. Han et al. showed that there were viscosity decrease and the first normal stress difference increase for CaCO_3 /PP composites regardless of the type of coupling agent used (Han et al., 1981). In contrast, in the case of glass bead filled PP the effect of surface treatment was not so distinct, the viscosity increased after treatment by aminosilane coupling agent, and decreased when octylsilane and titanate coupling agents were used (Khan & Prud'Homme, 1987). Similar complex rheological behavior appeared as the results of surface treatment of CaSiO_3 filled PA6 (Luo et al., 1983) and ferrite filled PP (Saini et al., 1985).

Recently, we studied the effect of silane coupling agents on the rheological properties of short and long glass fiber reinforced polypropylene composites in molten state (Nishitani et al., 1998b, 2007). Surface treatment by silane coupling agents increased the storage modulus and reduced the peak in the loss tangent. Furthermore, decrease in the dynamic viscosity was affected by the concentration of coupling agents. Nevertheless, according to our survey of the previous results, the effect of surface treatment on the rheological properties is still not well known. It is therefore necessary to investigate systematically for further understanding of it. The objective of this chapter is to report the results on the effect of surface treatment by silane coupling agent on the rheological properties of short and long glass fiber reinforced polypropylene composites in the molten state which were obtained mainly in our previous studies.

2. Rheological properties of surface treated short glass fiber reinforced polypropylenes

Short fiber reinforced thermoplastic composites have been employed extensively in the plastic industry because of the excellent combination of their mechanical properties, chemical resistance, moderate cost, and recyclability performance. Short glass fiber reinforced polypropylene composites (GF/PP) are of particular interest (Nishitani et al., 2007). Despite great effort expended on research into GF/PP composites, their properties can still be improved by control of the interphase adhesion between GF and PP. One of the methods of improving the adhesion between polymer and fiber is the use of surface treatment agents (Shenoy, 1999). Treatment agents, when properly chosen, bring considerable improvement, particularly in mechanical and thermal properties. A typical surface treatment for GFs is a coupling agent. Another method involves the addition of PP modified by maleic anhydride (mPP) (Sasagi & Ide, 1980). Mechanical properties are improved by the increase in interfacial adhesion. The lower the degree of grafting of maleic anhydride to the modified PP and the higher its molecular weight is, the more effective the improvement is. Recently, a combination of these methods was investigated (Peltonen et al., 1995; Nishitani et al., 1998c, 2007), but the mechanism is still not fully understood. In particular, there have been few efforts to investigate the rheological properties of GF/PP

composites by these combinations. The aim of this section is to report the results of the effect of the fiber surface treatment with aminosilane coupling agent on the rheological properties of short glass fiber reinforced polypropylene composites (GF/PP) and of GF/PP composites supplemented by maleic anhydride modified PP (GF/mPP/PP). Rheological functions in the molten state were measured under steady state shear (viscous and elastic properties) and oscillatory flow (viscoelastic properties) regimes.

2.1 Materials and methods

The effect of surface treatment on the rheological properties of short glass fiber reinforced polypropylene (GF/PP) in molten state was investigated in this section. The materials used in this section were GF/PP and the same materials added with maleic anhydride modified PP (GF/mPP/PP). The polymers used were polypropylene (PP, Sumitomo Novolen, Sumitomo Chemical Co., Japan) and maleic anhydride modified PP (mPP, Sumitomo Chemical Co.) Glass fiber (GF, Micro Glass Fiber, Nippon Glass Fiber Co., Japan) was filled with PP. Surface treatment by aminosilane coupling agent (ASC, γ -aminopropyltriethoxysilane, A1100, Nippon Unika Co., Japan) with different concentrations was performed on glass fibers. The GFs were pre-treated with ASC in the following way. ASC was mixed with 20 times its volume of water, then the hydrolyses ASC was further diluted in water to concentrations of 0.2, 0.5 and 1.0 wt.%, and the aqueous solutions were applied to GFs. The GF content was fixed with 20wt.% and 40wt.%. The compositions and average fiber lengths of the samples are shown in Table 1.

Composition (wt.%)	PP	20GF								40GF			
		GF/PP				GF/mPP/PP				GF/PP		GF/mPP/PP	
PP	100	80	80	80	80	75	75	75	75	60	60	55	55
mPP	-	-	-	-	-	5	5	5	5	-	-	5	5
GF	-	20	20	20	20	20	20	20	20	40	40	40	40
ASC	-	-	0.2	0.5	1	-	0.2	0.5	1	-	1	-	1
Fiber length (mm)	Original	1.038	-	-	1.177	1.020	-	-	1.134	-	-	-	-
	Remixed	0.648	-	-	0.731	0.620	-	-	0.674	-	-	-	-

Table 1. Composition and average fiber length of GF/PP and GF/mPP/PP composites.

The compounding of PP with GF was carried out at 200°C in a specially developed elastic extruder (Kataoka et al, 1976; Zang et al, 1995, Nishitani et al 1998c, 2007). The weighed amounts of the pellets used for making the 3mm thick compression molded samples were placed into the mold cavity. They were compressed for 3min under 5MPa at 200°C. Finally, the test specimens for the rheological measurements were cut from the molded sheets. And second time-mixed composites were also prepared in order to investigate the influence of this process on the effect of surface treatment.

The steady-state shear flow properties in the low shear rate region and the dynamic functions were measured using a rotational viscometer (cone-plate type, RGM 151-S, Nippon Rheology Kiki Co., Ltd., Japan). The cone radius R was 21.5mm, the gap between the central area of the cone and plate H was kept at 175 μ m, and the cone angle θ was 4°. The measurements were carried out at 200°C. Steady state shear properties (shear viscosity η , and the first normal stress difference N_1) as well as dynamic functions (storage and loss moduli G' , G'' , respectively,

dynamic viscosity η' and complex viscosity $|\eta^*|$) were determined as functions of the shear rate $\dot{\gamma}$ and angular frequency ω from 10^{-2} to 10 1/s (rad/s), respectively. The strain amplitude was chosen to be 25% (oscillatory angle $\pm 1^\circ$) which is considered to be a large value in order to compare the results of the oscillatory and steady shear regimes.

2.2 Shear rate dependences

The shear viscosity η and the first normal stress difference N_1 are plotted against shear rate $\dot{\gamma}$ for both the untreated and 1wt.% ASC treated GF/PP composites in Fig.1. In the lower shear rate region, between 0.05 and 0.5 1/s, the character of the viscosity curves of all the GF filled systems were similar to that of pure PP – i.e. they were nearly independent of the shear rate. It is thought that increase in shear viscosity was caused by enhanced resistance to shear flow arising from structure composed by reinforcing fibers in the system, and also from the increased fiber-polymer matrix interactions supported by surface treatment. In the shear rate region higher than 0.5 1/s, where the PP behaves in a pseudoplastic manner, the fibers tend to orient in the flow direction, and the effect of surface treatment by ASC diminishes (Fig.1(a)). The first normal stress difference N_1 data shown in Fig. 1(b) indicates an increase in elastic property as a result of the surface treatment by ASC. In general, the first normal stress difference N_1 increases with an increase in fiber length, with structure formation by the fibers, and with the elastic properties of fibers themselves. The degree of dispersion of fibers in a polymer matrix is also an important factor influencing on the elastic properties of fiber reinforced composites in the molten state. When the fibers are surface treated, the structure formed can be changed easily. Furthermore, the apparent fiber modulus of a treated system will be higher than that of an untreated one because of the softened phase, which is able to change the structure in the region of the polymer-fiber interface. Although the first normal stress differences of untreated GF/PP composites in the high shear rate region reach the values close to those of the pure polymer matrix, those of the treated materials are higher.

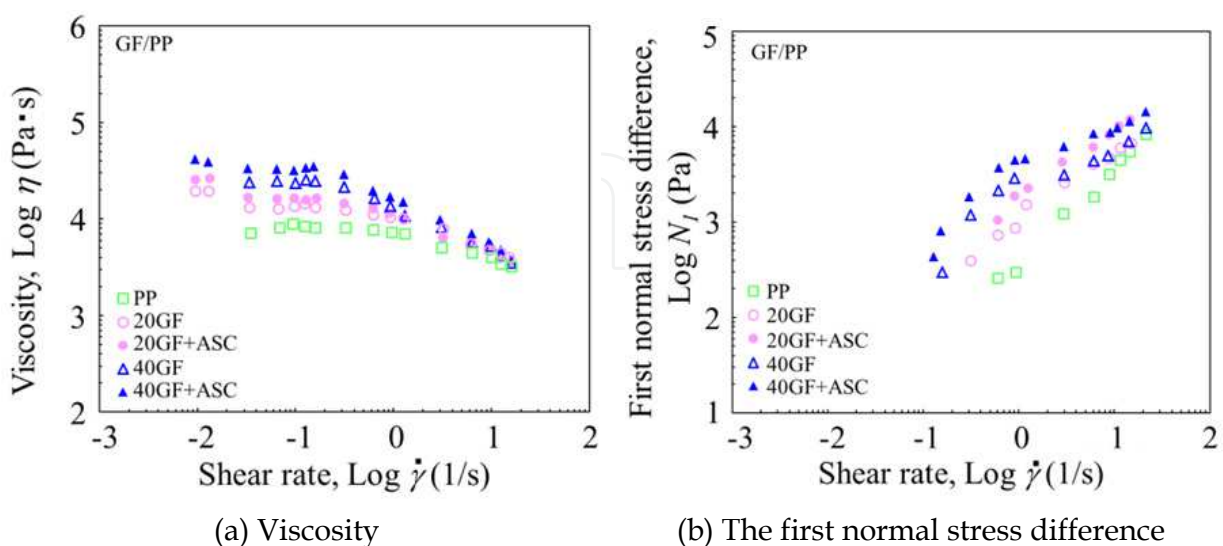


Fig. 1. Influence of silane coupling agent on steady shear flow properties of GF/PP composites: (a) viscosity as a function of shear rate, (b) the first normal stress difference as a function of shear rate

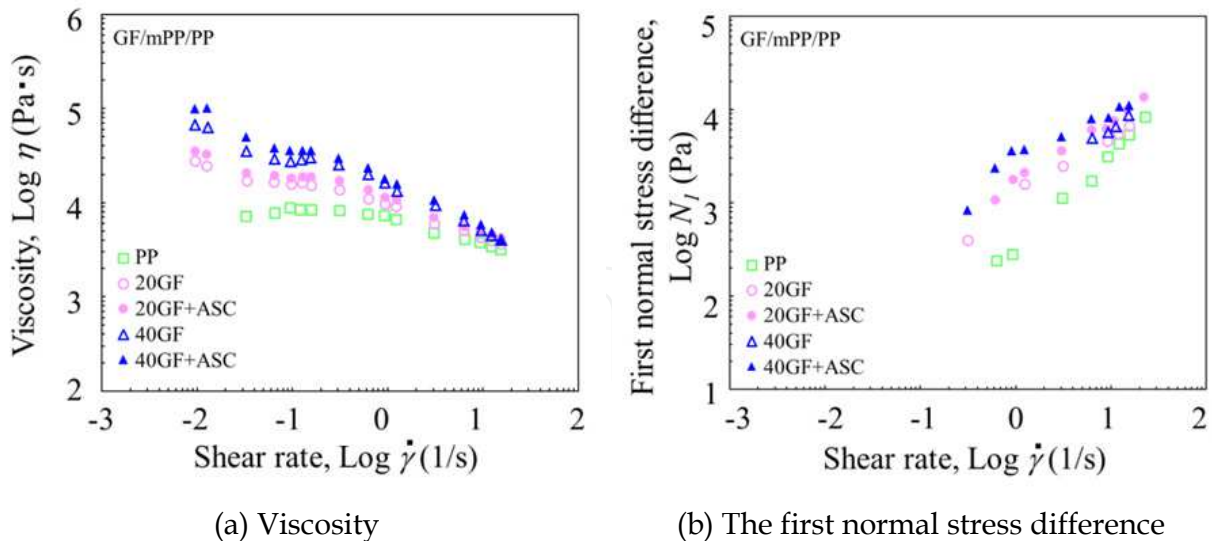


Fig. 2. Influence of silane coupling agent on steady shear flow properties of GF/mPP/PP composites: (a) viscosity as a function of shear rate, (b) the first normal stress difference as a function of shear rate

In the low shear rate region, the first normal stress difference increases with the fiber content, which may be due to the hydrodynamic effect associated with fiber orientation in the flow direction. The effect of surface treatment was identical to that in the high shear rate region. The shear viscosity and the first normal stress difference as a function of shear rate for maleic anhydride modified PP (5wt.%) added composites (GF/mPP/PP composites) are plotted in Fig. 2. Although the overall level of the both functions η and N_1 was higher than that in GF/PP composites (Fig. 1), the effect of surface treatment by 1wt.% ASC on η and N_1 of GF/PP composites is similar to that of GF/mPP/PP.

The results demonstrated in Figs. 1 and 2 are somewhat different from those obtained in studies of particulate filled polymer systems, for example, mica filled PP (Boaira & Chaffey, 1977) or calcium carbonate filled PP (Han et al., 1981), where the increased values of shear viscosity and the first normal stress difference caused by the filler addition could be reduced to a greater or lesser extent - by surface treatment. Such discrepancies in the results can be explained by the different roles played by the coupling agent during processing as follows. First, it forms chemical bonds between the inorganic filler and polymer matrix, and assists physical adhesion by Van der Waals's forces. Second, it may behave as a lubricant, which decreases the friction between the filler and polymer matrix. Third, it changes the interfacial energy of the filler, and simultaneously supports better filler dispersion in the polymer matrix, and reduces agglomeration by wetting. Finally, a surface treatment agent can behave as an additive to make deformation of fiber assembly easier and to make the viscoelastic properties of a matrix polymer lower. It is thought that the mechanisms mentioned above do not occur separately, and therefore it is difficult to distinguish a particular type.

Regarding GF/PP and GF/mPP/PP composites investigated in this section, the adhesion between fiber and polymer matrix was improved. In addition, because of the improved protection against the breakage of fibers, the fiber length of treated materials can be kept

longer throughout the compounding and processing than that of untreated ones. Finally, the addition of maleic anhydride modified PP (mPP) increases the rheological properties (viscosity and the first normal difference), because mPP probably not only improves the surface treatment, but also forms chemical bonds between fiber and polymer matrix.

2.3 Angular frequency dependences

The storage and loss moduli G' and G'' as a function of angular frequency ω for GF/PP composites are shown in Fig. 3. The storage modulus G' of the GF/PP composites treated by 1 wt.% ASC was scarcely higher than that of the untreated ones, and it was almost independent of fiber content (20 or 40 wt.%), although generally G' should increase with fiber loading level (Fig.3(a)). Also, the loss modulus G'' of the treated GF/PP composites (Fig. 3(b)) was only slightly higher than that of the untreated composites. Unlike G' , G'' increased with increasing the fiber content. Although G'' of the untreated composites (20 and 40 wt.% GF) increased over the whole angular frequency range covered by the experiments, this trend was valid only for angular frequencies higher than 0.1 rad/s in the case of the treated materials. In the frequency region lower than 0.1 rad/s, the surface treatment by ASC initiated the behaviour in which G'' was independent of ω , indicating a second rubbery plateau, i.e. the long-scale relaxation time. This behaviour implies the presence of an apparent yield stress, which will be attributed to the strong fiber structure formation imparted by the surface treatment. The properties of GF/mPP/PP composites, demonstrated in Fig. 4, showed the same trend of G' against frequency dependency as for GF/PP composites in Fig. 3(a). However, with 20wt.% GF and no ASC treatment, there was no evidence of plateau behaviour in the loss modulus.

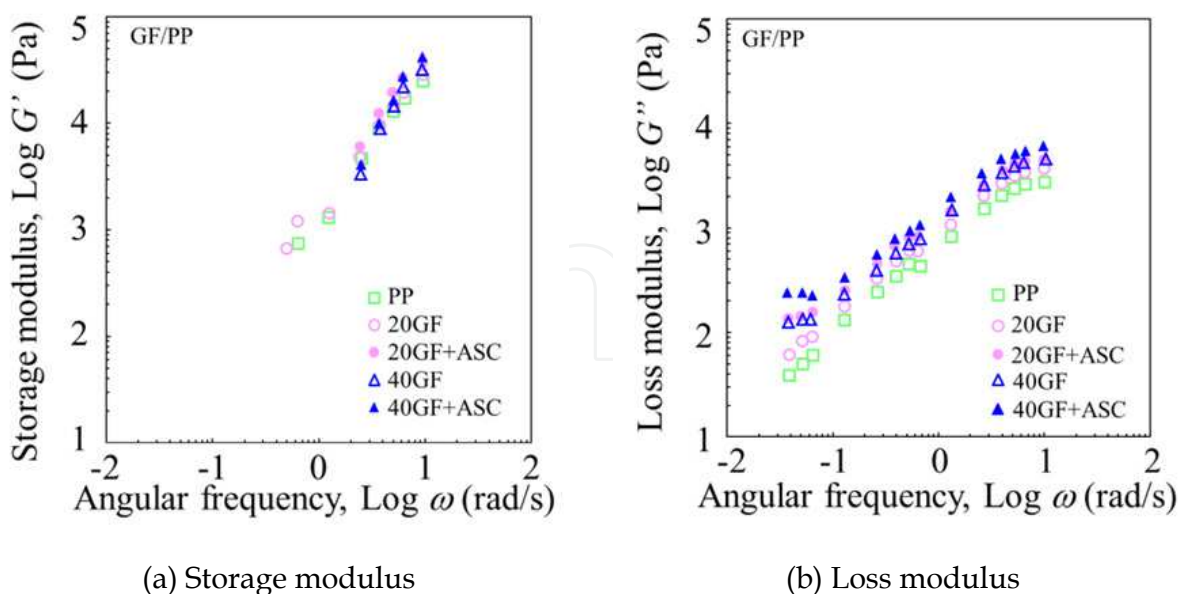


Fig. 3. Influence of silane coupling agent on dynamic viscoelastic properties of GF/PP composites: (a) storage modulus as a function of angular frequency, (b) loss modulus as a function of angular frequency

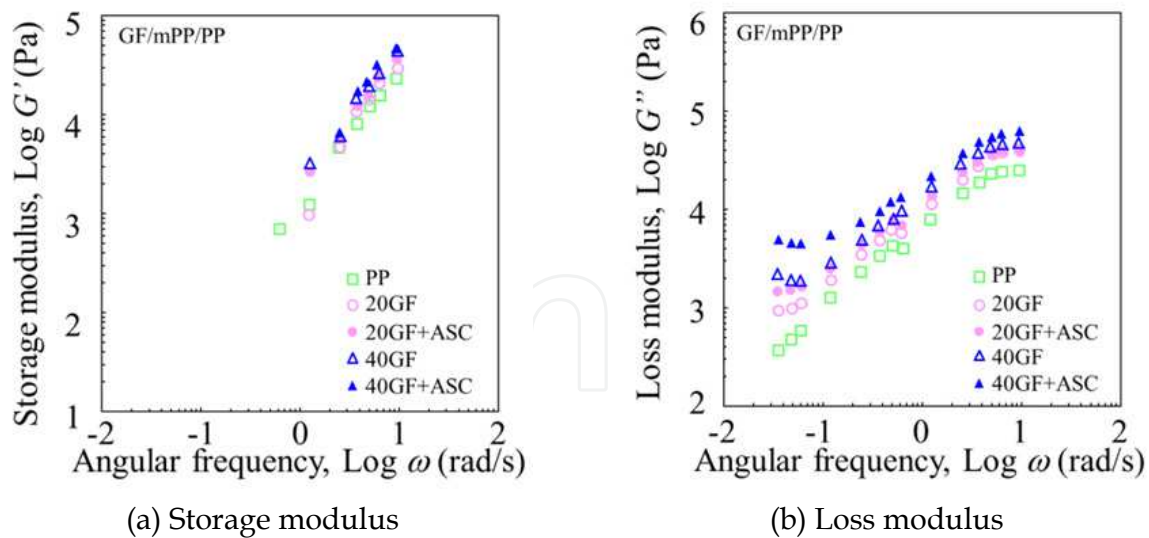


Fig. 4. Influence of silane coupling agent on dynamic viscoelastic properties of GF/mPP/PP composites: (a) storage modulus as a function of angular frequency, (b) loss modulus as a function of angular frequency

2.4 Comparison of steady shear and dynamic flow data

Cox and Merz (Cox & Merz, 1958) observed a close similarity between the steady state shear and complex viscosities determined at corresponding values of the shear rate and angular frequency, respectively. This empirical rule can be written as follows:

$$\dot{\eta}(\dot{\gamma}) = |\eta^*(\omega)| = \sqrt{\eta'^2(\omega) + \eta''^2(\omega)} \quad (1)$$

Where η , $|\eta^*|$ are the shear and complex viscosities, and η' , η'' are the real and imaginary parts of the complex viscosity $|\eta^*|$, respectively. The validity of this relation for polymer melts and concentrated solutions has been amply verified. The steady state shear and complex viscosities both approached their limiting (zero viscosity) values as their arguments go to zero, and they decreased in a similar way with increasing $\dot{\gamma}$ or ω , although at high shear rates (angular frequency) $|\eta^*|$ may fall more rapidly than η . As proposed by Dealy (Dealy & Wissbrun, 1990), the Cox-Merz rule should be generally valid for flexible molecules; however, it is not suitable for almost any fiber filled polymer systems (Kitano et al., 1984a, 1984b; Li et al., 1997; Nishitani et al., 2007), since the viscosity increment caused by the fiber addition would be different under the two types of flow.

In Fig. 5, double-logarithmic plots of η vs. $\dot{\gamma}$ and $|\eta^*|$ vs. ω are shown for both GF/PP and GF/mPP/PP composites. The η and $|\eta^*|$ curves coincided relatively well in their plateau (Newtonian) regions at shear rates (angular frequencies) from 0.1 to 1 1/s (rad/s) for untreated samples. Nevertheless, the $|\eta^*|$ values of the GF/PP treated by 1wt.% ASC, shown in Fig. 5(a), were clearly higher than the η level. In the case of the treated GF/mPP/PP, in Fig. 5 (b), η vs. $\dot{\gamma}$ and $|\eta^*|$ vs. ω curves showed the same tendency as the untreated systems. Such behaviour supports the idea of the ASC surface treatment having different roles in GF/PP and GF/mPP/PP composites.

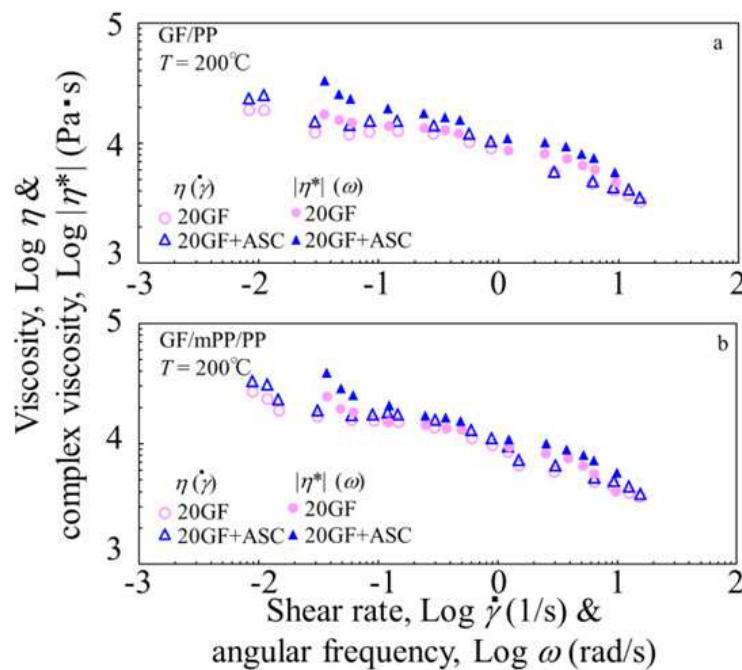


Fig. 5. Shear viscosity versus shear rate and complex viscosity versus angular frequency: (a) GF/PP composites, (b) GF/mPP/PP composites

2.5 Effect of coupling agent concentration

In order to clarify the influence of the concentration of the aminosilane coupling agent (ASC) on the rheological properties of GF/PP and GF/mPP/PP composites, both steady shear (η , N_{1r}) and dynamic ($|\eta^*|$, G') functions are plotted against the ASC concentration C in Figs. 6 and 7. The content of fibers was fixed at 20wt.%, and the relative values representing the ratio of treated GF/PP and GF/mPP/PP to untreated GF/PP and GF/mPP/PP, respectively, are shown at two shear rates (angular frequencies) of 0.1 and 9.2 1/s (rad/s). The relationship between the relative viscosity η_r obtained from the steady shear flow measurements, and the ASC concentration C (wt.%) is demonstrated in Fig. 6(a). Generally, η_r increased slightly with increasing C , and for higher shear rate (9.2 1/s) it was almost independent of C for both systems. In order to discuss about the elastic response, the relation between the relative normal stress difference N_{1r} , and C is plotted in Fig. 6(b). It was found that whereas the N_{1r} of GF/mPP/PP composites showed a maximum at 0.5 wt.% ASC, that of GF/PP composites increased monotonously with increasing C . To conclude, the N_{1r} variation with amount of aminosilane coupling agent was much larger than that of η_r . Figs. 7(a) and 7(b) show the effect of the ASC concentration C on the viscoelastic properties. While the relative complex viscosity $|\eta^*|_r$ of the GF/PP system, in Fig. 7(a), increased with increasing C , it was almost independent of the amount of ASC for the GF/mPP/PP composite. The dependency of the relative storage modulus G'_r on the ASC concentration C of both composites shown in Fig. 7(b) was similar to that of $|\eta^*|_r$ vs. C curve for the GF/PP composites. However, the G'_r vs. C curve for GF/mPP/PP composites showed a peak at 0.2 wt.% ASC. In general, G'_r reached smaller values than N_{1r} shown in Fig. 6(b). As one explanation of this phenomenon, different deformation modes under the particular flow can be considered.

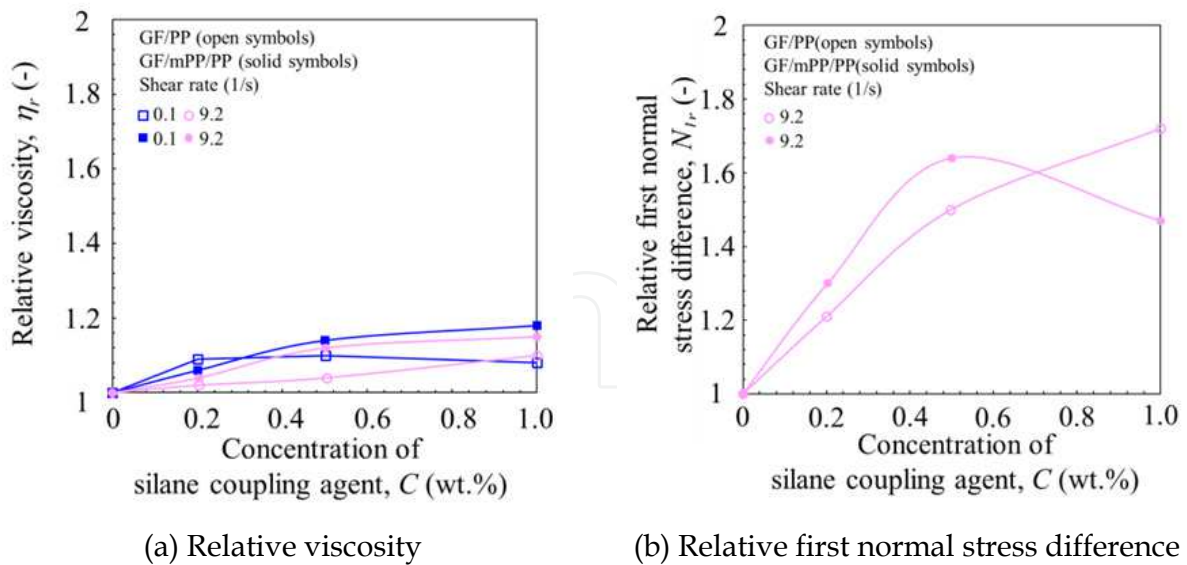


Fig. 6. Relationship between relative values of steady shear flow functions and concentration of silane coupling agent for GF/PP and GF/mPP/PP composites: (a) relative viscosity, (b) relative first normal stress difference

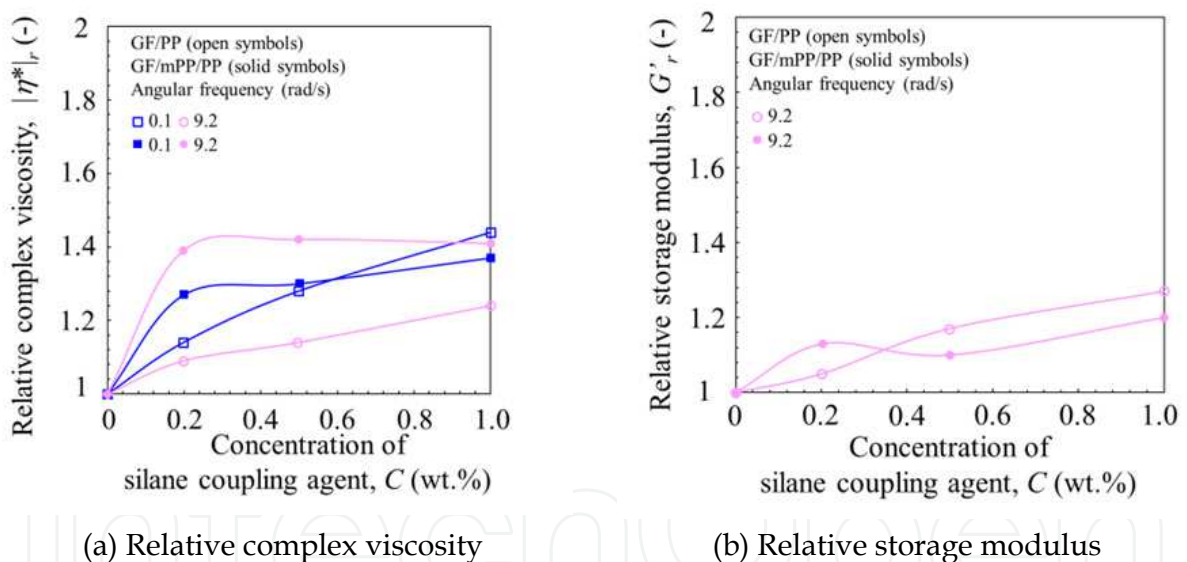


Fig. 7. Relationship between relative values of oscillatory flow functions and concentration of silane coupling agent for GF/PP and GF/mPP/PP composites: (a) relative complex viscosity, (b) relative storage modulus

Finally, the effect of surface treatment with regard to the fiber content is described and summarized in Table 2. The increase in the ASC concentration seems to make the processing of composites more difficult due to the increase of viscous and elastic properties of the composites. However, mechanical properties such as tensile, bending and impact strength are highly enhanced by ASC treatment (Nishitani et al. 1998b, 1998d). Consequently, the optimum concentration of surface treatment agent has to be determined individually, according to the performance required for a particular product.

Relative values	$\dot{\gamma}$ (1/s) or ω (rad/s)	1 wt.% ASC			
		GF/PP		GF/mPP/PP	
		20 wt.% GF	40 wt.% GF	20 wt.% GF	40 wt.% GF
η/η_0	0.1	1.06	1.35	1.18	1.16
	9.2	1.10	1.16	1.17	1.02
$ \eta^* / \eta^* _0$	0.1	1.45	1.46	1.38	1.91
	9.2	1.25	1.18	1.42	1.13
N_1/N_{10}	0.1	-	1.82	-	-
	9.2	1.72	1.68	1.47	1.42
G'/G'_0	0.1	-	-	-	-
	9.2	1.27	1.24	1.20	1.17

Table 2. Relative values of rheological properties for GF/PP and GF/mPP/PP composites

2.6 Yield stress

The presence or absence of a yield stress is of great importance in the molding of filler filled or fiber reinforced polymers, and also for the physical stability of many industrial products. Casson proposed an equation describing the steady state shear flow properties of the suspensions of solid particles in Newtonian liquids (Casson, 1959), so as to easily evaluate yield stresses:

$$\tau^{1/2} = \tau_0^{1/2} + k_1 \dot{\gamma}^{1/2} \quad (2)$$

Where τ is the shear stress, τ_0 represents its yield value, $\dot{\gamma}$ stands for shear rate, and k_1 is a constant. If the plots of $\tau^{1/2}$ against $\dot{\gamma}^{1/2}$ give straight lines, the yield stress can be obtained by extrapolation to $\dot{\gamma}=0$.

In this section, we discuss about the existence of the yield stresses of the GF/PP and GF/mPP/PP composites in the molten state and their relationship among the yield stress, content of dispersed fillers (fibers), and the structure of fiber assembly (Figs. 8 and 9). Fig.8 shows Casson's plots for GF/PP and the GF/mPP/PP composites. The line for pure PP is straight ones passing through the origin, suggesting the absence of a yield point. Concerning filled PP, the yield stresses, σ_y is determined only in the very low shear rate region ($\dot{\gamma}^{1/2}$ less than 0.4 1/s^{1/2}), where the flow data can be fitted by the straight lines. The σ_y of GF/PP composites, which is estimated from Fig. 8(a), seems to increase slightly with increasing GF content, and also by the ASC surface treatment of GF. The rate of σ_y increase for the GF/mPP/PP, Fig. 8(b), is larger than that for the GF/PP. This means that the addition of modified PP strongly influences on the yield stress appearance.

Such a trend can be seen clearly in Fig. 9, where the yield stresses of both composites are plotted as a function of the weight fraction of glass fiber ϕ_v in semi-logarithmic co-ordinates. The surface treatment of GF by silane coupling agent, and further the addition of modified PP increases the yield stress of the composites in the same manner as the increment of fiber

content. This behaviour is attributed to the strong structure formed by the fiber assembly, which are coupled by ASC, and strengthened by modified PP. Finally, it should be noted here that a yield stress is usually responsible for long scale relaxation times (the second rubbery plateau behaviour).

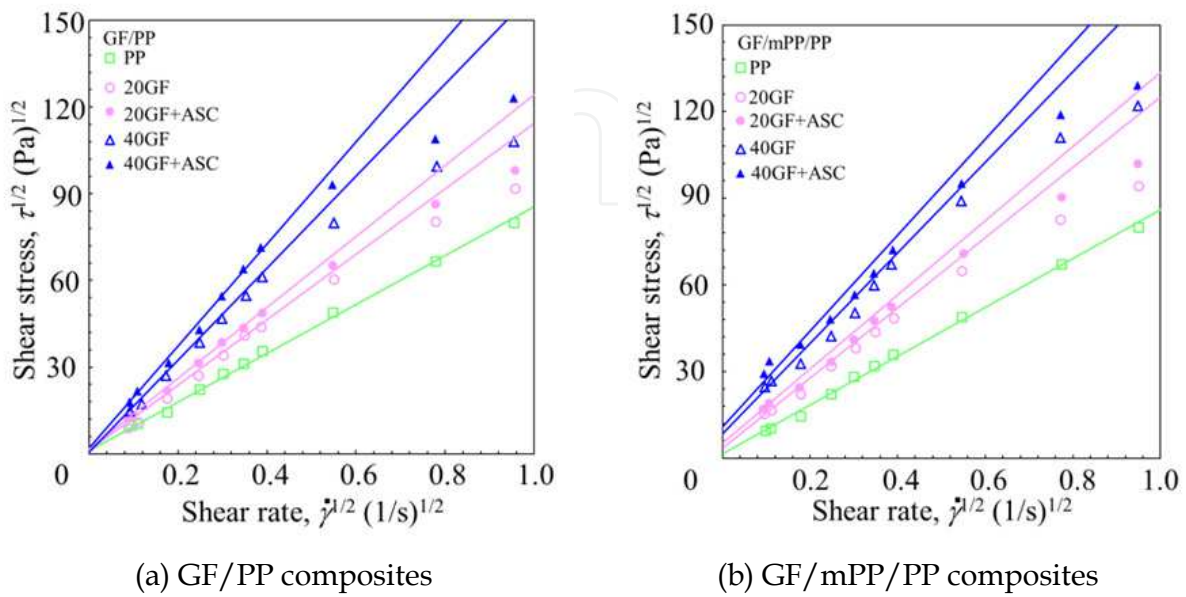


Fig. 8. Casson's plots: (a) GF/PP composites, (b) GF/mPP/PP composites

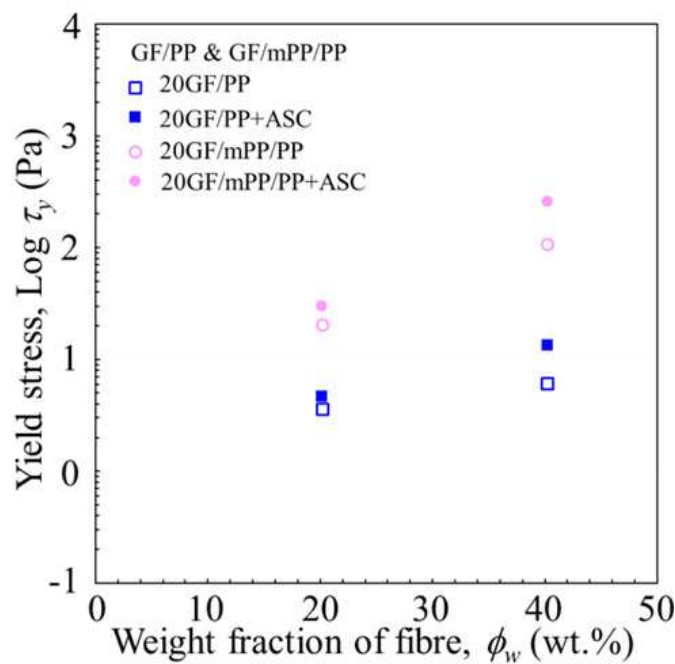
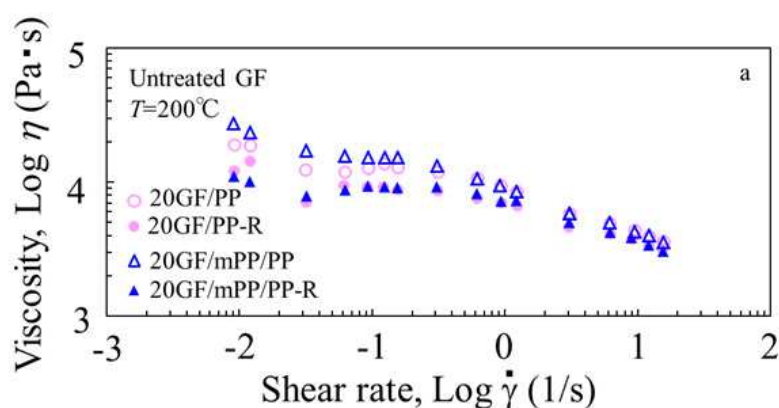


Fig. 9. Relationship between yield value of shear stress and weight fraction of fiber for GF/PP and GF/mPP/PP composites

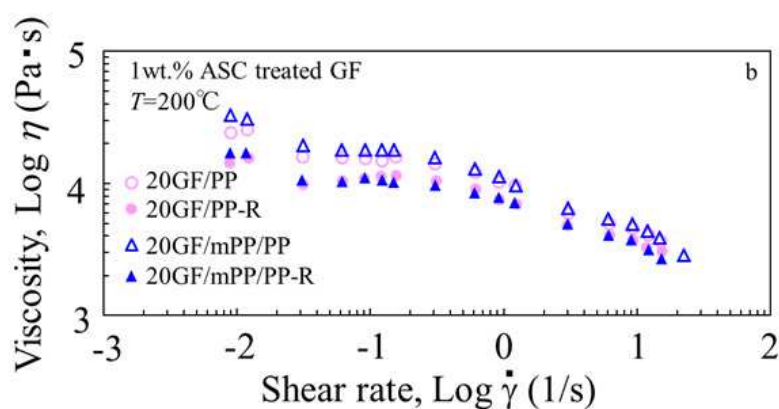
2.7 Effect of re-mixing process on rheological properties

Re-mixing (second compounding) of short fiber reinforced polymers is generally carried out to avoid the non-uniform dispersion of fillers or fibers in a polymer matrix. Composites processed by injection molding undergo the second mixing in an extruder or injection molding machine. In this section, we investigated the influence of re-mixing on the ASC surface treatment. The plots of η vs. $\dot{\gamma}$ for the mixed GF/PP and GF/mPP/PP composites and remixed GF/PP-R and GF/mPP/PP-R ones are depicted in Fig. 10. The viscosities of the re-mixed composites were lower, and there was no clear difference between untreated and treated materials. The reason might be the decrease in the fiber length after re-mixing (see Table 1), and the simultaneous diminution of the influence of fiber length on the viscous properties.

In addition, the viscosity difference between GF/PP and GF/mPP/PP composites was reduced after second mixing. In contrast, the complex viscosity of re-mixed composites was different for treated and untreated materials, as shown in Fig. 11. The former showed the same tendency as the shear viscosity, but the latter values were not much affected by re-mixing.

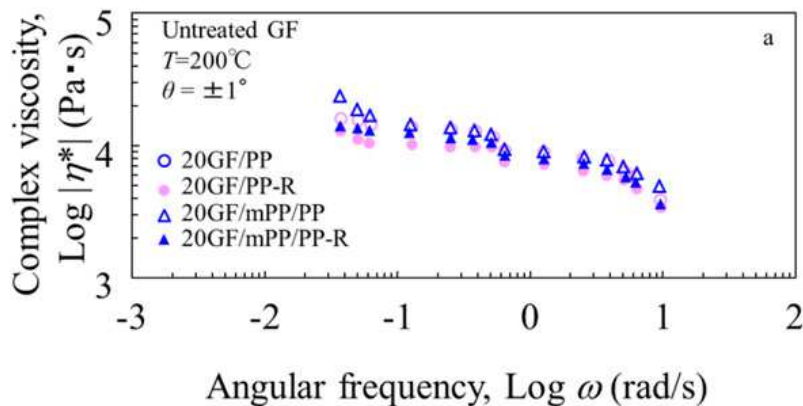


(a) Untreated composites

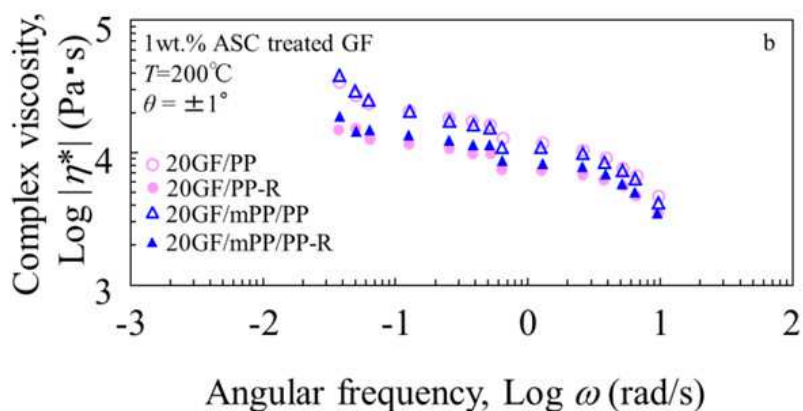


(b) ASC treated composites

Fig. 10. Effect of re-mixing on viscosity as a function of shear rate curves: (a) untreated composites, (b) ASC treated composites



(a) Untreated composites



(b) ASC treated composites

Fig. 11. Effect of re-mixing on complex viscosity as a function of angular frequency curves: (a) untreated composites, (b) ASC treated composites

3. Rheological properties of surface treated long glass fiber reinforced polypropylenes

Fiber reinforced thermoplastic composites are usually fabricated by a flow molding process. For high performance fiber reinforced composites it is important to analyse the flow /deformation behaviour of fiber filled systems during the polymer processing, and to investigate the flow mechanisms and any changes in the internal structure of these systems. The flow properties of short fiber filled systems, whose reinforcement fiber length is up to several 100 micrometers, have been studied extensively (Czarnecki & White, 1980; Laun, 1984; Mutel & Kamal, 1986; Ausias et al, 1992; Basu et al, 1992; Greene & Wikes, 1995; Kim & Song, 1997). For these systems, non-uniformity of orientation or dispersion of fibers arises, depending on flow conditions, and it is well known that this anisotropic or heterogeneous structure will cause anisotropic physical properties (Kitano et al, 1981). On the other hand, researches into continuous or long fiber filled systems have not been widespread, because the measuring or analysing methods required are not established yet, and the flow behaviour becomes more complicated in this case (Davis & Mcalea, 1990; Groves & Stocks, 1991; Groves et al, 1992; Davis & Manson 1993; Greene & Wikes, 1995; Nishitani et al 1998a, 1998b, 2001).

The measuring methods for short fiber filled systems are seldom valid for long fiber filled ones. Steady shear flow measurements, usually used for short fiber filled systems, cannot be applied to long fiber filled ones, since the heterogeneity of the latter system is higher than that of the former, and the structure composed by the long fiber assembly changes gradually under large shear deformations. Then, the stable flow state cannot be obtained. Therefore, it is common for the flow properties of long fiber filled systems to be evaluated by dynamic viscoelastic properties, measured by means of oscillatory flow experiments under small strain/deformation amplitudes (Nishitani et al 1998b, 2001). When measuring the flow properties of fiber filled systems it is desirable to retain the initial state of fiber orientation or dispersion. The change in the initial state is easily occurred during the setting up of a sample when a cone-plate typed rheometer is used. Therefore, it is more appropriate to use a parallel-plate typed rheometer for the viscoelastic properties of long fiber filled systems. In addition, it is desirable to know the flow properties of continuous or long fiber filled composites in order to clarify unsolved problems such as the impregnation of matrix resin and the uniformity of the fiber distribution in composites.

Furthermore, various surface treatments are used in order to achieve the high performance. The methods of surface treatment for long fiber filled systems are the same ones as for short fiber filled systems, however the effect of the surface treatment on the rheological properties of long fiber filled composites is not understood enough yet.

In our previous works (Kitano et al, 1994, 2000; Nishitani et al, 1998a, 1998b, 1999, 2001) we investigated the fabrication methods and physical properties of long fiber reinforced polypropylenes, which were compression molded polypropylene fibers mixed homogeneously with long reinforcement fibers such as glass fiber, carbon fiber, aramid fiber, polyvinyl alcohol fiber and polyamide 6 fiber by an apparatus called a "fiber separating and flying machine". The fabrication method employed here is a discontinuous and dry process similar to the stampable sheet molding method. This is superior to other manufacturing methods from the point of view of thermal efficiency, isotropic physical properties (because of the completely separated and homogeneously dispersed reinforcement fibers), and applicability to hybrid composites.

The objective of this section is to report the effect of surface treatment on the rheological properties, which is the dynamic viscoelastic properties in the molten state, investigated experimentally, for long glass fiber reinforced polypropylene composites (GFL/PP) prepared by the mentioned above. The present section discusses the dynamic viscoelastic properties in terms of various factors: angular frequency, concentration of silane coupling agent, various kinds of silane coupling agents, volume fraction of fiber, temperature and strain amplitude.

3.1 Materials and methods

The materials used in this section were surface treated long glass fiber reinforced polypropylene melts. Polypropylene fiber (PP, Showa aroma, Showa Denko K. K., Japan) was used as the matrix. Glass fiber (GF, Micro Glass Roving, Nihon Glass Fiber Co., Ltd., Japan, fiber diameter $d=13\mu\text{m}$) was used as reinforcement fibers. Surface treatment by different kinds of silane coupling agents with different concentrations was performed on glass fibers. Four types of silane coupling agents: aminosilane (ASC, A-1100, Nippon Unicar

Co. Ltd., Japan), diaminosilane (DAS, SH-6020P, Dow Corning Toray Co., Ltd., Japan), acrylsilane (ACS, A174, Nippon Unicar Co., Ltd.) and epoxysilane (ESC, A187, Nippon Unicar Co., Ltd.) were used as surface treatment agent. These details: code, component name and concentration are listed in Table 3.

Coupling agent	Code	Component Name	Concentration C (wt.%)	Volume fraction of fiber V_f (vol.%)
Aminosilane	ASC	γ -aminopropyltriethoxysilane	0.2, 0.5, 1.0	5, 10, 20, 30
Diaminosilane	DAS	γ -(2-aminoethyl)aminopropyltrimethoxysilane	0.5	10, 20
Acrylsilane	ACS	γ -methacryloxypropyltrimethoxysilane	1.0	10, 20
Epoxysilane	ESC	γ -glycidxypropyltrimethoxysilane	1.0	10, 20

Table 3. Name of coupling agent, its component and code, its concentration and volume fraction of GF

All of the composite materials were compression molded from mixed mats prepared by the apparatus called a “fiber separating and flying machine” (Nishitani et al, 1999, 2001). This apparatus is schematically illustrated in Fig. 12. Continuous GF with volume fraction of 5, 10, 20 and 30 vol.% were fed into the “fiber separating and flying machine” apparatus simultaneously with PP fibers which are previously cut in 100 to 150mm. The collected mixed mats prepared by this apparatus were used as a base material for compression molding. Then the mixed mats were cut into 150 x 150 mm pieces, the weighed amounts of the mats for molded samples with 3mm thickness were piled into the mold cavity. These mats were kept in an air circulation oven at 120°C for 3 hours in order to remove the absorbed water in the fibers. Then the dried mats were compression-molded by a hot press in 3mm thick sheets for 3minutes under 5MPa at 200°C. Test specimens for viscoelastic properties measurements were cut from the sheets. The average length of glass fibers was 21.6mm, their orientation was generally three dimensional, and the degree of orientation gradually changed with the fiber content.

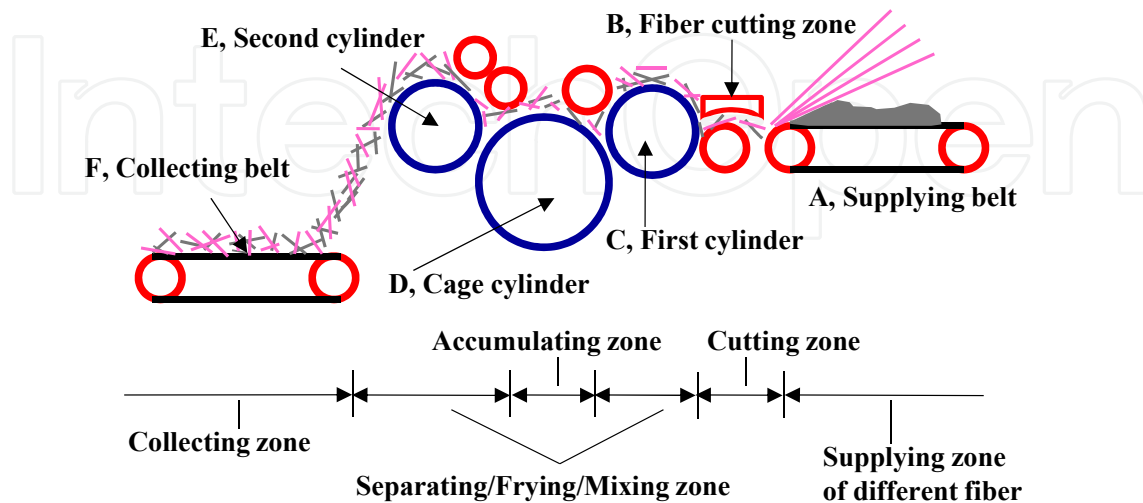


Fig. 12. Schematic diagram of the mixture mats production by the “Fiber separating and flying machine” apparatus

For long fiber reinforced composites it is difficult to estimate their rheological properties by using a cone-plate typed or capillary typed rheometer under steady shear flow. Therefore, specially designed rheometer is used for continuous fiber reinforced composites (Nishitani et al, 1998b, 1998c, 2001). In our experiments, a parallel-plate typed rheometer (151-S, Nippon Rheology Kiki Co., Ltd., Japan) was used to measure the dynamic viscoelastic properties of the samples. The specimens were compression-molded sheets cut into disks of 27 to 28 mm diameter. The gap between the two plates of 12.5mm radius was fixed at 3mm. Under such gap condition, a test specimen was slightly compressed in the molten state. The angular frequency varied from 10^{-2} to 10^2 rad/s, and the forced oscillatory angle of lower plate was used at 0.5, 1.0 and 2.0 degree, corresponding to the strain amplitude of 4.4%, 8.7% and 17.5% in shear unit, respectively. The measurements were carried out for all the samples at 180, 200 and 220°C. Linear viscoelastic properties such as storage modulus G' , loss modulus G'' , dynamic viscosity η' and loss tangent $\tan \delta$ were determined.

3.2 Angular frequency dependence

First, the effect of the surface treatment on the rheological properties of long glass fiber reinforced polypropylene composites (GFL/PP) is discussed. The rheological properties are evaluated by the dynamic viscoelastic properties in the molten state, which are strongly dependent on the internal micro structure formation of the polymer composites. We shall discuss the angular frequency dependence, which is the basic variable in dynamic viscoelastic properties. All the results discussed in this section were measured under an oscillatory angle of 0.5° (strain amplitude 4.4%) and the range of angular frequency was from 10^{-2} to 10^2 rad/s. Fig. 13(a) shows the effect of the concentration of aminosilane coupling agent (ASC) on the relationship between the storage modulus G' and angular frequency ω of GFL/PP composites. G' of untreated GFL/PP increases with increasing ω . G' of ASC treated GFL/PP increases with increasing the concentration of ASC (from 0.1 to 1.0 wt.%) and shows the typical G' curve similar to highly filled systems although the content of GF in the composites is 10vol.%. The slopes of G' against ω become small in low ω region, indicating the "second rubbery plateau" i.e. the long-scale relaxation time (Ferry, 1980; Nishitani et al, 2001, 2007, 2010a, 2010b). This tendency is highly enhanced by the increase of the ASC concentration. This behaviour may be attributed to the fiber network formation, which is due to high aspect ratio, and the interfacial interaction between GF and PP. Fig. 13(b) shows the effect of the concentration of ASC on the relationship between the dynamic viscosity η' and ω of GFL/PP composites. η' decreases monotonously with increasing ω , and the slopes of η' against ω have a slope of an angle of approximately -45° . This behaviour shows the presence of an apparent yield stress in the low ω region. The effect of the concentration of ASC on η' or loss modulus G'' seems to show more complex behaviour. η' of the ASC treated GFL/PP composites having the concentration of ASC of less than 0.5 wt.% is less than that of untreated ones, although 1.0wt.% ASC treated GFL/PP composites shows higher η' than that of untreated ones, which means the treatment with low ASC concentration rather decreases η' or G'' (viscous properties) although increase G' (elastic property). These behaviour may be due to the action of the coupling agent as a wetting agent, lubricant or plasticizer.

In Fig. 14(a), the storage modulus G' is plotted against the angular frequency ω for various silane coupling agents treated GFL/PP composites. G' of all treated GFL/PP is higher than

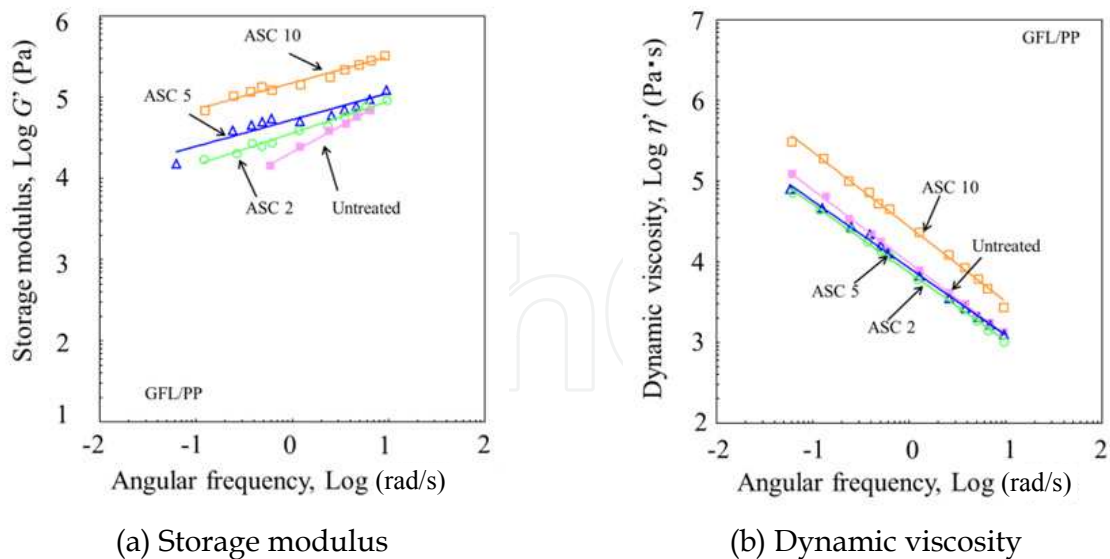


Fig. 13. Influence of concentration of aminosilane coupling agent on dynamic viscoelastic properties for GFL/PP composites: (a) storage modulus versus angular frequency, (b) dynamic viscosity versus angular frequency

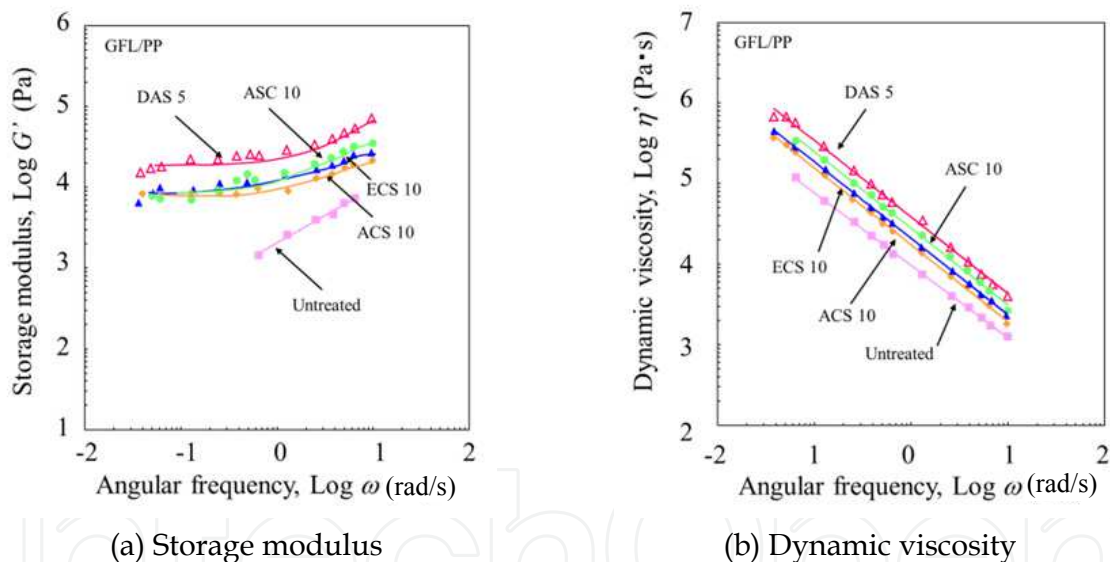
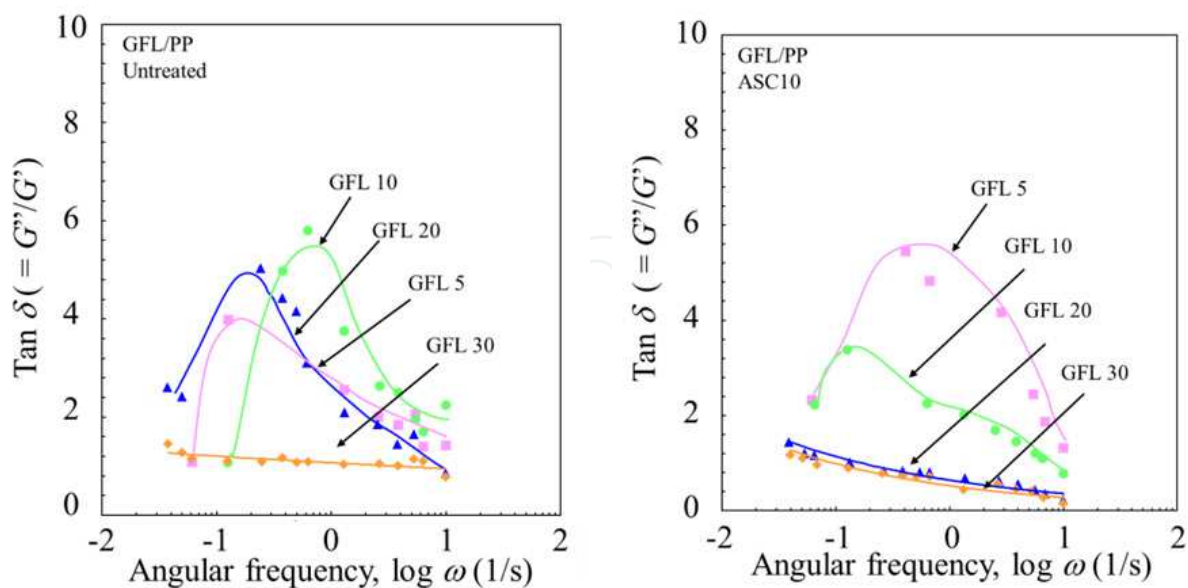


Fig. 14. Influence of different kinds of silane coupling agent on dynamic viscoelastic properties for GFL/PP composites: (a) storage modulus versus angular frequency, (b) dynamic viscosity versus angular frequency

that of untreated GFL/PP composites in a wide range ω region and shows the typical G' curve similar to that of highly filled systems, indicating the “second rubbery plateau”, however the values of G' change with the types of silane coupling agents and increase in the following order: untreated < acylsilane (ASC) < epoxysilane (ESC) < aminosilane (ASC) < diaminosilane (DAS). Fig. 14(b) shows the dynamic viscosity η' of various silane coupling agent treated GFL/PP composites as a function of ω . η' decreases monotonously with increasing ω , and the slopes of η' against ω have a slope of an angle -45° . As with G' , η' of various silane coupling agent treated GFL/PP increases in comparison with η' of untreated

GFL/PP composites, and this increase of η' is in the same order as G' . In particular, both properties such as G' and η' appear conspicuously to be high for the GFL/PP composites with diaminosilane coupling agent (DAS). This trend showed the same tendency also by the mechanical properties such as impact strength and so on (Nishitani et al., 1998a)

Loss tangent $\tan \delta$, which is defined as the ratio of the loss modulus G'' and storage modulus G' , can clarify the correlation between the elastic and viscous properties of the materials. Fig. 15 shows the relationship between $\tan \delta$ and angular frequency ω for untreated and ASC 10 (1.0wt.%) treated GFL/PP composites with various volume fractions of fiber from 5 to 30 vol.%. $\tan \delta$ of untreated GFL/PP composites (Fig. 15 (a)) with volume fraction of fiber V_f less than 10vol.% (GFL10) increases with V_f and $\tan \delta - \omega$ curves have the peak. In high V_f region with V_f higher than 10vol.%, $\tan \delta$ becomes smaller with increasing fiber content, and independent of ω in 30 vol.% (GFL30). It may be thought from these results that GF in the composites with higher fiber content contributes to a more dominant role for the elastic properties than the viscous ones. $\tan \delta$ of GFL30 is independent of ω , and these composites behave like solid materials because of the high rigidity of the structure composed with rigid fibers. On the other hand, $\tan \delta$ of ASC 10 treated GFL/PP composites are shown in Fig. 15 (b) as a function of ω . $\tan \delta$ decreases gradually with increasing V_f . For composites with V_f higher than 20 vol.%, $\tan \delta$ is independent of ω , behaving like solid materials. Although $\tan \delta - \omega$ curves of untreated GFL/PP composites have the peak values up to 20 vol.% (GFL20), those of ASC 10 treated GFL/PP composites have them up to 10 vol.% (GFL10). This fact indicates the decrease in viscous properties with high fiber content. By the surface treatment with ASC, this tendency is sifted to low fiber content region compared with untreated GFL/PP composites. These behaviour may be attributed to the strong interfacial interaction between GF and PP.



(a) Untreated GFL/PP composites

(b) ASC 10 treated GFL/PP composites

Fig. 15. Influence of volume fraction of fiber on loss tangent for GFL/PP composites: (a) Untreated GFL/PP composites, (b) ASC 10 treated GFL/PP composites

In general, the influence of surface treatment by coupling agents on the dynamic viscoelastic properties of the polymer composites is complex. This is because the surface treatment by silane coupling agents play two of multiple roles simultaneously, as a coupling agent which improves the adhesion between fiber (filler) and polymer, a lubricant which reduce the friction, a plasticizer which helps to make the fiber and the polymer softer, a wetting agent which reduces agglomeration and a an additive to make deformation of fiber assembly easier and to lower the viscoelastic properties of a matrix polymer. It is thought that the mechanisms mentioned above do not occur separately, and therefore it is very difficult to distinguish a particular type. From the results in this section, it can be concluded that the surface treatment by the various silane coupling agents improves the viscoelastic properties. Although the viscous properties are dominant in low concentration of silane coupling agent, which remarkably shows the role acting by plasticizer and internal lubricant, the elastic properties increase with the concentration of silane coupling agent. Thus, it is found that the role of the coupling agent, which forms chemical bonds between GF and PP and physical adhesion, becomes lager gradually with the increase of the concentration. Moreover, with increasing fiber content, the effect of fiber itself on the viscoelastic properties of GFL/PP composites becomes higher than the effect of surface treatment on them, and then the elastic properties increase gradually.

3.3 Effect of coupling agent concentration

In general, rheological properties such as storage modulus G' and dynamic viscosity η' are considered to be sensitive indicators for the quantitative analysis of morphological change in the composite materials. To more clarify the influence of silane coupling agent on the rheological properties of GFL/PP composites, both the storage modulus G' and the dynamic viscosity η' are plotted against the aminosilane coupling agent (ASC) concentration C as a parameter of angular frequency ($\omega=0.127, 1.257$ and 9.488 rad/s) in Figs. 16 and 17. In Fig. 16 (a), G' of GFL5 (GF content is 5vol.%) increases gradually with the increase of the ASC concentration C , except for data at 0.127 rad/s in low C region. G' of GFL10 (Fig. 16(b)) increases monotonously with increasing C as with G' of GFL5, and the increasing ratio of GFL10 is higher than that of GFL5. G' of GFL20 (Fig. 16(a)) increases rapidly with the surface treatment and has a constant value with C higher than 0.5 wt.%. However, in high fiber content region (GFL30, Fig. 16 (b)), G' shows the complex behaviour and has a minimum value. Moreover, the difference by the angular frequency becomes smaller with increasing the fiber content. On the other hand, η' against C curves, in Fig. 17, shows the different dependence on fiber content. η' of GFL5 and GFL20 shows the same tendency as G' , and η' of GFL10 and GFL30 has a minimum value. It is found from these results that the storage modulus G' , although showing the complex behaviour in high fiber content increases with the ASC concentration C according to fiber content. The dynamic viscosity η' shows the two kinds of tendencies, which increase with increasing C and have a minimum value. Therefore, the effect of ASC concentration on the viscoelastic properties shows the existence of an optimum concentration for systems at each volume fraction of fiber. In addition, these tendencies are similar in a wide range of angular frequency.

3.4 Effect of volume fraction of fiber

In order to clarify the effect of volume fraction of fiber on the viscoelastic properties of surface treated GFL/PP composites in this section, the relationship between the storage

modulus G' and the dynamic viscosity η' and volume fraction of fiber V_f at a typical angular frequency ω ($\omega=1.257$ rad/s) are shown in Fig. 18 as a parameter of ASC concentration. The dependence of G' on V_f changes remarkably with the ASC concentration. G' of untreated GFL/PP composites increases with increasing V_f . On the other hand, G' of treated systems increases monotonously with V_f until it reaches the value of 2 to 5 $\times 10^6$ Pa, and finally levels off at high V_f . This means that the elastic properties of treated GFL/PP composites are more dominant at relatively low contents than that of untreated systems. As with G' , η' reaches the value of 2 to 5 $\times 10^6$ Pa. In addition, the degrees of the increase of G' and η' become higher according to the ASC concentration order.

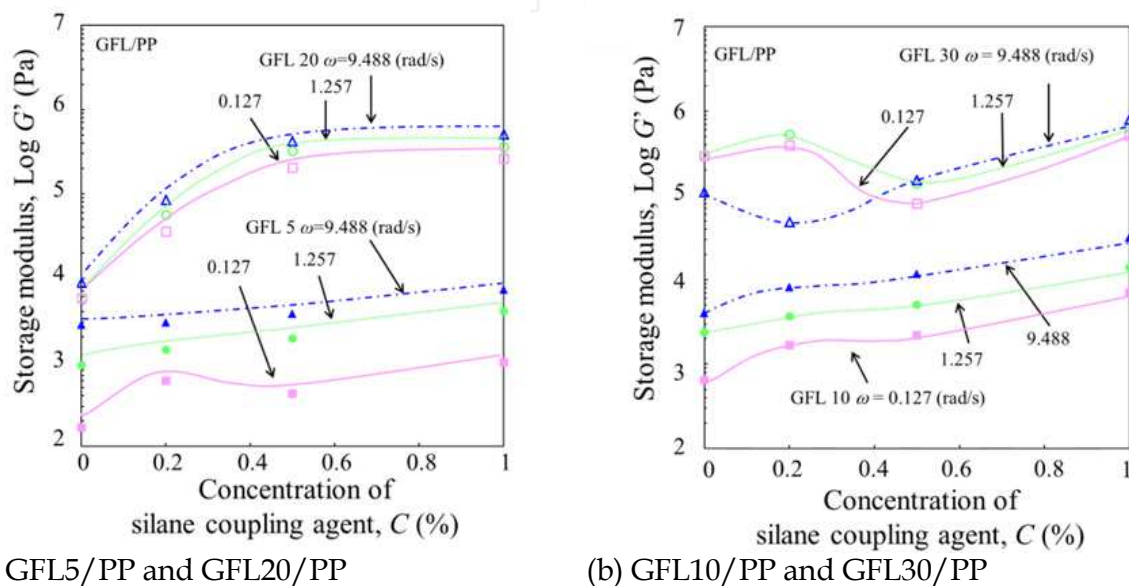


Fig. 16. Relationship between storage modulus and concentration of aminosilane coupling agent for GFL/PP composites: (a) GFL5/PP and GFL20/PP, (b) GFL10/PP and GFL30/PP

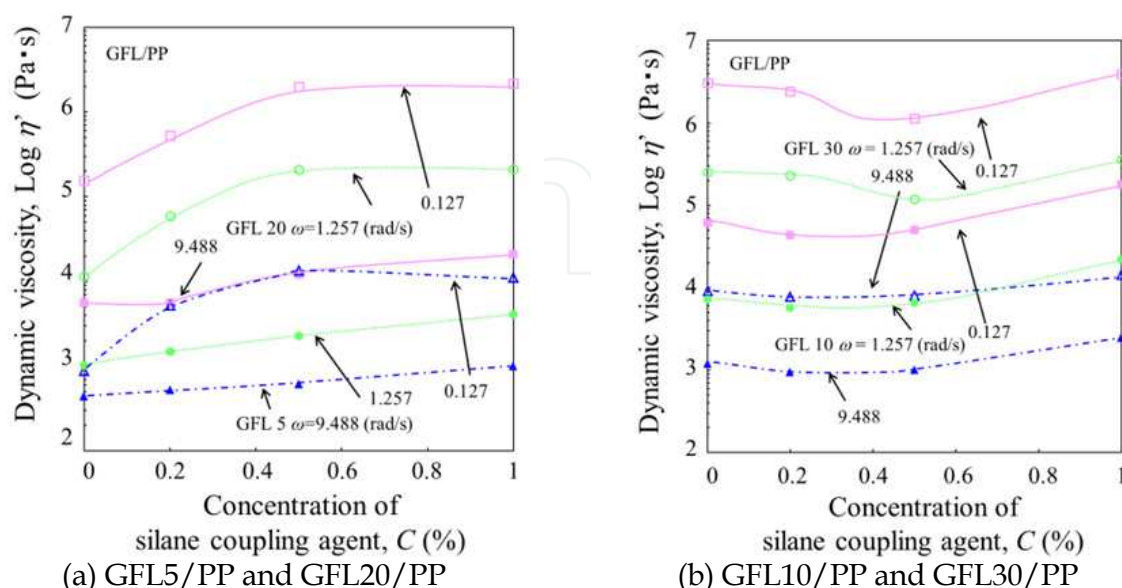


Fig. 17. Relationship between dynamic viscosity and concentration of aminosilane coupling agent for GFL/PP composites: (a) GFL5/PP and GFL20/PP, (b) GFL10/PP and GFL30/PP

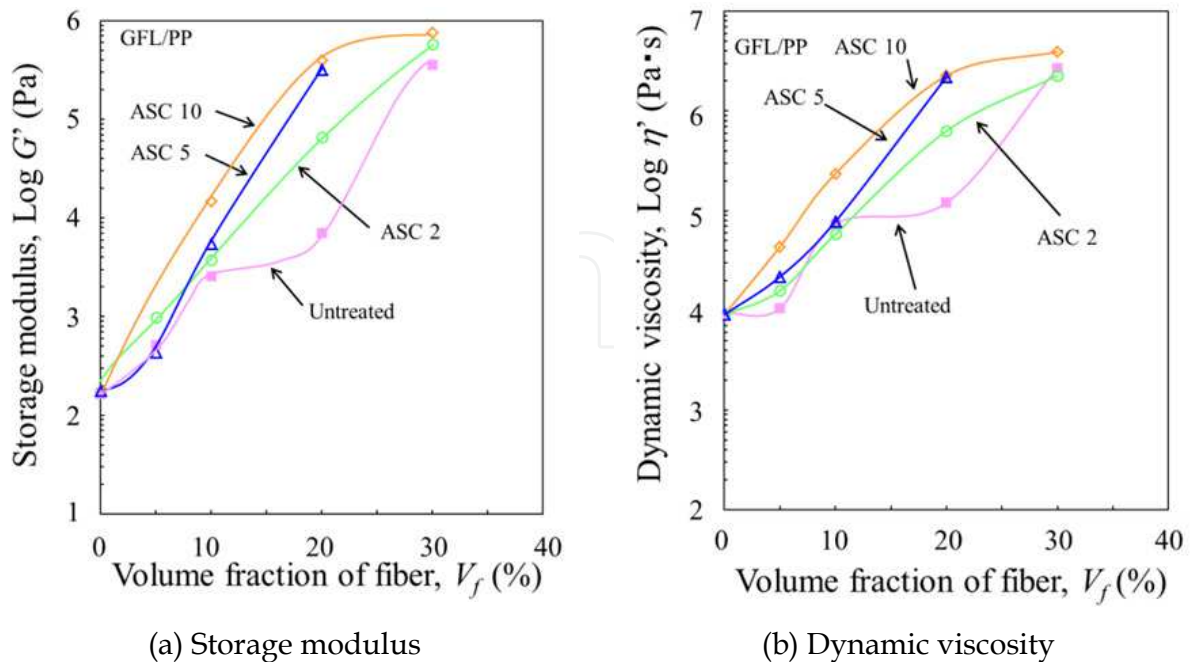


Fig. 18. Relationship between dynamic viscoelastic properties and volume fraction of fiber for GFL/PP composites at the angular frequency of 1.257 rad/s: (a) storage modulus, (b) dynamic viscosity

3.5 Temperature dependences

The influence of temperature on the viscoelastic properties of surface treated GFL/PP composites will be discussed here. Fig. 19 shows the storage modulus G' (Fig. 19(a)) and the dynamic viscosity η' (Fig. 19(b)) as a function of angular frequency ω as a parameter of temperature T for untreated and surface treated GFL10/PP composites. G' of untreated GFL/PP composites decreases with increasing T . However, G' of ASC10 treated GFL/PP composites corresponds approximately to the measurements at different temperatures. As with G' , η' of treated systems at different temperatures are in accord with the one in a wide range of ω . It is found from the results of the measurements at different temperature that the surface treatment decreases the temperature dependence of viscoelastic behaviour, especially of elastic ones, although the untreated systems show the clear temperature dependences. Thus, the difference of processability with different temperatures is minimal by performing the surface treatment by silane coupling agent. These temperature dependences were almost same for the systems with different fiber content although not shown here. Accordingly, it is found from the results that the viscoelastic properties originating in the fiber network formation are dominant in the measuring ω region, the temperature dependences of them are relatively small and also these tendencies become stronger by the surface treatment of long GF.

3.6 Strain amplitude dependences

According to the report of Mutel and Kamal (Mutel & Kamal, 1986), the viscoelastic properties such as the storage modulus G' and the loss modulus G'' of polymer in the

molten state show the strain amplitude dependence if Lissajous figure (torque – shear rate loop) does not draw the perfect (harmonic) ellipse. A strain dependent but harmonic stress region was observed for filled melts in oscillatory shear as well as an non-harmonic stress region at low frequencies and large strain amplitudes. The strain dependent harmonic stress region is thought to be the result of the much longer time scales for the relaxation of fluid compared to the period of oscillations. In our experimental data in this section, the Lissajous figures almost draw the perfect ellipses.

To more clarify the effect of strain amplitude dependence on the viscoelastic properties of surface treated GFL/PP composites, the influence of the oscillatory angle θ or strain amplitude on the storage modulus G' and the dynamic viscosity η' of untreated and treated GFL/PP composites at different angular frequencies ω is shown in Figs. 20, 21, 22 and 23. The strain amplitude was chosen to be 4.4, 8.7 and 17.5 % (which is corresponding to oscillatory angle of 0.5, 1.0 and 2.0°, respectively). Here, all the data were calculated by assuming the linearity was maintained. Although the effect of surface treatment on the strain amplitude dependences does not remarkably appear, G' decreases with increasing the strain amplitude and also with increasing V_f . And the degree of decrease of G' decreases with increasing the angular frequency. Thus, the smaller the angular frequency is, the higher the strain amplitude dependence for G' is in the same strain amplitude. The strain amplitude dependence of dynamic viscosity η' has the same tendency as that of G' although its dependence of η' is smaller than that of G' .

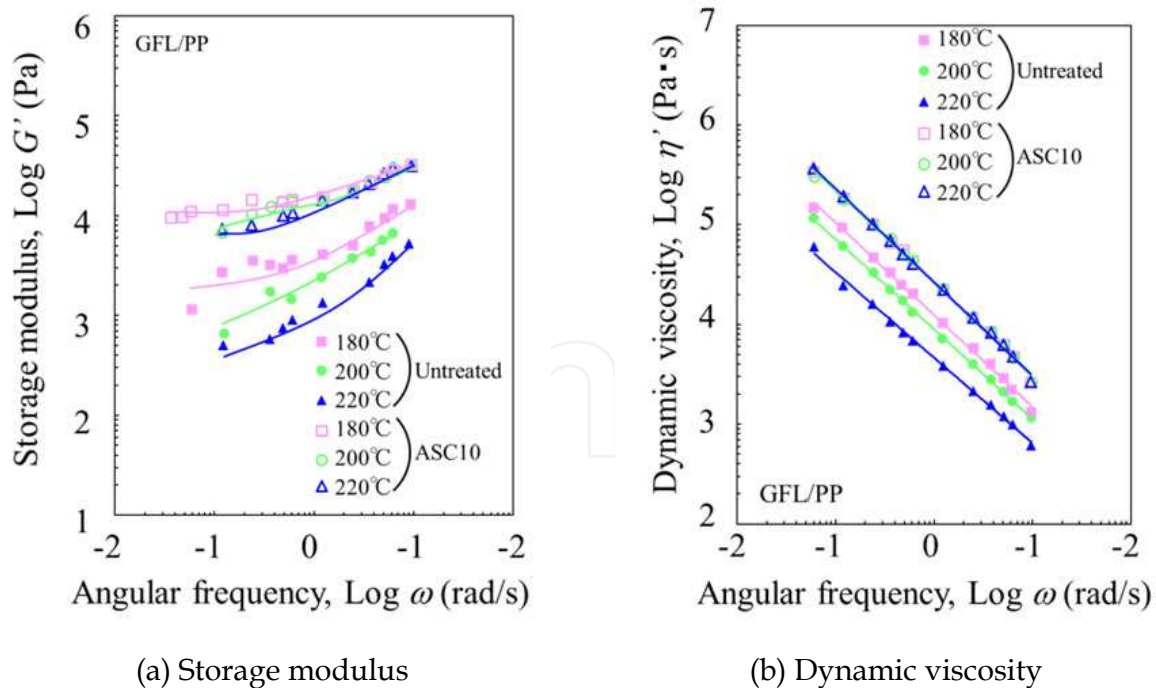


Fig. 19. Influence of temperature on dynamic viscoelastic properties for GFL/PP composites: (a) storage modulus, (b) dynamic viscosity

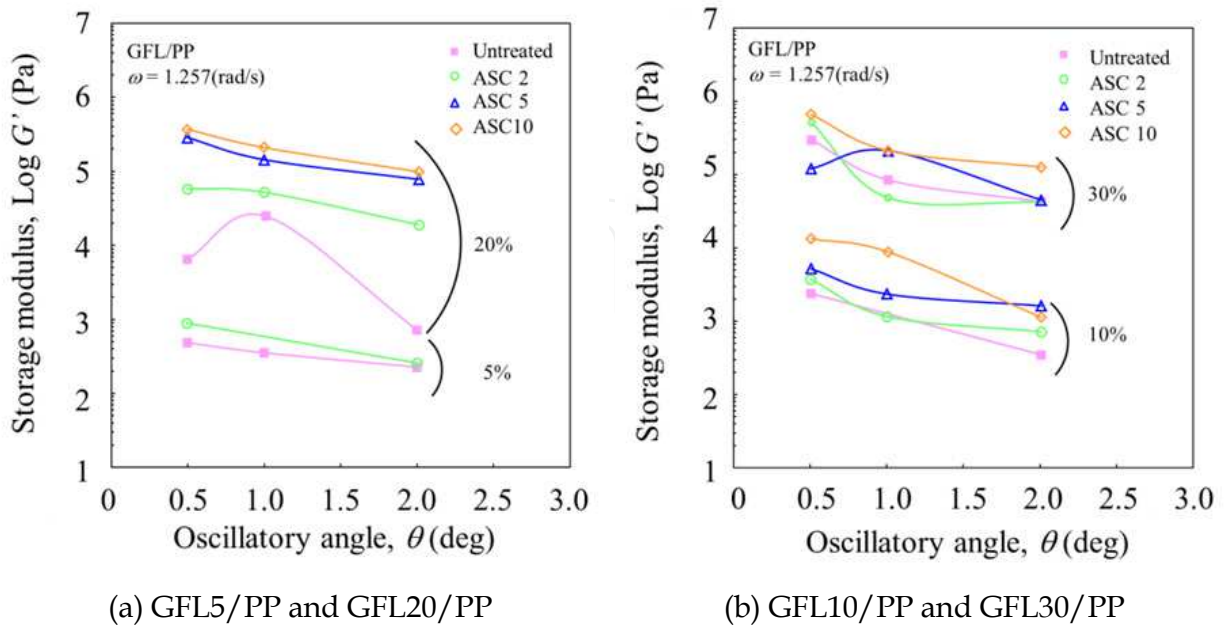


Fig. 20. Influence of oscillatory angle (strain amplitude) on storage modulus for GFL/PP composites at the angular frequency of 1.257 rad/s; (a) GFL5/PP and GFL20, (b) GFL10/PP and GFL30/PP

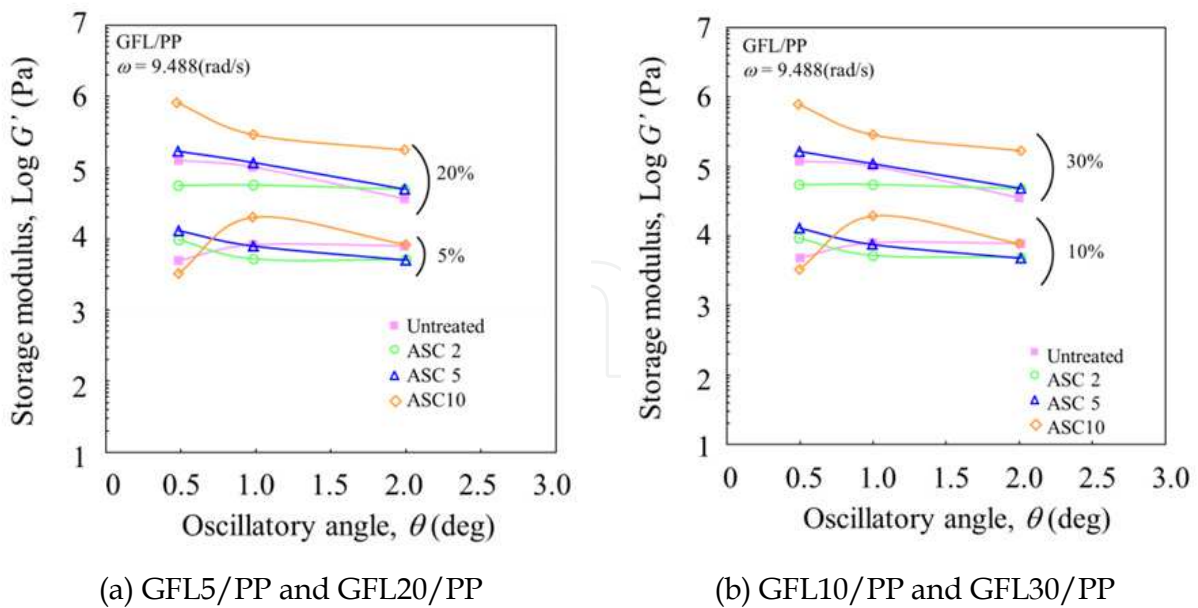


Fig. 21. Influence of oscillatory angle (strain amplitude) on storage modulus for GFL/PP composites at the angular frequency of 9.488 rad/s; (a) GFL5/PP and GFL20, (b) GFL10/PP and GFL30/PP

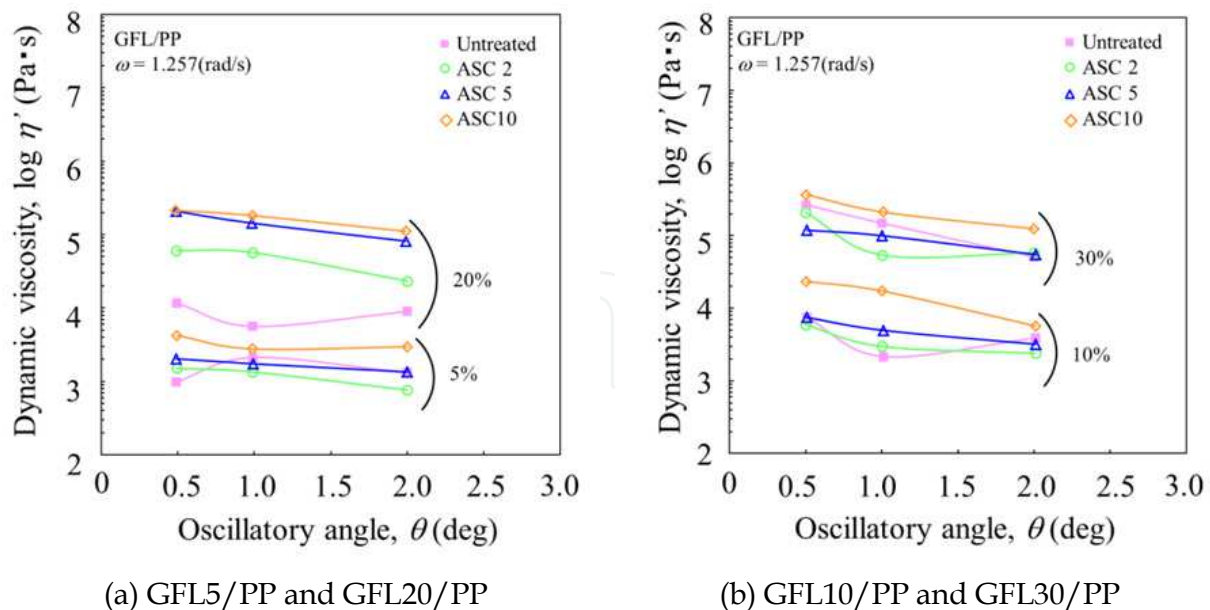


Fig. 22. Influence of oscillatory angle (strain amplitude) on dynamic viscosity for GFL/PP composites at the angular frequency of 1.257 rad/s; (a) GFL5/PP and GFL20, (b) GFL10/PP and GFL30/PP

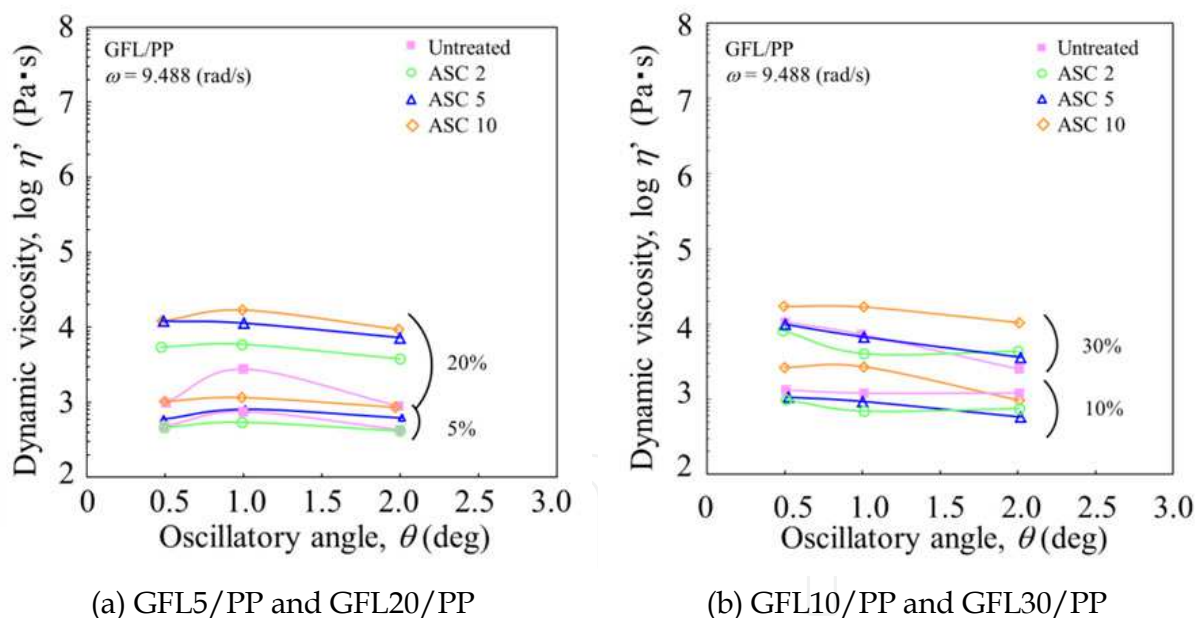


Fig. 23. Influence of oscillatory angle (strain amplitude) on dynamic viscosity for GFL/PP composites at the angular frequency of 9.488 rad/s; (a) GFL5/PP and GFL20, (b) GFL10/PP and GFL30/PP

4. Conclusion

This chapter discusses the rheological properties of surface treated short and long glass fiber reinforced polypropylene composites in molten state. Glass fibers were surface-treated by silane coupling agent.

The first part deals with the effect of surface treatment on the rheological properties of 20 and 40 wt.% short glass fiber reinforced polypropylenes (GF/PP) and of the same composites containing maleic anhydride modified polypropylene (GF/mPP/PP). These GF/PP and GF/mPP/PP composites were extruded by an extruder specially designed for mixing. Steady state shear and dynamic viscoelastic properties in the molten state were measured using a cone plate typed rheometer. Surface treatment increased the rheological properties of the molten composites. This trend was more pronounced for composites containing modified PP (mPP). In the case of the GF/PP composites the increase was monotonous for all measured functions, while in the case of the GF/mPP/PP ones, the parameters representing elasticity showed peaks at 0.5wt.% aminosilane coupling agent (ASC, γ -aminopropyltrimethoxysilane). The Cox-Merz empirical law was found to be applicable to untreated GF/PP and GF/mPP/PP composites at low shear rates (or angular frequencies), where the materials showed the Newtonian plateau. As for ASC surface treated composites, GF/mPP/PP followed the same trend. On the other hand, GF/PP exhibited a higher complex viscosity than the steady state shear one over the whole range of angular frequencies (shear rates) covered by the experiments. Surface treatment enhanced apparent yield stress, as did with increasing the glass fiber content. The effect of the latter was more pronounced in the case of the GF/mPP/PP series. The viscosities of the re-mixed composites became lower than those of the original ones, and the difference between untreated and ASC treated systems was detectable only in the case of the complex viscosity of the GF/mPP/PP composites.

The second part deals with the influence of surface treatment on the rheological behaviour of long glass fiber reinforced polypropylene melts (GFL/PP). Surface treatment by different kinds of silane coupling agents (aminosilane, diaminosilane, epoxysilane and acrylsilane) with different concentrations was performed on glass fibers. Glass fiber and polypropylene fiber mixed mats were prepared by a mixing machine which is called "Fiber separating/flying machine" and then compression molded. Rheological properties on a rotational parallel plate rheometer were evaluated. Dynamic viscoelastic properties are discussed in terms of various factors: angular frequency, concentration of silane coupling agent, various kinds of silane coupling agents, volume fraction of fiber, temperature and strain amplitude. Surface treatment was shown to increase storage modulus and also reduce the peak of loss tangent, which means that the adhesion between the polymer matrix and the fibers is improved. Dynamic viscosity, however, was changed by the concentration of silane coupling agent. This is because the coupling agent acts to couple the fiber to the polymer matrix, as a wetting agent or as an internal lubricant. Diaminosilane coupling agent was the most effective of the various silane systems for enhancement of rheological behaviour. The dependence of the viscoelastic properties on the concentration of silane coupling agent showed the existence of an optimum concentration for systems at each volume fraction of fiber from the point of view of the processing of these composites. From the results of the measurement at different temperatures and strain amplitude, it was found that surface treatments decrease the temperature dependence of rheological behaviour, and that the dependence of viscoelastic properties on strain amplitude was minimal.

5. Acknowledgment

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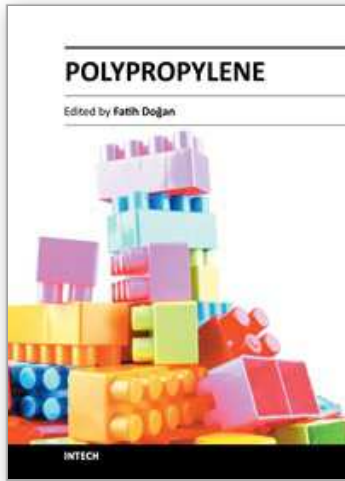
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This book aims to bring together researchers and their papers on polypropylene, and to describe and illustrate the developmental stages polypropylene has gone through over the last 70 years. Besides, one can find papers not only on every application and practice of polypropylene but also on the latest polypropylene technologies. It is also intended in this compilation to present information on polypropylene in a medium readily accessible for any reader.

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