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An Investigation on Dispersion State of Graphene in Polypropylene/Graphite Nanocomposite with Extensional Flow Mixing

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Abstract. Graphene nanoplatelets (GNP) have attracted considerable attention because of their excellent mechanical, thermal and electrical properties. Many researchers have tried to exfoliate GNP directly from graphite (Gr) in polymer by shear flow mixing process with twin-screw extruder, internal mixer and so on. By usual shear mixing, however, exfoliation of Gr into GNP is very difficult because of inefficiency process. Therefore, we focused on the extensional flow for exfoliating to GNP from Gr. In this study, the mixing effect of pure extensional flow for exfoliating into GNP was investigated by comparing with shear flow. Primary, PP/Gr masterbatch pellets were extruded by capillary rheometer equipped with orifice die (i.e. extensional flow) and capillary die (i.e. shear flow). Then, mixing effect was discussed by morphological and rheological analysis. As the results, extensional flow can exfoliate into few layer GNP with keeping larger sure face area by comparing shear flow and storage modulus G' was improved as the extensional stress is higher.

Keywords: Nanocomposite, Polymer, Graphene, Extensional Flow, Dispersive Mixing

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INTRODUCTION

Graphene is one of the most attractive nanocarbon materials, because it has excellent mechanical properties and functional properties (i.e. thermal or electrical conductivity and barrier properties). Many companies and researchers have been attempted to manufacture the high quality graphene by chemical process (e.g. Chemical Vapor Deposition (CVD)) or exfoliate to graphene from graphite directly by mechanical process (e.g. ultra-sonication, melt mixing). However, the cost of graphene by chemical process is very expensive, and the quality of the graphene by mechanical process is lower than by chemical process because the graphene is broken into small pieces.

We have been focused on extensional flow to obtain the better dispersion state of nanofillers (i.e. MWCNT [1-3]) with twin-screw extruder. Typically, shear flow is used for compounding the nanofillers and thermoplastic resin by melt mixing process. Experimentally, extensional flow is more efficiently than shear flow in terms of dispersive mixing [4]. The exfoliation to graphene by shear mixing is difficult because the van der Waals force between the layers works strongly. To use this graphene for reinforcement of polymer, graphene should be exfoliated to nanoscale layer with keeping large surface area.

Therefore, we attempt to use the extensional flow for exfoliating graphite to graphene directly in polypropylene (PP) matrix. The purpose of this study is making clear the mixing effect of pure extensional flow by using orifice die which is installed in capillary rheometer. The effect of extensional flow can be evaluated by measured entrance pressure drop ΔP_e while extruding melted composite and entrance pressure drop can be measured directly with orifice die [5]. Furthermore, the mixing effect of extensional flow was compared with that of shear flow in terms of exfoliated (dispersion) state of graphene and particle size (i.e. surface area).

EXPERIMENTAL

Material

PP (J108M, Prime Polymer Co., Ltd.) was used as matrix with MFI 45g/10min at 2.16kg/230°C. Flake Graphite (XD150, Ito Graphite Co., Ltd., Japan) which is 150μm in average particle size was used as filler. The reason of selection this graphite with large surface area is that the morphology observation of graphene is easy. Then, graphite

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based PP composite pellets (masterbatch) were produced by masterbatch process with twin-screw extruder (ZSK18 MegaLab, Coperion GmbH, Germany). The filler loading was 1wt%. The compounding temperature was 200°C, the screw speed was set at 150 rpm and the through put was 4.5kg/h. To avoid the fracture of graphite, the screw configuration with little mixing effect was used (see Fig.1).

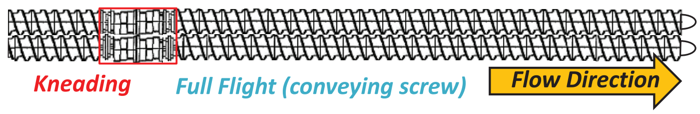


FIGURE 1. Screw configuration of twin-screw extruder with little mixing effect (low shear).

Extrusion for Exfoliation of Graphite into Graphene

Extensional Flow Mixing

The obtained pellets of graphite based PP composite were extruded by capillary rheometer (Rosand RH2200, Bohlin Instruments Ltd.) equipped with orifice die (see Fig.2 (a)). The extruded temperature was set at 200°C. The masterbach was extruded in various piston speeds with different diameter of orifice die to measure the wide range of entrance pressure drop ΔP_e. The entrance pressure drop was measured while extruding the material. The condition of extrusion is shown in Table 1. Then, extensional stress σ was calculated by Cogswell approach:

$$\sigma = \frac{3}{8}(n+1)\cdot \Delta P_e \tag{1}$$

where n is global shear power law index. This index could be obtained from shear viscosity data.

Shear Flow Mixing

At the high shear rate (>10 s^{-1}), the masterbach pellets were extruded by capillary rheometer that capillary die (see Fig.2 (b)) was installed at 200°C. By using capillary die, the materials were applied high shear stress. However, the measured pressure drop ΔP includes entrance pressure drop ΔP_e and shear pressure drop ΔP_{sh}. Therefore, the materials were affected by both extensional and shear stress. The condition of extrusion is shown in Table 1. Shear stress τ was calculated by Hagen-Poiseuille equation with Bagley correction:

$$\tau = \frac{(\Delta P - \Delta P_e)D}{4L} = \frac{\Delta P_{sh} D}{4L} \tag{2}$$

where D is diameter of capillary die and L is length of capillary die.

On the other hand, at the low shear rate (<10 s^{-1}), the rotational rheometer (Gemini II, Bohlin Instruments Ltd.) was used under the steady shear stress condition. The 25mm parallel plate was equipped, the gap height was 1 mm, and the temperature was 200°C. The applied shear stress was 50 Pa, 100Pa, 500Pa and 1000Pa for 30 sec.

TABLE (1). The experimental condition of extensional and shear flow extrusion.

ID	Extensional Flow		(High) Shear Flow	
	Diameter of Orifice die[mm]	**Piston speed [mm/min]**	**Geometry of Capillary Die $D \times L$ [mm]**	**Piston speed [mm/min]**
1	1	20	1 × 16	20
2	1	100	1 × 16	100
3	1	500	1 × 16	500
4	2	20	2 × 16	20
5	2	100	2 × 16	100
6	2	500	2 × 16	500
7	3	20	3 × 16	20
8	3	100	3 × 16	100
9	3	500	3 × 16	500

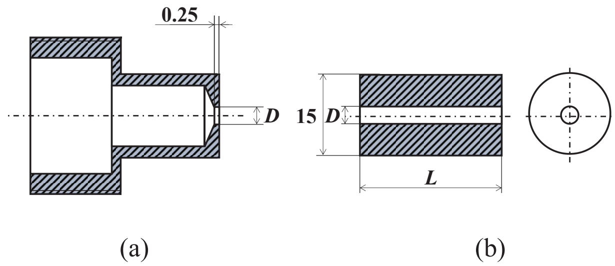


FIGURE 2. Geometry of extrusion die for capillary rheometer; (a) Orifice die (b) Capillary die.

Morphological and Rheological Analysis

Primary, to investigate the state of graphite particle roughly after extensional and shear extrusion, the particle size above 10μm were measured by laser microscopy (VK-X210, KEYENCE CORP.) for 100 graphite particles. The graphite particle was obtained by burned the composite with Electric Furnace (KDF 300-Plus, DENKEN-HIGH DENTAL Co., Ltd., Japan) at 500°C for 1h. Then, to observe the state of graphene in nanoscale, TEM (JEM-2100F, JEOL Ltd., Japan) investigation was conducted. The specimen for TEM observation was prepared by microtome and the thickness of specimen was about 100nm.

Furthermore, the rheological characterization in oscillation mode was conducted with rotational rheometer equipped with 25mm parallel plate because this method can characterize the nanostructure in nanocomposite more accuracy. The storage modulus G' increases by improving the dispersion of nanofiller [6]. In this study, the storage modulus G' was measured under a strain of 5% at angular frequency 0.5 rad/s for all composite after extrusion.

RESULTS AND DISCUSSION

Pressure Drop Measurement and Stress Calculation

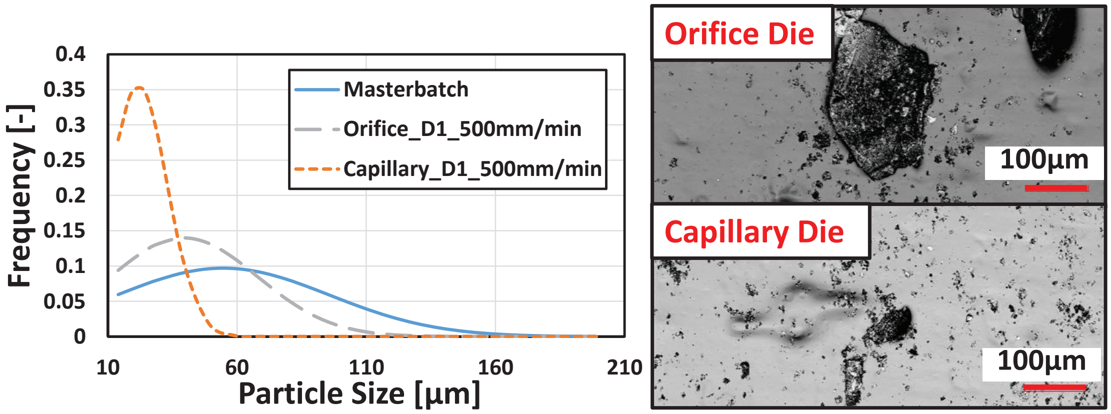
The results of pressure drop measurement and stress calculation are shown in Table 2 for extensional and shear flow mixing. From these results, the entrance pressure drop and shear pressure drop increased as the piston speed is higher and diameter of each extrusion die are smaller. Hence, the tendency of each stress magnitude exhibited the same behavior as that of each pressure drop.

TABLE (2). The results of pressure drop measurement and stress magnitude calculation.

ID	Extensional Flow			Shear Flow		
	Entrance Pressure Drop ΔP_e [kPa]	Stretch Rate[s^{-1}]	Extensional Stress σ [kPa]	Shear Pressure Drop ΔP_e [kPa]	Apparent Shear Rate [s^{-1}]	Shear Stress τ [kPa]
1	253	123	140	2877	600	45
2	768	575	364	5277	3000	82
3	2174	5794	865	8778	15000	137
4	68	11.2	44	387	75	12
5	222	56.3	127	1002	375	31
6	663	267	330	1978	1875	62
7	16	2.86	11	61	22	2.9
8	65	15.9	41	226	111	11
9	301	80.9	167	814	556	38

Morphological Analysis

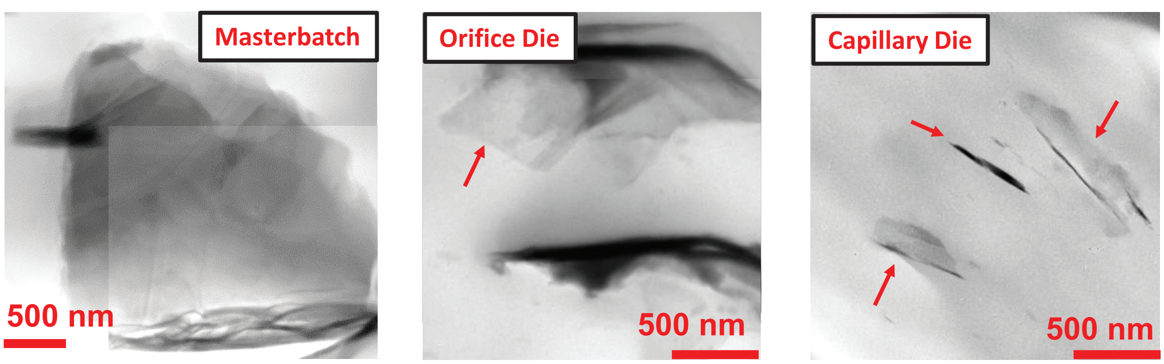
Primary, the result of particle size measurement for only graphite particle is shown in Fig.3 (a) and observed images of graphite were shown in Fig.3 (b). To evaluate the each mixing effect, the particle size distribution was compared between masterbatch, orifice die with 1mm diameter at 500mm/min piston speed (i.e. maximum extensional stress) and capillary die with 1mm diameter at 500mm/min piston speed (i.e. at maximum extensional stress and shear stress). From this result, the particle size decreased dramatically by high shear stress.



(a) (b)

FIGURE 3. The results of particle size measurement for flake graphite after extrusion; (a) Comparison of particle size distribution (probability density function) (b) Observation images of flake graphite.

Furthermore, observed TEM micrographs were shown in Fig.4 to discuss the mixing effect for each flow in more detail. TEM micrograph of masterbatch pellets was shown in Fig.4 (a). The thick layers which have about 3.5μm particle size can be observed and the layers didn't exfoliate into one layer. Then, TEM micrograph of extruded materials under maximum of extensional stress was shown in Fig.4 (b). From this image, the layers didn't exfoliate into one layer completely yet. However, thinner layers were observed by comparing with thick layers in materbatch. Finally, the TEM image of the extruded materials under maximum of shear stress was shown in Fig.4 (c). The smaller (<500nm) and thinner layers were observed in this image. However, the surface area of graphene layer by shear extrusion was smaller than that of graphene by elongational extrusion. This tendency coincided with the results of particle size measurement for flake graphite.



(a) (b) (c)

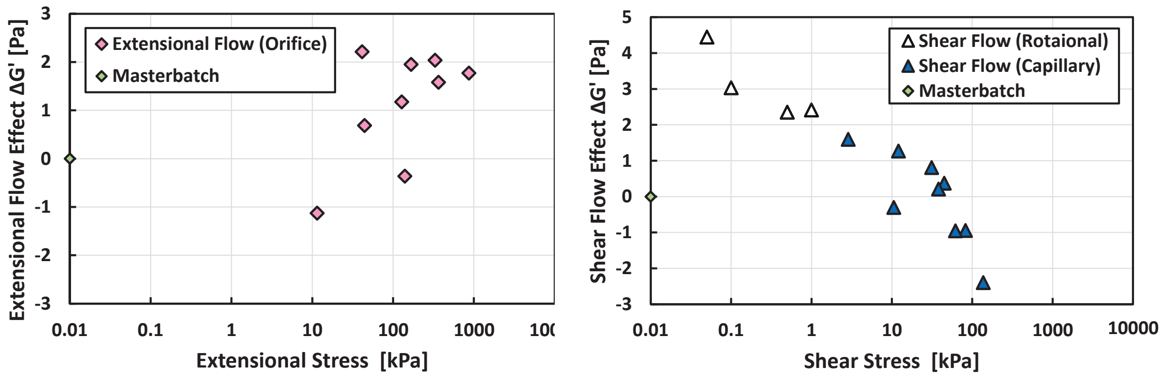
FIGURE 4. TEM micrographs of the cross-section of the extruded materials; (a) Masterbatch (b) Orifice die (at maximum extensional stress) (c) Capillary die (at maximum shear and extensional stress).

Rheological Analysis

The results of storage modulus G' for each flow were shown in Fig. 5. To separate the mixing effect, equation (3) and (4) were used. From these results, the $\Delta G'$ for extensional flow increased as extensional stress is higher. On the other hand, the $\Delta G'$ for shear flow decreased as shear stress is higher. These results indicates that the $\Delta G'$ was depend on the surface area (i.e. length to thickness ration) of graphene layer and the exfoliate state or dispersion state. Therefore, it is suggested that graphene was destroyed not by extensional flow rather but by high shear flow.

$$\Delta G'_{ExtensiondFlowEffect} = G'_{ExtensiondExtrusion} - G'_{Masterbatch} \quad (3)$$

$$\Delta G'_{ShearFlowEffect} = G'_{ShearExtrusion} - G'_{Masterbatch} \quad (4)$$



(a) (b)

FIGURE 5. The results of storage modulus G’ in rheological analysis; (a) Extensional flow (b) Shear flow.

CONCLUSIONS

This research work investigated the effects of extensional flow mixing for exfoliation the graphite into graphene in PP matrix on morphological and rheological analysis by comparing with shear flow mixing. From morphological analysis, the flake graphite particles and graphene layers were broken by shear flow and the extensional flow can exfoliate the graphite into graphene with keeping large surface area by comparing with shear flow. Furthermore, from rheological analysis, storage modulus G’ of extrusion material by extensional flow was improved by 200%. However, storage modulus G’ of extrusion material by shear flow was decreased as shear stress is higher. Therefore, it is suggested that extensional flow is more effective for exfoliate graphite or disperse the graphene than shear flow.

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