



# Article Effects of the Simultaneous Strengthening of the Glass Fiber Surface and Polyamide-6 Matrix by Plasma Treatment and Nanoclay Addition on the Mechanical Properties of Multiscale Hybrid Composites

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Abstract: To strengthen the mechanical properties of a fiber-reinforced plastic without deteriorating its toughness caused by adding nanomaterial, multiscale hybrid composites (MHC) composed of polyamide 6 (PA6), woven glass fibers (WGFs), nanoclay, and various additives were fabricated and characterized. A surfactant was used to improve the dispersion of the nanoclay in the composite, and a compatibilizer and toughening agent were added to enhance the interfacial interactions between the nanoclay and PA6 and the toughness of the MHC, respectively. In addition, the WGFs were pretreated with atmospheric-pressure air plasma to enhance the interfacial bonding between the WGF and the mixture composed of PA6/nanoclay/compatibilizer/toughening agent, which constitutes the matrix. The optimal composition of the PA6 mixture, optimal content of the nanoclay, and optimal conditions of the plasma pretreatment of the WGF surface were experimentally determined. A suitable manufacturing process was employed using a material composition that maximizes the mechanical properties of the MHC by mitigating the toughness deterioration owing to nanoclay addition. An appropriate quantity of the nanoclay increased the tensile properties as well as the elongation at the break of the MHC because the toughening agent prevented the reduction in the degree of elongation caused by increasing the clay content to a certain extent. Moreover, the plasma treatment of the WGF enhanced the flexural properties and impact resistance of the MHC. Therefore, not only the tensile strength, modulus, and elongation at the break of the PA6 nanocomposite, which constitutes the matrix of the MHC, increased up to 39.83, 40.91, and 194.26%, respectively, but also the flexural strength and modulus, absorbed impact energy, and penetration limit of the MHC increased by 20.2, 26.8, 83.7, and 100.0%, respectively.

Keywords: glass fibers; nanoparticles; surface treatment; composites; mechanical properties

## 1. Introduction

Currently, the attention of the industrial community is focused on developing advanced composites composed of polymer matrix and fibers with complementary properties, and the use of fiber-reinforced composites has been steadily increasing in various fields, such as the automotive and aviation industries, military, and civil engineering [1,2]. Compared with fiber-reinforced composites consisting of short and long fibers with inferior physical properties, continuous fiber-reinforced composites demonstrate superior properties and can replace certain metal parts in the military and automobile fields, which demand both mechanical properties and lightweight. For carbon fiber-reinforced thermoset composites, the cost of carbon fibers is still significantly higher than that of glass fibers; therefore, most thermosetting polymers have been used in high-value-added industries, such as structural parts of vehicles and aircraft. However, when such composites are subjected to repeated vibration and impact, critical defects may occur because of the high



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). rigidity of carbon fibers and thermosetting polymer and the weak interfacial bonding between them. For these reasons, carbon fiber-reinforced thermoset composites are unsuitable for interior parts for vehicles and aircraft, such as seat back frames, battery storage, and the outer case of electronic control systems. Therefore, continuous glass fiber-reinforced thermoplastics (C-GFRTPs) are more practical materials for inner components of military vehicles and aircraft to provide higher toughness and impact resistance than thermoset composites [3–5]. In order to meet the increasing demands for military applications of C-GFRTPs in severe environments, an advanced reinforcement technology is required to increase both toughness and general mechanical properties, such as tensile and flexure strengths; however, this is challenging because of the trade-off relationship between them. In general, to improve the mechanical properties of fiber-reinforced composites, reinforcing both fiber and resin [6–8] or strengthening the fiber–resin interaction at the interphase is necessary [9].

The complementary relationship between the resin and fiber can typically be improved in two ways: (i) adding certain additives, such as a reinforcing agent and compatibilizer to the resin to improve the functionality of the resin itself and (ii) modifying the fiber surface to enhance the interaction between the fiber and resin. Excellent interfacial interactions can prevent stress concentration at certain sites of the composite, leading to an overall improvement of the mechanical properties. Many fiber surface treatment methods have been developed, and they can be subdivided as follows: increasing the interfacial surface area of fibers by employing nanowires [10,11] and nanorods [12–14], functionalizing the fiber surface with organic functional groups using a coupling agent [14–16] or through an appropriate chemical reaction [17-19], and changing the composition of the fiber surface by oxidative surface treatment [20]. Although increasing the interfacial adhesion of the fiber using a single method, such as whiskerization, coupling with a functional silane molecule, and chemical treatment, has provided promising results, certain limitations in terms of the price and productivity for industrial application remain to be resolved. Moreover, in the cases of heat and oxidative surface treatments, the improvement of certain properties could be compromised owing to the damage of the fiber itself [21,22]. As an alternative method, plasma surface treatment has been widely applied in recent years to modify material surfaces [13,22]. In particular, atmospheric-pressure air plasma is a suitable technique for the surface treatment of metal plates, circuit boards, and fibers because of its merits, such as mass and continuous in-line processing capability, simple equipment installation, and non-requirement of a vacuum chamber or a specific gas [23,24]. Plasma treatment can increase the number of oxygen functional groups and the roughness of the fiber surface and render the fiber surface hydrophilicity.

Among the commercially available thermoplastic polymers, nylon 6 (also known as PA6) is one of the most attractive and widely employed engineering polymers because of its good performance parameters, such as a high impact resistance, low friction coefficient, high wear resistance, and relatively high thermal resistance [25]. More specifically, the amine groups of PA6 can readily react with maleic anhydride-grafted compatibilizers, which can result in the stabilization of the interfacial tension. Therefore, PA6 can be a suitable candidate for reinforcing the interactions between the glass fiber and polymer matrix [26,27].

Compared with carbon nanomaterials, which have been extensively studied as reinforcing agents [28], nanoclay derived from natural clay has excellent dispersibility and is eco-friendly and cost-effective [29]. Melted thermoplastics exhibit an extremely high viscosity during the manufacturing process; therefore, nanoclay particles cannot maintain good dispersibility in the resin matrix. Therefore, a compatibilizer and surfactant are required to improve the dispersion and compatibility between the glass fibers, clay particles, and polymer in fiber-reinforced polymer composites. In particular, many earlier studies have utilized polypropylene-graft-maleic anhydride (PP-g-MA) [30–32] and polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-graft maleic anhydride (SEBS-g-MA) [30,33] as the compatibilizer and toughening agent, respectively, and a cationic

surfactant, viz., octadecyl-trimethyl-ammonium bromide (ODAB) for the dispersion and exfoliation of the nanoclay particles [34,35]. PP-g-MA has better ductility than PA6, and it can blend homogeneously with the PA6 resin through melt compounding at temperatures exceeding 200 °C. The resulting composite demonstrates improved crystallinity and tribological properties because maleated PP acts as a nucleating agent, stabilizes the crystalline site, and accelerates the nucleation of the polymer [36–38], but also reduces the interfacial tension between the PA6 chains, facilitating the uniform clay intercalation to polymer chains [27,39]. SEBS-g-MA acts both as a compatibilizer and as a toughening agent that prevents the reduction of the impact resistance of PA6 following the addition of nanomaterial reinforcement (i.e., nanoclay). The maleic anhydride (MA) groups in both PP-g-MA and SEBS-g-MA copolymer at the PA6-PP-g-MA interface. This co-polymerization stabilizes the interfacial tension of the interfacial tension of the interfacial tension of the composite [26].

This study focused on improving the functionalities of PA6 and glass fibers to increase the flexural properties and the toughness of multiscale hybrid composites (MHC) fabricated using three additives, viz., ODAB, PP-g-MA, and SEBS-g-MA, and nanoclay as the reinforcing agent of PA6. PA6 films reinforced with the nanoclay and various additives (i.e., the blend of PA6, ODAB, PP-g-MA, and SEBS-g-MA, and nanoclay, referred to as the PA6 nanocomposite blend) were prepared by a film extrusion method through melt compounding to subsequently fabricate MHCs by combining with woven glass fibers (WGFs). The tensile properties of the PA6 nanocomposite films were investigated in terms of the clay concentration to determine the optimum composition of the nanocomposite matrix to develop MHCs by mixing with WGFs. Before the production of MHCs, the WGF was pretreated by varying the distance of the nozzle of the plasma apparatus from its surface (hereafter referred to as the nozzle height). The effects of plasma treatment on the surface composition of the WGF and the mechanical properties of the MHCs were evaluated and discussed.

#### 2. Experimental Section

## 2.1. Materials

Plain woven E-glass fibers (7628, tensile strength: 500 ksi; tensile modulus: 10.5 msi) produced by JMC (Republic of Korea) were used in this study. The general tensile strengths of the WGFs in warp and fill directions were 39.5 and 30.4 N/m, respectively, and the yarn density (Tex) was 68 g. PP-g-MA (427845, 8–10 wt.% MA), SEBS-g-MA (432431, 2 wt.% MA), ODAB (359246), and montmorillonite (MMT) nanoclay (682632) were obtained from Sigma-Aldrich, USA. To improve the adhesion properties, the surface of the MMT clay particles was modified using silane coupling agents (0.5–5 wt.% aminopropyltriethoxysilane and 15–35 wt.% octadecylamine). Dry PA6 pellets (KOPA KN177N, extrusion grade) were purchased from KOLON PLASTICS, INC. (Republic of Korea). The pellets of PA6, PP-g-MA, and SEBS-g-MA were separately pulverized in a cryogenic environment at the Research Institute of Industrial Science and Technology (RIST) to obtain powders with particle sizes of <100  $\mu$ m.

## 2.2. Plasma Treatment of the WGF Surface

The surface-cleaned WGF was subjected to continuous surface treatment by varying the height (17, 13, 9, and 5 mm) of the plasma nozzle with respect to its surface. An atmospheric-pressure air plasma apparatus (830W, Applied Plasma Inc., Gumi, Republic of Korea) composed of a gas pressure regulator, plasma reactor, nozzle, air filter, power supply, and conveyor belt was used for plasma treatment. An electrode in the nozzle generated a strong electrical arc, which produced a potential-free plasma flow from fresh air at a flow rate of 70 L/min. After being generated, the plasma hit the surface of the WGF and altered its chemical composition. A schematic and photograph of the plasma treatment of the WGF surface are shown in Figure 1, and the treatment conditions are listed in Table 1.



Figure 1. Schematic of the atmospheric-pressure plasma pretreatment of the WGF surface and photograph of the apparatus.

			Nozzle Parameters			
Sample Number	Fiber	Plasma Treatment	X-Axis	Y-Axis	Z-Axis	
			Speed [m/min]	Transfer Distance [mm]	Height [mm]	
1	Untreated WGF	Х	Х	Х	Х	
2	WGF_17 mm	О	20	10	17	
3	WGF_13 mm	0	20	10	13	
4	WGF_9 mm	О	20	10	9	
5	WGF_5 mm	0	20	10	5	

Table 1. Conditions of the plasma treatment of the WGF surface
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## 2.3. Preparation of PA6 Nanocomposite Films and MHCs

Before melt compounding to fabricate a nanocomposite matrix comprising PA6, MMT nanoclay, PP-g-MA, and SEBS-g-MA, the MMT clay was modified with ODAB to induce intercalation and exfoliation of the clay particles, based on the procedure reported by Deka et al. [40] and our previous study [35]. First, the MMT clay (20 g) and ODAB (24 g) were dispersed separately in 400 mL of distilled water/ethanol (5:5 vol%) at 80 °C for 24 h using a hot plate with a magnetic stirrer. Then, 19.2 mL of 1.0 N HCl was added to the ODAB solution under stirring. After 2 h, this solution was slowly poured into the MMT clay dispersion and stirred at 80 °C for another 24 h. Subsequently, the mixture was sonicated for 3 h using a horn-type sonicator (Sonictopia, Cheongju, Republic of Korea). Then, the homogeneously dispersed organoclay suspension was placed in a centrifugal separator (1236R, Labogene, Allerød, Denmark) to extract the intercalated and exfoliated organoclay, and the resulting organoclay slurry was filtered and washed four times with distilled water until no chloride ions were detected using  $AgNO_3$  solution [34]. The clean organoclay sample was dried overnight in a vacuum oven at 60  $^{\circ}$ C, ground, and kept in a dark color bottle to avoid sunlight and moisture for subsequent use.

Next, the powders of PA6, PP-g-MA, SEBS-g-MA, and organoclay were mixed using a fine blender (7010HS, Waring, Stamford, CT, USA) for 15 min and then dried in a vacuum oven for 24 h at 80 °C. With respect to the weight of PA6, the content of the organoclay was varied from 1 to 5 wt.%, while the content of PP-g-MA was fixed at 3 wt.% [35,41]. In addition, 6 phr (parts per hundred resin) of SEBS-g-MA was added to the PA6/organoclay/PP-g-MA mixture, regardless of the clay content (refer to Table 2). To prepare the PA6 nanocomposite films, a lab-scale extrusion system (Randcastle Extrusion, USA) with a custom-designed rotating screw was used. The fully dried powder mixtures

were fed into the feed hopper and extruded into a nanocomposite film (t = 0.1 mm) through five different temperature zones in sequential order: dosing, metering, melting, mixing, and pumping. The temperature zones were maintained at 213, 221, 249, 241, and 221 °C, respectively. The dosing and metering zones applied a consistent screw speed to transfer a uniform volume per unit of time and automatically modulated the feeder rate according to the feedback of the load cell. As the mixture passed through the melting and mixing zones, the particle size decreased, and the dispersibility of the components increased owing to strong shear stress imposed by the screw. In addition, division and recombination of the components occurred, resulting in excellent distribution and uniform homogenization of the blend [42]. Thus, the nanocomposite films were prepared by extruding the homogeneously blended PA6/organoclay/PP-g-MA/SEBS-g-MA compound through a film die. The drawing rate of the receiving roller was maintained at 62 rpm (take-up speed: 8.8 m/min).

Table 2. Manufacturing conditions of the PA6 films.

Sample	Polymer Matrix	Organoclay (ODAB-Nanoclay) (1:5)	Organo Clay Content (wt.%)	PP-g-MA (3 wt.%) SEBS-g-MA (6 phr)	Screw Speed (RPM)	Take-Up Speed [m/min]
Neat	PA6	Х	0	Х	4	8.8
0	PA6	Х	0	0	4	8.8
1	PA6	ODAB-Clay	1	О	4	8.8
2	PA6	ODAB-Clay	2	О	4	8.8
3	PA6	ODAB-Clay	3	0	4	8.8
4	PA6	ODAB-Clay	4	0	4	8.8
5	PA6	ODAB-Clay	5	О	4	8.8

To fabricate the MHCs, the plasma surface-treated WGFs and nanocomposite films were laminated in a layer-by-layer manner on a female mold, and then the mold was sealed with the male mold. Thereafter, a 30-ton semi-automatic hydraulic hot press (COAD 1205a, Ocean Science, Uiwang, Republic of Korea) was used to melt-impregnate the fabric with the resin matrix. The temperature was fixed at 260 °C, and the pressure was initially maintained at 2 MPa for 5 min and subsequently increased up to 10 MPa for 2 min to effectively induce melt impregnation. The schematics of the overall manufacturing process of the MHCs is provided in Figure 2.

## 2.4. Characterization of the Nanocomposite Film

To evaluate the variation in the viscosity of PA6 with different nanoclay contents, dynamic viscosity measurements were performed using a rheometer (Haake MARS III-ORM Package, Thermo Fisher Scientific, Waltham, MA, USA) in the shear rate range of 0-1000/s at 260 °C.

The melting temperature and crystallinity of the nanocomposite films were evaluated through differential scanning calorimetry (DSC; TA instruments Q800, New Castle, DE, USA). The DSC analysis was carried out over a wide temperature range of 10–300 °C in a nitrogen atmosphere, and the heating rate was 10 °C/min. The percentage crystallinity ( $X_c$ ) of the films was calculated from the endothermic peak using the following equation:

$$X_{c} = (\Delta H_{m, \text{ experiment}} / \Delta H_{o, \text{ literature}}) \times 100\%$$
(1)

where  $\Delta H_{m, experiment}$  and  $\Delta H_{o, literature}$  are the melting heat enthalpies of the measured sample and 100% crystalline PA6, respectively ( $\Delta H_{o, literature} = 190 \text{ J/g}$ ).



Figure 2. Manufacturing process of the PA6 nanocomposite film and MHC.

Tensile test specimens (2 mm  $\times$  30 mm) were prepared using a laser cutting apparatus (Versa Laser 25 W, Universal Laser Systems, Scottsdale, AZ, USA). Tensile properties of the nanocomposite film, such as the ultimate tensile strength, elastic modulus, and elongation at break, were evaluated at the same gauge length and strain rate using a universal testing machine (Shimadzu AGX-100NX, Kyoto, Japan).

## 2.5. MHC Characterization

## 2.5.1. X-ray Photoelectron Spectroscopy (XPS) of the WGF

The surface composition of the plasma-treated surfaces was determined using XPS (K-Alpha, Thermo Fisher Scientific, USA). During the XPS, the spot size and energy step size were maintained at 400  $\mu$ m and 0.1 eV, respectively. High-resolution O1s, Si2p, C1s, Ca2p, N1s, and Al2p spectra were obtained using an Al *K* $\alpha$  monochromatic X-ray source (1486.6 eV). To analyze the type and extent of functional groups in detail, the C1s scan was deconvoluted into four Gaussian peaks using a curve-fitting program (CasaXPS 2.3.24PR1.0).

#### 2.5.2. Scanning Electron Microscopy on Fractured Surface of the MHCs

The plasma-treated WGF surface and the fractured MHC surface were observed using a high-resolution scanning electron microscope (HR-SEM; FEI, Nano-nova 230). The specimens were fractured at an extremely low temperature using liquid nitrogen to obtain fractured surfaces. All SEM samples were coated with platinum before observation.

## 2.5.3. Three-Point Bending and Drop Weight Impact Testing of the MHCs

Flexural properties were evaluated using a universal testing machine (Instron 5982, Norwood, MA, USA). The specimen information and test procedure for three-point bending were referred to ASTM D790. A crosshead motion speed of 1 mm/min was constantly applied to push the center of the flexural test specimens. Flexural tests were conducted on five specimens of each condition, and the results were averaged.

To evaluate the impact resistances of the MHCs, drop weight impact tests were conducted using a drop tower impact tester (CEAST 9350, Instron, Norwood, MA, USA) according to ASTM D3763 test specifications. A test specimen with a surface area of  $100 \times 100 \text{ mm}^2$  was fixed with a ring-type clamp (diameter: 40 mm) at 100 N, and then a striker with a nominal diameter of 12.7 mm was dropped at the rate of 1.27 m/s, which corresponded to an impact energy of 4 J. The impact energy absorbed by the MHC specimens was calculated by collecting the data of the photoelectric sensor from the striker's first impact point on the surface until penetration by the striker.

#### 3. Results and Discussion

#### 3.1. Interaction Mechanism of the PA6 Nanocomposite Blend

The fabrication of thermoplastic resin-based nanocomposites has been investigated for several decades. The internal chemical bonding mechanism of these nanocomposite blends was extensively studied in the past with numerous validations. Cationic surfactants could neutralize the surface charge of the nanoclay and reduce inter-particle interactions. As a result, the nanoclay particles readily dispersed homogenously in the solvent [43]. In addition, cationic surfactants played a significant role in promoting the exfoliation of nanoclay platelets by adsorbing onto or intercalating into the nanoclay surface [43]. Thus, the terminal amino group of the intercalated PA6 chains and the organofunctional groups (primary amines) of aminopropyltriethoxysilane and octadecylamine on the surface of the nanoclay could form covalent bonds via chemical interactions with the MA groups of PP-g-MA and SEBS-g-MA during the melting compounding process [44–49]. Furthermore, the polymer chains of PP, SEBS, and PA6 underwent entanglement at the same time. These chemical and mechanical interactions enhanced the compatibility between the polymers and between the polymers and the nanoclay, improving the dispersion and stability of the nanoclay particles. Ultimately, the mechanical and thermal properties of the nanocomposite blends were significantly strengthened [50]. A schematic of the interaction mechanism of the PA6 nanocomposite blend is presented in Figure 3.



Figure 3. Interaction mechanism of the PA6 nanocomposite (i.e., PA6/Organo-clay/SEBS-g-MA/PPg-MA). Red line: PP chains, Green line: SEBS chains, Blue line: PA6 chains.

## 3.2. Dynamic Viscosity of the Nanocomposite Films

In general, high-viscosity resins obtained by the addition of a nano-reinforcing agent do not infiltrate the fibers adequately, which can lead to poor interfacial bonding and delamination of the composites. Therefore, a rheometer was used to evaluate the change in the viscosity of the PA6 nanocomposite with the organoclay content. The viscosity-shear rate characteristics at the processing temperature of 260 °C are presented in Figure 4. The melt viscosity of the PA6 nanocomposites increased with nanoclay content owing to the enhanced intermolecular interactions, such as van der Waals forces, hydrogen bonding, and covalent bonding between PA6 and organoclay particles. All samples exhibited shear thinning behavior (non-Newtonian fluid characteristic); however, the flow behavior in the specific shear rate range of 20 to 300/s revealed that all samples, except for the sample with 5 wt.% organoclay showed Newtonian fluid behavior because an increase in the shear rate led to the alignment of organoclay particles along the shear direction [51]. A sharp decline in the viscosity was observed at shear rates exceeding 300/s owing to increased agglomeration of the clay particles. The sample with 5 wt.% clay exhibited a slightly different characteristic: the viscosity decreased sharply at a lower shear rate as compared to the other cases owing to the excess clay content. Although the increase in interactions between PA6 and organoclay is desired, a very high viscosity leads to decreased impregnation of the fabric with the polymer matrix, which can severely deteriorate the mechanical properties of the MHC. Therefore, adding an appropriate quantity of organoclay

is important to obtain an MHC with optimal mechanical properties. For samples with up to 2 wt.% clay content, the dynamic viscosity did not increase noticeably owing to the added toughening agent, SEBS-g-MA.



**Figure 4.** Dynamic viscosity of neat PA6 and PA6 nanocomposites as a function of the organoclay concentration at the processing temperature of 260 °C.

#### 3.3. Crystallinity and Melting Temperature of the Nanocomposite Films

Figure 5 presents the DSC thermograms of the PA6 nanocomposites (PA6/SEBS-g-MA/PP-g-MA/organoclay) with different nanoclay contents as well as the variation in the crystallinity and melting temperature according to the content of the organoclay. In the case of the sample without the organoclay (i.e., PA6/SEBS-g-MA/PP-g-MA), the melting point shifted to a lower temperature because the melting temperatures of the PP and SEBS copolymers are lower than that of PA6. In contrast, the addition of the organoclay increased the melting point of the nanocomposite, and the melting point gradually shifted to a higher temperature as the nanoclay content increased. This is because the nanoclay acts as a nucleating agent and helps polymer phase nucleation in PA6 blends, increasing melting point. This factor reduces the crystal size of the polymer, stabilizes the interface, accelerates the rate of crystallization, and increases the crystallinity of the composite [27]. The degree of crystallinity calculated using Equation (1) and the melting temperatures of the nanocomposites are listed in Table 3. The crystallinity of PA6 decreased in the absence of the organoclay because of the added compatibilizer/toughening agent, SEBS-g-MA. Interactions between the PA6 and SEBS-g-MA phases through hydrogen bonding would restrict the chain mobility of PA6 and eventually suppress crystal formation, resulting in a decrease in its crystallinity [52]. However, the decrease rate was not large due to the small amount of SEBS-g-MA added to the composite. In contrast, the crystallinity of the nanocomposite increased as the clay content was increased up to 3 wt.% and then decreased with a further increase in the clay content; this is because a high clay content induced particle agglomeration and reduced the interfacial area, which weakened its effect as a nucleation agent. Therefore, the PA6/SEBS-g-MA/PP-g-MA/organoclay sample with 2 and 3 wt.% organoclay exhibited greater crystallinity than neat PA6.



**Figure 5.** DSC endothermic peaks of neat PA6 and PA6 nanocomposites (PA6/Organo-clay/SEBS-g-MA/PP-g-MA) at different organoclay concentrations.

**Table 3.** Percentage crystallinity and melting temperature of the PA6 nanocomposite as a function of the organoclay content (\* PA6 nanocomposite = PA6/organoclay/6 phr SEBS-g-MA/3 wt.% PP-g-MA).

Sample Melting Enthalpy $(\Delta H_{\rm m}, J/g)$		Crystallinity (%)	Melting Temperature (°C)
Neat PA6	67.04	35.28	211.70
PA6 nanocomposite (0 wt.% organoclay)	67.00	35.26	208.82
PA6 nanocomposite (1 wt.% organoclay)	68.16	35.87	214.28
PA6 nanocomposite (2 wt.% organoclay)	72.57	38.19	214.45
PA6 nanocomposite (3 wt.% organoclay)	72.93	38.38	215.38
PA6 nanocomposite (4 wt.% organoclay)	71.23	37.49	214.79
PA6 nanocomposite (5 wt.% organoclay)	71.03	37.38	214.41

3.4. Tensile Properties of the Nanocomposite Films

Figure 6 and Table 4 present the change in the tensile properties of the PA6/SEBS-g-MA/PP-g-MA/organoclay nanocomposite according to the clay content.

**Table 4.** Tensile properties of the PA6 nanocomposite films (PA6/0–5 wt.% organoclay/6 phr SEBS-g-MA/3 wt.% PP-g-MA) at different organoclay concentrations.

Sample	Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at Bsreak (%)
Neat PA6	$0.88\pm0.13$	$32.74 \pm 2.67$	$12.36\pm3.33$
PA6 nanocomposite (0 wt.% organoclay)	$0.69\pm0.05$	$46.22\pm3.58$	$65.05\pm15.17$
PA6 nanocomposite (1 wt.% organoclay)	$0.72\pm0.09$	$47.85 \pm 1.64$	$37.07\pm8.57$

Sample	Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at Bsreak (%)
PA6 nanocomposite (2 wt.% organoclay)	$1.24\pm0.22$	$45.78\pm0.85$	$36.37\pm5.70$
PA6 nanocomposite (3 wt.% organoclay)	$1.29\pm0.04$	$43.90\pm2.18$	$18.24\pm2.33$
PA6 nanocomposite (4 wt.% organoclay)	$1.23\pm0.09$	$37.74\pm0.22$	$12.13\pm0.80$
PA6 nanocomposite (5 wt.% organoclay)	$1.41\pm0.18$	$37.33\pm0.68$	$6.61\pm0.33$

Neat PA6 Nanocomposite, 0 wt.% Nanocomposite, 1 wt.% Nanocomposite, 2 wt.% Nanocomposite, 3 wt.% Nanocomposite, 4 wt.% Nanocomposite, 5 wt.% 50 40 **Fensile Stress (MPa)** 30 (a.u.) 20 10 0.10 0.15 0.05 0.20 0.25 0.30 0.35 20 40 60 Tensile Strain (%)

**Figure 6.** Stress–strain curves of neat PA6 and PA6 nanocomposite films (PA6/ODAB-clay/SEBS-g-MA/PP-g-MA) as a function of the organoclay content.

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The tensile modulus of the PA6/SEBS-g-MA/PP-g-MA specimen without the organoclay decreased as compared with that of neat PA6, whereas the tensile strength and elongation increased significantly. Owing to the role of the organoclay as an outstanding nucleating agent, the tensile modulus increased after the addition of the organoclay. The maximum tensile modulus, tensile strength, and elongation at break were observed for samples with 5 wt.%, 1 wt.%, and 0 wt.% clay content, respectively. Considering the overall properties, the film samples with 2 and 3 wt.% clay content exhibited better tensile properties. However, the sample with 2 wt.% clay content appeared to have the best mechanical properties in view of its viscosity and the rate of reduction in elongation. Moreover, the ultimate tensile strength, tensile modulus, and elongation at break of this sample increased by 39.83, 40.91%, and 194.26%, respectively, as compared to those of the neat PA6 film.

## 3.5. Surface Morphology of the Plasma-Treated WGF

The surface morphologies of the WGFs before and after plasma treatment were investigated using high-resolution SEM. As shown in Figure 7, no remarkable changes occurred in the surface morphology of the fibers after plasma treatment. However, the surfaces of both the non-treated WGF and the mildly plasma-treated WGF had large amounts of impurities, although the samples were washed with a mixed solvent of acetone/ethanol

 Table 4. Cont.

for ~1 h. After moderate to strong plasma treatment, the impurities that adhered to the fiber surface disappeared. When the height of the plasma nozzle from the fiber surface was lower than 13 mm, the fiber surface hardly contained any impurities. This is because the fiber surface was etched and cleaned through the high-energy ion collisions caused by the plasma [53]. Moreover, this cleaning effect improves the interfacial bonding between the fiber and resin.



**Figure 7.** SEM images of the WGF surface plasma-treated from different nozzle heights (5, 9, 13, and 17 mm).

#### 3.6. Surface Composition of the Plasma-Treated WGF

The change in the composition of the WGF surface was analyzed using XPS. The survey XPS scan (0–1400 eV) of all the samples commonly exhibited the following peaks: C1s (280-295 eV), O1s (525-540 eV), N1s (394-410 eV), Si2p (97-107 eV), Ca2p (343-355 eV), and Al2p (70–77 eV), and the atomic percentage (at.%) of each element determined through peak analysis is listed in Table 5. The contents of Si, Ca, and Al did not change significantly with the plasma treatment, whereas the contents of C, O, and N varied substantially following the plasma treatment. The plasma surface treatment caused a decrease in the content of C and an increase in the contents of O and N atoms on the fiber surface; thus, the atomic contents of C and O were inversely related. In particular, the sample subjected to plasma treatment with 9 mm nozzle height from the surface showed the minimum C content (22.0 at.%) and the maximum O content (48.8 at.%); therefore, it had the largest O1s/C1s (221.8%) ratio. This is because of the increase in the oxygen functional groups after the plasma surface pretreatment. Further, the O1s spectrum and deconvoluted C1s spectrum were examined to confirm the functional groups on the surface of the WGF (see Figure 8). In the O1s spectrum, the O1s peak intensity increased with a decrease in the plasma nozzle height to 9 mm, and a further decrease in the nozzle height to 5 mm led to a decrease in the intensity owing to significant surface oxidation and damage of the fiber surface owing to excessive plasma exposure. The deconvoluted C1s spectrum contained peaks centered at 284.5, 286.1, 287.4, and 288.5 eV corresponding to the carbon-carbon single bond (C–C) and hydroxyl (C–OH), carbonyl (C=O), and carboxyl (COOH) groups, respectively [35,54,55]. Among these peaks, the C–C peak had the largest area, and the peak area gradually decreased with plasma treatment until the plasma nozzle height from the WGF surface was increased to 9 mm. In contrast, the peaks of the C–OH, C=O, and COOH groups increased gradually with the plasma surface treatment, and the maximum peak area was observed at plasma nozzle heights of 9 and 13 mm from the WGF surface. However, the peak intensities decreased considerably after plasma treatment at 5 mm height of the nozzle. These results are summarized in Table 6. The spectra and the data in Table 6 clearly reveal that the largest peak areas of the C-OH (21.4%) and C=O (15.2%) groups occurred at 9 mm height of the plasma nozzle on the sample surface, and the sample plasma-treated with 13 mm nozzle height had the maximum peak area of the-COOH groups (21.8%). These results indicate a considerable increase in the number of functional groups than those in untreated WGF; this is consistent with the O1s and C1s atomic contents in Table 5. The plasma pretreatment of the WGF surface strengthened the interfacial bonding between the fibers and polymer matrix because the oxygen functional groups on the fiber surface had multiple interactions with the PA6 chain, organoclay particles, and MA groups in the compatibilizers [56,57]. Overall, the plasma treatment of the WGF surface with a plasma nozzle height of 9 mm resulted in the largest number of functional groups with an optimal O1s/C1s ratio.

**Table 5.** Elemental compositions and atomic percentages of non-treated WGFs and WGFs subjected to plasma treatment with different nozzle heights.

Z-Distance (mm)	C1s (at.%)	O1s (at.%)	N1s (at.%)	Si2p (at.%)	Ca2p (at.%)	Al2p (at.%)	O1s/C1s (%)
Neat	32.3	40.2	0.9	18.0	4.5	4.1	124.5
17	24.7	45.9	1.8	18.8	4.6	4.2	185.8
13	22.9	48.0	1.3	18.5	5.0	4.3	209.6
9	22.0	48.8	1.4	18.5	4.7	4.6	221.8
5	24.1	47.5	1.7	17.4	4.9	4.4	197.1



**Figure 8.** XPS O1s scan and deconvoluted C1s peaks of the WGF surface plasma-treated by varying the height (5, 9, 13, and 17 mm) between the plasma nozzle and fiber surface.

Z-Distance (mm)	C–C (Area%) 284.5 eV	C-OH (Area%) 286.1 eV	C=O (Area%) 287.4 eV	COOH (Area%) 288.5 eV
Neat	81.6	4.4	5.2	8.8
17	74.4	13.4	3.0	9.2
13	47.6	18.5	12.1	21.8
9	45.2	21.4	15.2	18.2
5	75.5	11.2	5.1	8.2

**Table 6.** Relative area (%) of the deconvoluted peaks of C1s as a function of the plasma nozzle height.

#### 3.7. Mechanical Properties of the MHCs

Based on the results of the tensile tests of the nanocomposite films, the PA6/SEBS-g-MA/PP-g-MA/organoclay nanocomposite film reinforced with 2 wt.% organoclay was used as the matrix to prepare MHCs. A total of seven specimens, including neat PA6/ untreated WGF, PA6 nanocomposite/untreated WGF, neat PA6/plasma-treated WGF (9 mm nozzle height), PA6 nanocomposite/plasma-treated WGF (height of the plasma nozzle from the WGF surface was varied as 17, 13, 9, and 5 mm) were tested to investigate the flexural and impact properties according to the plasma intensity during WGF treatment, and the addition of the optimized organoclay and compatibilizers. Three-point bending tests (see Figure 9) revealed that the PA6 nanocomposite/untreated WGF (Figure 9b) had higher flexural modulus and strength than neat PA6/untreated WGF (Figure 9a). Remarkably, specimens (Figure 9d–g) with plasma-treated WGFs exhibited a considerably better increase rate of flexural properties. In particular, the flexural modulus and strength were increased by 26.82 and 20.16% for PA6 nanocomposite/9 mm plasma-treated WGF (Figure 9f) compared with those of neat PA6/untreated WGF. However, the flexural properties were degraded in the case of the specimen with a WGF subjected to stronger plasma treatment (5 mm nozzle height); this trend is almost similar to the trend of the XPS results, implying that excessive surface treatment adversely affects the flexural properties of the MHC. In general, the flexural properties of fiber-reinforced composites are influenced to a greater extent by the polymer matrix and interfacial properties than by the properties of the fiber. Similarly, the improvement in the flexural properties of the PA6 nanocomposite/untreated WGF (Figure 9b) was greater than that of neat PA6/9 mm plasma-treated WGF (Figure 9c), which indicates that the flexural property of the MHC is more affected by the modification of the matrix than by the plasma treatment of the fibers. Overall, the use of the PA6 nanocomposite considerably improved the flexural modulus, while the plasma treatment of the WGF appeared to positively impact the flexural strength. Thus, we confirmed that the mechanical properties of the fiber-reinforced composites can be maximized by simultaneously tuning the properties of the polymer matrix as well as the reinforcing fibers.

The drop-weight impact testing is affected by the impact speed and energy of the striker. The impact energy of the striker should exceed the penetration and perforation threshold of the specimen [58,59]. Otherwise, the specimen does not puncture, and the overall impact energy cannot be determined. To ensure the striker perfectly passed through the specimen, the impact speed and energy of the striker were set at 1.27 m/s and 4 J, respectively. The total impact energy of the specimen can be divided into rebound energy and absorbed energy. Because the rebound energy is negligible for fiber-reinforced composites, the absorbed energy can be approximated as the total impact energy because most of the energy is completely absorbed by both the resin and the fibers [60]. The results of drop weight impact tests of the MHCs are presented in Figure 10, which reveals that the neat PA6/untreated WGF specimen had the lowest impact time, residual force, and absorbed energy. These parameters increased in the order of the neat PA6/plasma-treated WGF (9 mm), PA6 nanocomposite/untreated WGF, and PA6 nanocomposite/plasma-treated WGF (5–17 mm). As the height of the plasma nozzle was decreased for fiber pretreatment, the impact time, residual force, and absorbed energy of the MHC increased proportionally, and when the nozzle height was reduced to 9 mm, the absorbed energy increased by up

to 83.70% as compared to that of the neat PA6/untreated WGF specimen, whereas the specimen with the WGF treated with a further reduced nozzle height of 5 mm showed lower absorbed energy owing to fiber damage due to excessive surface treatment. These results are consistent with the XPS and flexural test results discussed above. As the plasma intensity was increased to a suitable level, the functional groups, such as carboxyl, hydroxyl, and carbonyl, were increased on the fiber surface, and they formed hydrogen and covalent bonds with PA6, organoclay, and MA groups of the compatibilizers, resulting in strong interfacial interactions; as a result, the material could effectively absorb and transfer the impact energy via the interfaces between the fiber and polymer matrix [57]. Figure 10c shows the velocity-time response curves for neat PA6/untreated WGF and MHCs. The difference between the incident and residual velocities is defined as the penetration limit [61]. Owing to the toughness improvement of the nanocomposite matrix caused by heterogeneous compatibilizers and interfacial strengthening between the matrix and plasma-treated fibers, the MHCs considerably decelerated the impact velocity of the striker during the impact test, as compared to that of the neat PA6/untreated WGF composite. The MHC reinforced using PA6 nanocomposite/9 mm plasma-treated WGF showed the highest penetration limit (100.0% increase) owing to the simultaneous enhancements, which considerably improved the load transfer between the polymer chain-intercalated clay particles and glass fibers. In summary, these results confirm that the use of the PA6 nanocomposite matrix and plasma-treated WGF improves the overall impact resistance of the MHC.



**Figure 9.** Ultimate flexural strength and flexural modulus of the MHCs as functions of the nanocomposite composition and the plasma nozzle height used for treating the WGF: (a) Neat PA6/Untreated WGF, (b) PA6 nanocomposite/Untreated WGF, (c) Neat PA6/Plasma-treated WGF\_9mm, (d) PA6 nanocomposite/Plasma-treated WGF\_17 mm, (e) PA6 nanocomposite/Plasma-treated WGF\_13 mm, (f) PA6 nanocomposite/Plasma-treated WGF\_9 mm, and (g) PA6 nanocomposite/Plasma-treated WGF\_5 mm. Note: PA6 nanocomposite = PA6/2 wt.% organoclay (ODAB-clay)/6 phr SEBS-g-MA/3 wt.% PP-g-MA.



**Figure 10.** Impact properties of the MHCs as functions of the nanocomposite composition and plasma nozzle height for WGF treatment (5, 9, 13, and 17 mm): (**a**) impact force, (**b**) absorbed impact energy, and (**c**) penetration limit.

## 3.8. Fractured Surfaces of the MHCs

SEM images of the cross-sections of the MHCs (see Figure 11) can provide information on the degree of polymer impregnation and interfacial bonding between the fibers and polymer matrix. For the untreated sample (untreated WGF, see Figure 11), the fiber pull-out traces due to fracture were clearly visible, and interfacial failures between the fiber and polymer matrix were also apparent. Moreover, the fibers were not optimally impregnated with the resin, that is, the PA6 nanocomposite, resulting in many voids. In the sample containing WGF subjected to plasma treatment at 17 mm nozzle height, which is the mildest plasma-treatment condition, the pull-out traces were reduced, and the impregnation of the resin was slightly improved, but clean interfacial failures were found owing to poor interfacial bonding. These defects decreased significantly after plasma treatment at a nozzle height of 13 mm, and thus, the improvement in interfacial bonding was visually confirmed. In particular, interfacial defects could hardly be detected in the sample containing plasmatreated WGF at 9 mm nozzle height because plasma treatment rendered the fiber surface hydrophilicity, which not only facilitates the infiltration of the fibers with the PA6 matrix but also strengthens interfacial adhesion between the WGF and PA6. Although the interface state and PA6 matrix impregnation of the WGF-5 mm nozzle height case were comparable to those of the WGF-9 mm nozzle height case, the mechanical properties were inferior to those of 9 mm or 13 mm nozzle-height cases, as indicated by the results of the impact and flexural tests. This result suggests that excessive plasma treatment of the WGF with 5 mm nozzle height from the surface damaged the fiber itself, thereby adversely affecting the interfacial bonding and resin impregnation.



**Figure 11.** SEM images of the fractured surfaces of the MHCs using WGFs subjected to plasma treatment with different plasma nozzle heights (5, 9, 13, and 17 mm).

## 4. Conclusions

To maximize the improvement in the mechanical properties of the C-GFRTP, the modification of the polymer matrix with the addition of organoclay and compatibilizers and the surface treatment of WGFs with atmospheric-pressure plasma were simultaneously considered and implemented. First, PA6 was pulverized and reinforced using various additive powders such as the ODAB-intercalated, exfoliated nanoclay, SEBS-g-MA, and PP-g-MA to facilitate homogeneous blending, crystalline behavior, and enhance tensile properties and elongation of the nanocomposite. Then, the tensile performance of the PA6 nanocomposite was optimized by identifying the optimal quantity of the organoclay. Furthermore, atmospheric-pressure air-plasma treatment of the WGFs was performed to further strengthen the interfacial bonding between the fibers and PA6 nanocomposite matrix of the MHCs. After plasma treatment, the number of oxygen functional groups, such as hydroxyl, carbonyl, and carboxylic acid groups, on the WGF surface increased. These groups could react with the MA groups in the compatibilizers, amine, and terminal carboxylic acid groups in PA6 and the organic functional groups in the silane-coated clay. These interactions facilitated hydrogen and covalent bonds and increased the interfacial bonding among the MHC components. Mechanical evaluations revealed that the PA6/ODAB-clay (2 wt.%)/SEBS-g-MA/PP-g-MA/plasma-treated WGF (9 mm nozzle height) sample had the best improvement rate of the flexural modulus, strength, impact absorbed energy, and penetration limit; its properties were significantly better than those of the neat PA6/untreated WGF specimen. However, an excessive addition of the organoclay and extremely strong plasma surface treatment did not contribute to the improvement of the mechanical properties. Thus, simultaneous strengthening of the PA6 matrix and glass fiber surface exerted synergistic effects on interfacial interactions between the components, leading to improved mechanical properties of the MHC.

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