

## Comparison of Mechanical and Thermal Properties of Polyamide-66/Rubber/Fiber Alloy Composites†

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This study compared and evaluated the mechanical and thermal properties of three-phase blends of polyamide-66. A series of polyamide-66/polymer blends were prepared using an extrusion and injection process and the blending polymers were rubber, TPU, polyester block polyamide and ionomer. The polymer contents was 10-30 %. The blending polymers were used to improve the moisture absorbance and elastic recovery of polyamide-66. The coupling agent impregnated in the glass fiber was melt blended to increase the miscibility of each composition.

**Key Words:** Polyamide-66, Alloy, Blend, Rubber, Elasticity, Flexibility, Strength.

### INTRODUCTION

Generally, a chemical method, such as a new synthesis or the introduction of a functional group and a physical method, which blends two or more polymers at certain ratios to create a desired product, can be used to improve the properties of polymers. Among these physical methods, a polymer blend is used widely because it is relatively simple and the desired properties can be adjusted depending on the polymers used. Polyamide (nylon) with its high crystallization, mechanical properties, thermal stability and excellent anti-abrasion resistance is a typical engineering plastic material and the demands and uses for it have increased steadily since 1940. Therefore, some studies in a range of fields have focused on improving the thermal and mechanical properties of nylon. Of the polyamides formed with polymers linked by monomers-chains of amide (CONH) bonds, polyamide-66 (chemical name: polyhexa methylene adipamide) has a high degree of crystallization and an excellent balance between its properties. A comparison of polyamide-66 (PA-66) and polyamide-6 revealed that polyamide-66 have superior thermal resistance and mechanical properties to polyamide-6. In addition, PA-66 has outstanding chemical resistance to hydrocarbon solvents, making it possible to reinforce these physical properties with glass fiber fillers. The heat deflection temperature can be improved remarkably when glass fibers are charged based on these properties, *i.e.* the mechanical strength and stiffness<sup>1,2</sup>.

This material also has perfect resilience. Figs. 1 and 2 show the chemical structure and synthesis mechanism of polyamide-66, respectively. The fiber filler is the most effective component of products that require strength, stiffness and heat resistance. Glass fibers are one of a range of additives used typically as reinforcements for plastics. Fiberglass reinforced plastics (FRP) is resistant to external shock and the strength of FRP materials is high. Fiberglass reinforced plastics was first used in the early 1940s. Since the 1960s, carbon fibers, which are superior to glass fibers, have been combined with plastic since the 1960s to replace existing metal and ceramic materials. The material is light weight and has good durability, impact resistance and wear resistance, as well as anti-rust non-thermal strain. Moreover, it is easy to process. Fiberglass reinforced plastics has been used in several products, such as building materials, the body of boats, skis, home baths, helmets, tennis rackets, chairs, living necessities and aircraft parts.

Generally, polyamide-66 has excellent anti-abrasion resistance, high thermal stability and mechanical strength. On the other hand, it is more expensive than other polymer and after injection, its properties are affected by moisture absorbance. In addition, it needs to dry before the injection. The polymer alloys by 2-phase or 3-phase blends are the best method for obtaining novel materials<sup>3-6</sup>.

Consequently, this study compared the mechanical properties and characteristics of polyamide-66 and polymer blending composites. The thermal and mechanical behaviour

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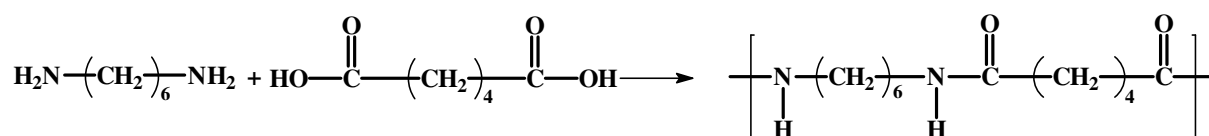


Fig. 1. Chemical structure of polyamide-66

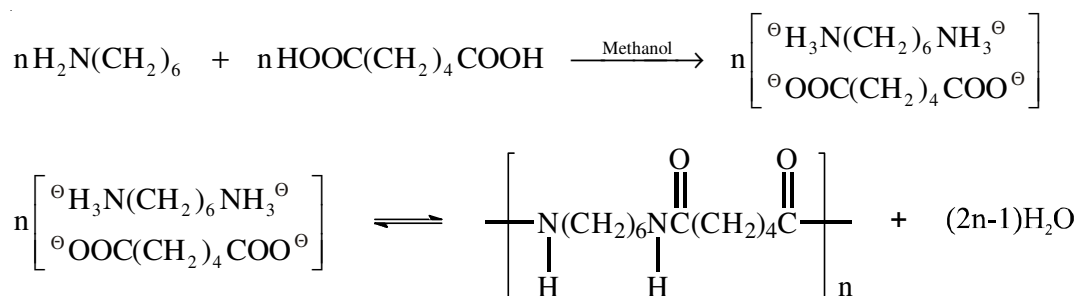


Fig. 2. Synthesis mechanism of polyamide-66

of polyamide-66 and its blends with high elasticity polymer were examined at various blending contents. A series of polyamide-66/polymer blends were prepared using an extrusion and injection process and the blending polymers were rubber, TPU, polyester block PA and Ionomer. The polymer contents was 10-30%. The polymers (rubber, TPU, polyester block PA, ionomer, etc.) were reported to be excellent candidates as a blending substitute because of their high elasticity, flexibility and strength<sup>7-12</sup>.

The thermal, mechanical and morphological characteristics of the compatibilized blends were examined from the tensile strength and Izod impact strength results judged by their compatibility and improved properties. The application possibility of glass-injection materials was assessed from the flexural strength and modulus<sup>13-16</sup>.

Their thermal properties (melting point, crystallization temperature and glass transition temperature of polyamide-66/polymer blends) were measured by differential scanning calorimetry (DSC). Scanning electron microscopy (SEM) was used to observe the microstructure of the blends in the surface and section<sup>17-20</sup>.

## EXPERIMENTAL

The polyamide-66 was a product from Kolon Plastics Co., Ltd. (KOPA KN3311) and GF was a Chinese product (L: 3 mm, D: 12 μm). The polyamide was used after drying in an 80 °C oven for 24 h to remove the absorbed moisture. Five polymers, polyether block amide (Pebax), ionomer (Surlyn),

EPM, TPV (santoprene) and TPU (each 10-30 wt %), were blended in polyamide-66. Table-1 lists the physical properties of blending polymer.

### General procedure

**Glass fiber (GF) surface treatment:** Many studies have focused on increasing the physical bonding by inducing chemical bonds or changing the surface characteristics, as a method of introducing functional groups to a reinforcing fiber surface. Similarly, in this study, the glass fiber surface was treated with a coupling agent to increase the miscibility of the composite within. First, the glass fiber was left in a drying oven at 80 °C for 24 h to remove the moisture completely. For a uniform surface, a blend silane coupling agent and acetone at a ratio of 95:5 was sprayed on the surface of the dried glass fiber, which was then dried again in a drying oven at 60 °C for 24 h.

**Manufacturing method of alloy composite:** The polyamide-66 was dry blended and its surface was treated with glass fiber and mixed for 10 min using a tumbler mixer for a sufficient length of time before being injected into an extruder using a feeder. A twin-screw extruder (L/D = 40, screw diameter = 32 mm, Model STS32) produced by Korea EM Co., Ltd was used. The temperature distribution of the extruder barrel was: feed zone - 220 °C, compression zone - 240 °C, metering zone - 260 °C, die - 285 °C. The screw was spun at 150 rpm and the output was 10 kg/h. The strand then passed through dies and through a water bath and was processed in pellet form using a pelletizer. Table-2 lists the composite formulations.

TABLE-1  
PHYSICAL PROPERTIES OF THE BLENDING POLYMER

Property	unit	PA66 KN3311	Pebax 7033	Surlyn 8150	TPU 5175DP	Test method
Specific gravity	g/cm <sup>3</sup>	1.14	1.02	0.97	1.28	ASTM D792
Hardness	shore D	120R	69	65	75±3	ASTM D2240
Flex modulus @RT	kg/cm <sup>2</sup>	30,000	4,700	500	-	ASTM D790
Tensile strength	kg/cm <sup>2</sup>	850	580	320	450	ASTM D638
Elongation at break	%	60	400	320	350	ASTM D638
Melt flow index	g/10 min	-	-	4.5	-	ASTM D1238
Vicat softening point	°C	-	165	53	180	ASTM D1525-70
Melting point	°C	255	174	84	210	ASTM D3418
Mold shrinkage	%	1.1~1.3	-	-	0.0040	ASTM D955
Water absorption equilibrium	23 °C, 60 % RH	1.3	0.6~0.8	-	-	ASTM D570

\*Quoting from the data sheet of each product (PA66 : Kolon plastic Co. Ltd., Pebax: Arkema, Surlyn: Dupont, TPU: Dongsung highchem Co. Ltd.)

TABLE-2  
COMPOSITE FORMULATIONS

		PA66 (wt %)	Ionomer (wt %)	Polyether block amide (wt %)	EPM (wt %)	TPV (wt %)	GF (silane treated) (wt %)
PA		100	-	-	-	-	0
PAG		95	-	-	-	-	5
Ionomer blend	S-1	65	30	-	-	-	5
	S-2	75	20	-	-	-	5
	S-3	85	10	-	-	-	5
Polyether block amide blend	P-1	65	-	30	-	-	5
	P-2	75	-	20	-	-	5
	P-3	85	-	10	-	-	5
EPM blend	E-1	65	-	-	30	-	5
	E-2	75	-	-	20	-	5
	E-3	85	-	-	10	-	5
TPV blend	R-1	65	-	-	-	30	5
	R-2	75	-	-	-	20	5
	R-3	85	-	-	-	10	5

TABLE-3  
CONDITIONS OF THE INJECTION MOLDING MACHINE

Resin	Nozzle temp. (°C)	Cylinder temp. (°C)			Injection pressure (MPa)	Injection speed (mm/s)
		H1	H2	H3		
PA66 alloy composite	268	265	255	245	150	185

**Making a specimen:** In the case of blending glass fibers, normally the viscosity of the composition increases, which causes a decrease in moldability. Therefore, the nozzle temperature during injection was set to be 8 °C higher than that general used for polyamide-66. Table-3 lists the injection molding conditions. For each composition, a specimen for the property evaluation was prepared using a mold prepared using a general plastic injection machine (Pro-WD80, Dongshin Hydraulics Co., Ltd., Korea) in accordance with the ASTM standards. Without heating, the mold was maintained at room temperature. The cooling time during injection was set to 35 seconds. Fig. 3 shows the structure of the injector.

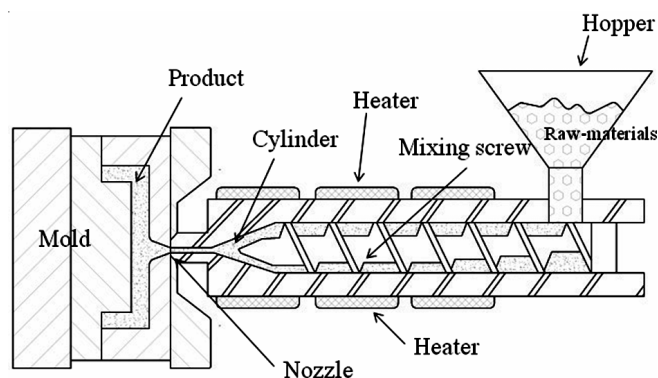


Fig. 3. Structure of the screw injector

#### Detection method: Analysis of physical properties

**Measuring the mechanical strength:** The tensile strength, flexural strength and flexural modulus of the ASTM standard specimens manufactured by injection molding were measured using a universal tester (UTM, Instron 4467) that was set to a crosshead speed of 50 mm/min using a load cell of 30 kN. Five specimens per condition were measured with the mean used for further analysis.

**Comparison of the thermal properties (DSC):** DSC was used to observe the glass transition temperature and melting behaviour of each material. "Q100" (TA company) was used and the measured temperature was 0-300 °C at a heating rate of 10 °C/min. The crystallization properties were measured by evaluating the thermal properties according to the secondary cooling-down followed by primary heating-up.

**Observing the phase structure by field emission scanning electron microscopy (FE-SEM):** FE-SEM (JSM-6701F, Jeol) was used to observe the dispersion and miscibility of the polymer and its phase structures. After cooling the blended sample in liquid nitrogen (-180 °C) for *ca.* 10 min, the morphology of the cross section was observed by breaking it. At this time, the sample was sputtered with gold and the acceleration voltage was 20 kV.

**Observing changes in surface chemical structure through FT-IR spectroscopy (FT-IR-430, JASCO):** Injection molded samples were analyzed to confirm the changes in chemical structure of the surface according to the blend materials and components of the alloy composites. The peaks were measured within the range of 4000-500  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

#### Mold shrinkage and density change based on blend:

For the products manufactured by injection molding, shrinkage affects the fraction defective and the moldability of the finished product. Therefore, mold shrinkage was measured according to the content of each blend system. The injection conditions were consistent and after stabilizing the prepared specimens at room temperature (*ca.* 20 °C) for 3 days, the level of mold shrinkage was measured by measuring the size of each. The hardness and density of the stabilized specimens were measured. Tables 4 and 5 listed the mold shrinkage and density of the polymer blended polyamide-66, respectively.

TABLE-4  
MOLD SHRINKAGE, WATER-ABSORPTION AND DENSITY OF POLYMER BLENDED POLYAMIDE-66

Blend ratio	Properties	Hardness (D type)	Density (g/cm <sup>3</sup> )	Mold shrinkage (%)	Water absorption (%)
PA66 (PA)		79D	1.124	1.33	2.02
PA66 + GF 5 wt % (PAG)		77D	1.158	1.12	1.44
PA66 + GF 5 wt % + Ionomer 20 wt % (S-2)		76D	1.139	1.33	1.39
PA66 + GF 5 wt % + Polyetherblockamide 20 wt % (P-2)		76D	1.144	2.04	0.71
PA66 + GF 5 wt % + EPM 20 wt % (E-2)		73D	1.111	1.46	0.68
PA66 + GF 5 wt % + TPV 20 wt % (R-2)		73D	1.147	1.75	0.78

TABLE-5  
MOLD SHRINKAGE, WATER-ABSORPTION AND DENSITY OF POLYMER BLENDED POLYAMIDE-66

Formulation No.	Properties	Hardness (D type)	Density (g/cm <sup>3</sup> )	Mold shrinkage (%)	Water absorption (%)
PA		79D	1.124	1.33	2.02
PAG		77D	1.158	1.12	1.44
Ionomer blend	S-1	75D	1.110	1.65	0.68
	S-2	76D	1.139	1.33	1.39
	S-3	78D	1.148	1.71	0.46
Polyether block amide blend	P-1	75D	1.128	1.73	0.70
	P-2	76D	1.144	2.04	0.71
	P-3	77D	1.153	1.59	1.39
EPM blend	E-1	69D	1.058	1.57	0.70
	E-2	73D	1.111	1.46	0.68
	E-3	76D	1.142	1.40	0.90
TPV blend	R-1	66D	1.130	1.78	0.67
	R-2	73D	1.147	1.75	0.78
	R-3	76D	1.151	1.39	0.88

The hardness decreased with increasing blend ratio because the blended polymer has lower hardness than polyamide-66 with its main chain. Among these, the hardness decreased the most when TPV was blended. On the other hand, the ionomer and polyether block amide have high hardness. Therefore, hardness does not decrease severely when they are blended. The density of the glass fiber blended PAG increased with increasing filler content.

From the appearance of the prepared specimens, polyamide-66 showed a slight yellow colour regardless of the amount of glass fiber. The colour changed to gray or brown when the retention time on the twin extruder was long or the temperature at molding injection or pressure condition was

unsuitable. This appears to have been caused by pyrolysis due to the high temperature conditions. To avoid this, the establishment of suitable conditions of molds and products are needed to reduce the incidence of these effects during machining or molding.

**Mechanical properties of polyamide-66/Rubber/fiber alloy composite:** Each property based on the blends was compared by measuring the mechanical properties, such as the tensile strength, flexural strength, flexural modulus and Izod impact strength. Table-6 presents the mechanical properties of polymer blended polyamide-66.

The mechanical strength of the blends tended to decrease because of the superior mechanical properties of polyamide-

TABLE-6  
MECHANICAL PROPERTIES OF POLYMER BLENDED POLYAMIDE-66

Formulation No.	Properties	Izod impact strength with Notch (kg cm/cm)	Tensile strength (kg/cm <sup>2</sup> )	Flexural strength (kg/cm <sup>2</sup> )	Flexural modulus (kg/cm <sup>2</sup> )
PA		7.03	835	1,349	27,450
PAG		5.44	795	1,394	31,065
Ionomer blend	S-1	8.5	675	942	15,500
	S-2	6.89	790	1,184	26,450
	S-3	5.95	845	1,397	30,845
Polyether block amide blend	P-1	6.16	795	1,060	22,530
	P-2	5.8	740	1,045	22,870
	P-3	4.71	780	1,243	26,125
EPM blend	E-1	6.45	875	759	20,580
	E-2	4.79	795	1,142	28,960
	E-3	4.71	935	1,144	29,800
TPV blend	R-1	6.02	880	927	25,380
	R-2	6.09	745	1,107	28,835
	R-3	6.53	785	1,421	33,475

66. The shock resistance of polyamide-66 was quite weak at temperatures less than  $T_g$ , but this was improved when the ionomer and EPM were used (S-1, E-1). This was attributed to the effect of the rubbery polymer distributed over the matrix phase by the introduction of a rubbery polymer. Moreover, the ionomer and EPM formed stress concentrators to obstruct failure cracks and their expansion in the polyamide-66 matrix phase. Miscibility or adhesion strength is essential between a matrix polyamide-66 and a dispersed phase blend polymer to minimize the decrease in mechanical tensile strength. From the tensile strength, diverse properties were shown depending on the blend polymer and considering the above concepts. The miscibility or adhesion strength between the three-phase blends was improved in the case of P-2, E-1, E-3 and R-1, showing an improvement in tensile strength.

The flexural strength did not show significant improvement, except in the case in which the ionomer was blended (S-3) or TPV is blended (R-3). Regarding the flexural modulus, despite blending materials having generally good resilience, property-improving effects were not observed except for the R-3 case, which blended 10 % TPV.

**Changes in the thermal properties based on blends:** DSC, with its versatility and strong data analysis capability, is the most widely used thermal analysis equipment. DSC was used to examine the heat of fusion of  $T_c$ ,  $T_m$ , *etc.*

The analysis revealed many irregular structures when  $T_m$  is low, which could be seen as a blended polymer that failed to disperse uniformly. The correlation between the molecular interaction and thermal properties was examined. Polymers with hydrogen bonds of the OH group or polar interaction (polyurea > polyamide > poly urethane) were observed to have a higher  $T_m$  when they contained the same repeating unit.

The melting point increased slightly during blending. The crystallization temperature shows the same tendency with regard to the melting point. Comparing the heats of fusion, PA66-GF5- Rubber20 using TPV type rubber was the lowest and followed in order by, PA66-GF5-PEBA20 > PA66-GF5-Ionomer20 > PA66-GF5 > PA66 > PA66-GF5-EPM20. The bonding and miscibility between PA66 and EPM were good when the heat of fusion was highest. Therefore, the miscibility between PA66 and TPV was the worst, as confirmed by FE-SEM.

Crystallization is a phenomenon in which an irregular material structure becomes regular by the gravitation between molecules and atoms and is opposite to melting. Generally, heating crystallization means that the amorphous structure of a solid becomes regular, which means that the amorphous structure of a liquid changes to solid with a regular structure for cooling crystallization. The crystallization temperature and crystallinity of each blended material can be observed through the 2nd cooling curve obtained as the blended materials in the

melt state cooled slowly. Figs. 4-6 and Table-7 present the results.

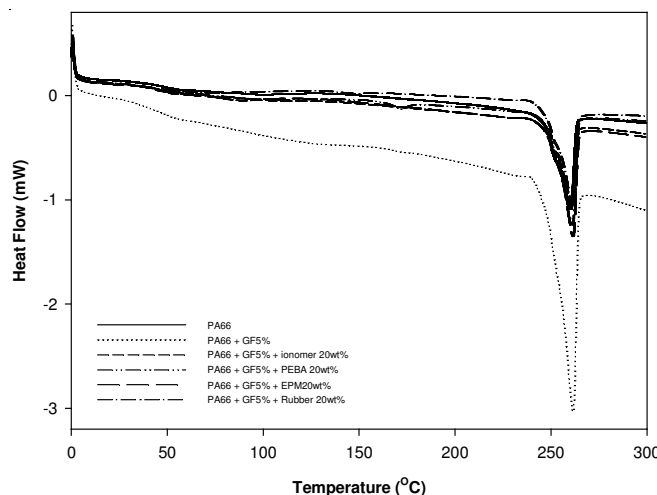


Fig. 4. Melting behavior of polymer blended polyamide-66 (1st heating curve)

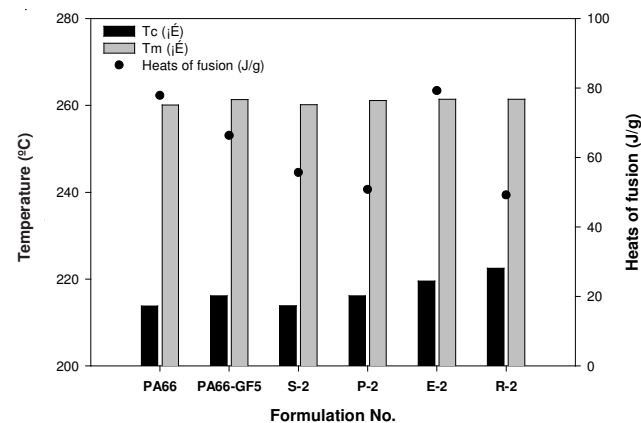


Fig. 5. Melting properties of polymer blended polyamide-66

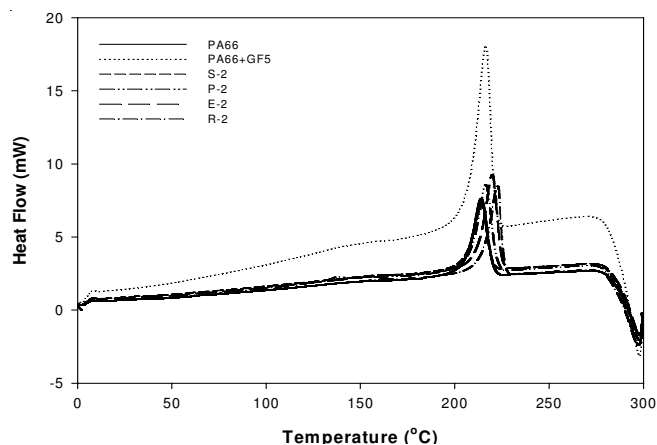


Fig. 6. Melting behavior of polymer blended polyamide-66 (2nd cooling curve)

	$T_c$ (°C)	$T_m$ (°C)	Extrapolated onset temp. (°C)	Heats of fusion (J/g)	$\Delta$ temp. (°C)
PA66	213.79	260.10	247.44	77.82	9.70
PA66-GF5	216.18	261.31	251.17	66.32	8.05
PA66-GF5-Ionomer20	213.89	260.19	249.82	55.67	7.85
PA66-GF5-PEBA20	216.13	261.13	251.28	50.83	7.43
PA66-GF5-EPM20	219.51	261.40	251.91	79.23	7.25

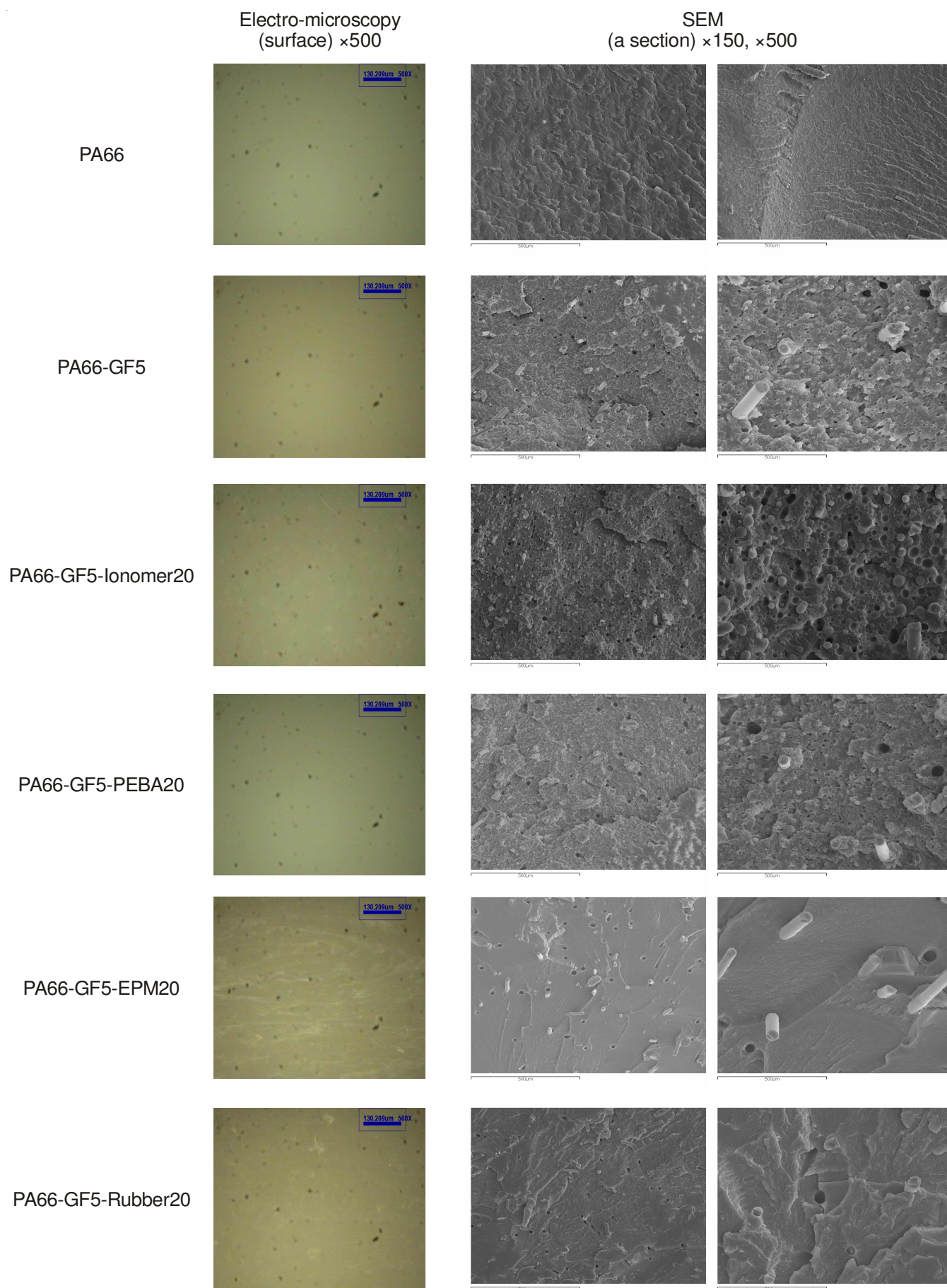


Fig. 7. Morphology of polymer blended PA66: surface by electron-microscopy ( $\times 500$ ) and a section by SEM ( $\times 150, \times 500$ )

The high crystallization temperature in the matrix can be explained by the difficult crystallization due to the high viscosity of the composition. As shown in this study, when EPM (E-2) or TPV(R-2) were blended, their viscosity increased because they are rubbery phase materials, not plastics and maintained more uniform shapes.

**SEM:** SEM was used to determine the miscibility between blended materials. Fig. 7 shows the morphology of polymer blended polyamide-66. The surface of the specimen prepared by injection molding was observed with a high magnification electron micrograph and the morphology of the cross-sections was observed by SEM. The cross-section and interior of polyamide-66 single product were quite clean. SEM showed that the surface has a relatively uniform shape. In the case of blending surlyn or TPV, agglomeration was observed on the surface, whereas a lamellar pattern was observed on the surface when blending EPM.

**Surface Structure Analysis: FT-IR:** Figs. 8 and 9 show the FT-IR spectra of the composite. The surface FT-IR spectra of the blends were compared to determine which chemical reaction is dominant. The IR spectra shows the abroad medium

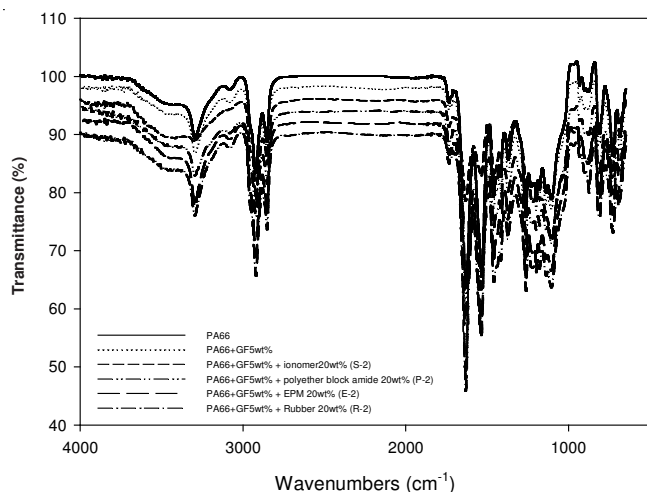


Fig. 8. FT-IR of the polyamide-66/Rubber/fiber alloy composites

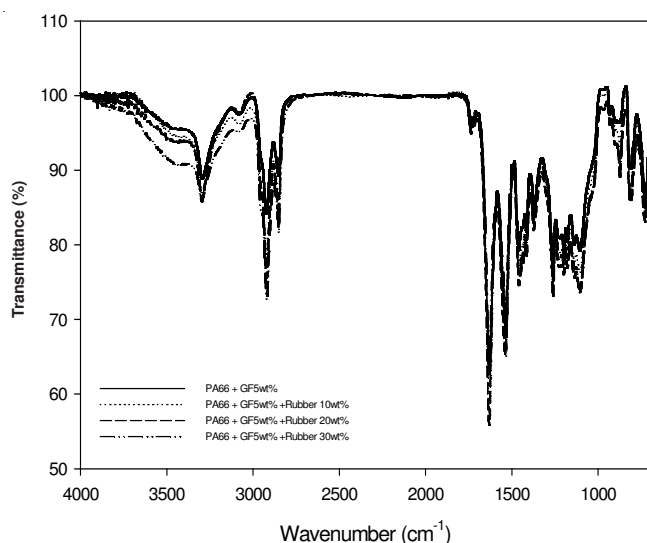


Fig. 9. FT-IR according to the rubber content of the polyamide-66/Rubber/fiber alloy composite

bands in the 3500-3200  $\text{cm}^{-1}$  ranges, attributed to intermolecular hydrogen bonding between OH and C=O groups in the same molecular and also NH groups.

## Conclusion

This study attempted to improve the resilience, shock resistance and water absorption by making an alloy complex composition by melt mixing 10-30 wt % of each polymer with a two-phase blended material, in which polyamide-66 and glass fibers were blended using 5 types of polymers: polyether block amide (Pebax), ionomer (Surlyn), EPM, TPV (santoprene) and TPU. The thermal behaviour and morphology of each composition were compared and the following conclusions were obtained.

1) The impact resistance of polyamide-66 was quite weak at temperatures below  $T_g$ , which could be improved using the ionomer and EPM (S-1, E-1). The tensile strength properties in the case of P-2, E-1, E-3 and R-1, in which Pebax, EPM and TPV were blended, were improved. The adhesion or miscibility between the polyamide-66 matrix and blend polymer was essential for minimizing the decrease in mechanical tensile strength. Adhesion or miscibility between these three-phase blends was improved due to the improvement in tensile strength. The flexural strength did not show any improvement except for when the ionomer was blended (S-3) or when TPV was blended. In the case of the flexural modulus, despite blending good-resilience materials, the effect of improving the physical properties was insufficient except for the case of R-3, which blended 10 % TPV.

2) The melting points and crystallization temperatures of the polyamide-66/rubber/fiber alloy composites were highest when EPM and TPV were blended. Products with high crystallization temperatures were considered to have uniform compositions with high melt viscosities. In addition, the orientation increased with increasing  $T_m$ , which was expected to improve the physical properties. PA66-GF5-Rubber20 using TPV-rubber had the lowest fusion temperature followed in order by PA66-GF5-PEBA20 > PA66-GF5-Ionomer20 > PA66-GF5 > PA66 > PA66-GF5-EPM20. The products with the greatest heats of fusion had the best adhesion and miscibility, of which blends of polyamide-66 and EPM were excellent.

3) The cross-section and interior of a polyamide-66 single product were quite clean according to morphological analysis. The miscibility with the matrix that blended polyamide-66, GF, EPM, TPV and rubber-polymer was excellent (E-2, R-2). In particular, in the case of E-2 in which EPM was blended, interface adhesion was good because the cross-section was quite smooth. In addition, the glass fiber has a uniform shape throughout all compositions examined.

Overall, injection products can be manufactured by designing the compositions of polyamide-66/Rubber/fiber alloy composites in the ratio of polyamide-66/EPM or TPV 20 %/glass fiber 5 % and be applied to a wide range of products requiring resilience and thermal resistance.

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