Thesis for the Degree of Master of Engineering

Study on Rheological, Mechanical and Thermal Properties of Ultrahigh Molecular Weight Polypropylene/Low Molecular Weight Polypropylene Blends

by

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(폴리프로필렌/저분자량 폴리프로필렌 블랜드의 유변학, 기계적, 열적 물성에 대한 연구)

Advisor : Prof. Won-Ki Lee

by

Byeonguk Kim

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CONTENTS

List of Tables

List of Figures

storage modulus (E′), (B) loss modulus (E″), and (C) damping factor (tan δ).

초고분자량 폴리프로필렌/저분자량 폴리프로필렌 블렌드의 유변학, 기계적, 열적 물성에 대한 연구

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요 약

초고분자량 폴리프로필렌(UHMWPP)는 분자량이 백만 이상으로 높은 기계적 강도, 높은 열적 특성, 높은 내화학성 및 우수한 마찰 특성을 가질 것으로 예상된다. 그러나 UHMWPP는 용융 점도가 아주 높아 가공하기 어렵다. 따라서 UHMWPP의 가공성을 향상시키기 위하여 저분자량 폴리프로필렌(LMWPP)와 용융혼합을 하였다. 이때 LMWPP는 다양한 용융 점도, 즉 분자량을 가진 LMWPP을 사용하여 UHMWPP와 혼합하였고 LMWPP는 용융 점도에 따라 크게 두 가지로 나눠서 실험을 진행하였다.

용융점도가 매우 낮은 PP는 UHMWPP의 가공성 개선을 목적으로 진행하여 가공성의 변화와 그에 따른 물성 변화를 측정하였다. 상업적으로 단독 사용되는 PP의 경우, UHMWPP와 혼합에 의한 기계적 물성변화에 대한 연구를 진행하였고 아울러 가공성에 대해서도 검토하였다.

CHAPTER 1. Introduction

Polypropylene (PP) is a commercially versatile polymer which has very useful properties such as chemical resistance, corrosion resistance, outstanding electrical insulation, sterilization, good processability, and low cost, compared to other commercial polymers. Thus, PP has been adopted for various applications in film, pipes, molded products, packing automotive, and construction industries [1-7]. PP has a low mechanical properties and wear resistance due to its flexible C-C backbones, thus, PP has been limited in using, compared to high-performance engineering polymers [8]. Ultrahigh molecular weight polypropylene (UHMWPP) is an engineering polymer with a molecular weight of over 1 million g/mol and plenty chain entanglement. UHMWPP has outstanding properties such as excellent mechanical properties and significant fatigue, and wear resistance. However, UHMWPP, which has a high viscosity and low melt index (MI) due to the entanglement of long chains, has low commerciality because of its low processability. Ultrahigh molecular weight polyethylene (UHMWPE) overcomes the properties of the normal polyethylene, such as its poor tribological and mechanical properties. Thus, UHMWPE has been studied to secure processability through various methods such as melt blending, solution blending, and ultrasonic blending, etc [9,10]. Similarity, in this study, we aimed to improve the processability of a UHMWPP by blending with various low molecular weight polypropylenes (LMWPP). We hypothesized that the dual structure (in Fig 1.) of the

UHMWPP/LMWPP blend system has a specific dual network structure, and entanglement of molecular chains. To demonstrate the properties of the UHMWPP/LMWPP blend, we discuss the mechanical, thermal, and rheological properties with a variety of measurements.

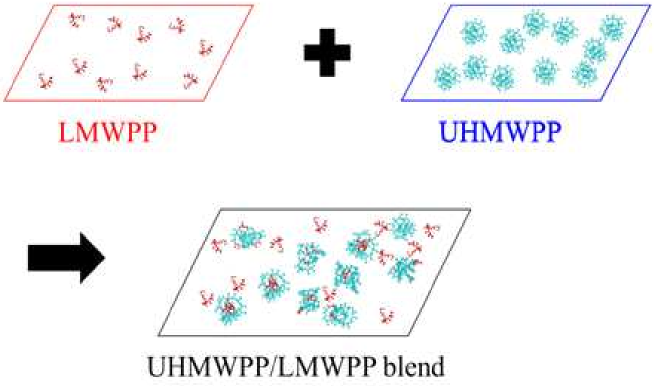

Figure 1. Schematic illustrations of a possible structure for the UHMWPP/LMWPP blend system.

CHAPTER 2. Theoretical Background

2.1. Ultrahigh molecular weight polyethylene

UHMWPE is a type of polyethylene polymer with an extremely high molecular weight. It is characterized by its long chains of polyethylene molecules, which contribute to its unique mechanical and chemical properties. Here are some key aspects of UHMWPE [9-17]:

- UHMWPE is defined by its molecular weight, which typically ranges from 3 to 6 million Daltons. This high molecular weight imparts exceptional strength and durability to the material.
- UHMWPE is known for its outstanding mechanical properties, including high tensile strength, impact resistance, and abrasion resistance. It is often used in applications where these properties are crucial, such as in the production of high-performance components.
- One of the notable features of UHMWPE is its low coefficient of friction. This makes it an excellent choice for applications where reduced friction is essential, such as in bearings and gears. Additionally, UHMWPE exhibits excellent wear resistance, making it suitable for components subjected to repetitive motion and high loads.
- UHMWPE is resistant to a wide range of chemicals, acids, and bases. This chemical inertness makes it suitable for use in environments where exposure to corrosive substances is a concern.
- UHMWPE is biocompatible, which means it is well-tolerated by the

human body. This property has led to its extensive use in medical applications, particularly in orthopedic implants such as hip and knee joint replacements.

- Despite its impressive strength, UHMWPE has a low density, making it a lightweight material. This is advantageous in applications where weight reduction is a priority without compromising on strength.
- UHMWPE poses challenges in terms of processing. Special techniques such as gel spinning and compression molding are often employed to shape the material into useful forms.
- UHMWPE exhibits good resistance to ultraviolet (UV) radiation, enhancing its outdoor durability. This makes it suitable for applications exposed to sunlight over extended periods.
- UHMWPE is generally considered to be environmentally friendly as it is inert and does not release harmful substances into the environment during its use. It is also recyclable.
- UHMWPE finds applications in various industries, including:
  - Medical Field: Orthopedic implants, prosthetic devices, and surgical components.
  - Industrial Sector: Gears, bearings, conveyor belts, and other components requiring high wear resistance.
  - Defense: Body armor and ballistic plates due to its high impact resistance.
  - Sports and Recreation: Skating rink liners, snowboard bottoms, and other sports equipment.

2.2. Ultrahigh molecular weight polypropylene

UHMWPP has a molecular weight of 1 million g/mol or more, and its properties are determined by its molecular weight and microstructure. UHMWPP is a semi-crystalline polymer with a lamella-type crystal in which chains are folded in the crystal phase and a random entanglement of chains in the amorphous phase [14]. However, in general, unlike PP and UHMWPE, UHMWPP has a high molecular weight and a very high melting viscosity, so it has poor processability. Therefore, it is necessary to improve processability for commercialization. In addition, UHMWPP has not been studied much and commercialized due to the poor processability of UHMWPP. HMWPP, like UHMWPE, has more specific properties than PP′s one and can be used for special purposes. Therefore, we study the improvement of processability by incorporating various processing methods of UHMWPE, according to observe the changes in various properties [18-20].

CHAPTER 3. Experimental section

3.1 Materials

UHMWPP with viscosity average molecular weight (M_v)of $1.57x10^6$g/mol and various LMWPPs with different melt indexes (MI) were provided by Korea Petrochemical Ind. Co., Ltd. (Korea). Properties of LMWPPs used in this study are shown in Table 1. 2,6-Di-tert-butyl-4-hydroxytoluene(BHT, Junsei, Japan) and Songnox 1010(Honshu Chemical Industry Co., Ltd, Japan) were used as antioxidants.

Table 1. Melt index(MI), molecular weights, and melting temperature (T_m) of PPs used in this study

Sample code	Melt index (g/10 min)**	M_n (g/mol)	M_w (g/mol)	M_v (g/mol)	T_m (℃)	Type
PP9*	9	42,000	224,000	-	165	Homo
PP60	60	24,300	242,830	-	165	Block
PP90	90	26,700	177,000	-	166	Block
LMWPP	1500	23,500			152, 160	Homo
UHMWPP	0.87	-	-	1,570,000	167	Homo

* The nubmer in sample code PP indicates its MI.
** 2.16 kg rod at 230 ℃.was applied, except UHMWPP (21.6 kg rod).

3.2 Preparation of UHMWPP/PP blends

UHMWPP and LMWPPs were dried in the vacuum oven at 60 ℃ to remove moisture and then premixed with antioxidants. Compositions of blends, PP/BHT/Songnox 1010 = 100 : 0.2 : 0.2 by weight. First, various compositions of LMWPP/UHMWPP blends with antioxidants were physically mixed. After homogeneous premixing, the blend of LMWPP/UHMWPP were melted at 180 ℃ and the mixtures of PP9, PP60 and PP90/UHMWPP were blended at 200 ℃ for 10 min in a kneader(PBV-0.1, Irle Shokai Co., Ltd., Japan) with a screw speed of 70 rpm. Homopolymer and blend films were fabricated with compression press at a 200 ℃ molding temperature under 25 MPa of pressure for 10 min and cooled to room temperature by putting on a table top. The thickness of the films was measured to 200~300 ㎛.

3.3. Characterizations.

The Universal tensile machine (UTM, H1KT, Tinius Olsen, USA) was connected to a 10 g load sensor applying a stretching rate of 5 mm/min. A minimum of six dog-bone-shape replicas of each blend film were cut and used for the testing. The thermal properties of the blend films were characterized by using a differential scanning calorimetry (DSC1, Mettler Toledo Inc., Switzerland) measured at a heating rate of 10 ℃/min and a cooling rate of 300 ℃/min under a nitrogen atmosphere. The degree of crystallinity, X_c, was determined by Equation (1).

$$\%) = \frac{\triangle H_{sample}}{\triangle H_{reference}} \times 100 \text{ --------------------(1)}$$

where is the value of the enthalpy of fusion obtained during the second heating scan(following an initial heating to 180 ℃, which was maintained for 5 min and then cooled at a rate of 300 ℃/min), and is the enthalpy of fusion of 100% crystalline (PP = 209 J/g). Thermogravimetric analysis (TGA 7, PerkinElmer Inc., USA) was used to define the thermal stability, decomposition temperature, rate of degradation and mass loss of samples. The thermal properties of the UHMWPP/LMWPP blends were obtained in a nitrogen atmosphere at a heating rate of 10 ℃/min to 600 ℃. The morphology of tensile-fractured samples was observed with a SEM (Tescan MIRA3, Tescan Orsay Holding a.s., Czech Republic). The viscosities of the UHMWPP/LMWPP blend samples were assessed by using a melt index tester (MFI 9, AMETEK Lloyd Instruments Ltd., USA) which was identified the standard test die and 2.16 kg rod or 21.6 kg rod at 230 ℃. The dynamic mechanical properties of the UHMWPP/LMWPP blend films were measured with Ares G2 (TA instruments, USA) over a temperature range of −50 ℃ to 100 ℃ with a heating rate of 5 ℃/min under a constant frequency of 1.0 Hz.

CHAPTER 4. Results & discussion

4.1. Low viscosity PP/UHMWPP blend

4.1.1. Rheological properties

The melt flow index (MI) is a measurement value that indicated the mass of the polymer flowing through a die at a standard temperature and pressure for 10 min. The MI value of a certain polymer depends on its viscosity and molecular weight, that is inversely proportional to the MI value, thus it is a simple measurement method for calculating rheological properties [12]. The MI of blends containing various amounts of LMWPP was characterized the effect of LMWPP content on the rheological properties. Figure 2 and Table 2 are shown the MI of the UHMWPP/LMWPP blends. The MI of UHMWPP which is 0.87 g/10 min using a 21.6 kg load at 230 ℃ was very low because of its high melt viscosity. To improve the processability of UHMWPP, it was blended with LMWPP processing simple. As shown in Fig. 2 and Table 2, the content of LMWPP and the MI value observed a proportional relationship, and the MI value of maximum UHMWPP content (50%) showed 90.5 g/10 min. However, the mechanical properties of UPP40 and UPP50 blends were shown that dramatic decrease with increasing MI values, as shown in Fig. 3. It is that weak interaction between LMWPP and UHMWPP interfered with the shear distribution of blends and UHMWPP could not be completely disentangled during the melt blending, thus its dispensability in

LMWPP matrix was decreased due to the viscosity difference UHMWPP and LMWPP in UPP40 and UPP50, resulting in poor miscibility [6,21].

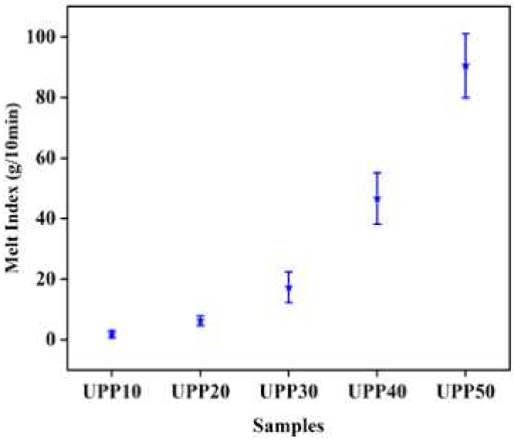

Figure 2. MI values of UHMWPP/LMWPP blends. (2.16 kg load, 230 ℃)

Table 2. MI values of UHMWPP/LMWPP blends

Sample name and designations	UPP10	UPP20	UPP30	UPP40	UPP50
UHMWPP/LMWPP (by weight%)	90/10	80/20	70/30	60/40	50/50
MI(g/10 min)	1.8±1.2	6.3±1.6	17.3±5.1	46.7±8.5	90.5±10.6

4.1.2. Mechanical properties

The stress-strain curves of the UHMWPP/LMWPP blends (UPP10, UPP20, and UPP30) was characterized the stress-yielding and strain-hardening behaviors in Fig. 3. The neat UHMWPP was tried to melt blending with the antioxidants at 190 ℃ for 10 min. It was not completely melted due to its high viscosity even after increasing the melt temperature. The UHMWPP blends were oxidized and become yellowing despite exceeding the amount of oxidants, when increasing the temperature. Thus, the mechanical properties of UHMWPP were expected through the overall trend and change of content of UHMWPP in UHMWPP/LMWPP blends. As shown in Figures 3B and 3C and Table 3, the tensile yield strength, tensile strength at the break point, and % elongation decreased dramatically, the increasing in the amount of LMWPP. The highest mechanical properties was the UPP10 blend with an average of 36.11 MPa tensile yield stress and 47.99 MPa tensile stress as break, as shown in Fig 3A. As many broken fibrils were observed in Fig 3E, it might be because the molecular chain entanglement and viscoelasticity were considerably due to interfacial molecular diffusion between UHMWPP and LMWPP and a dense and sturdy dual network structure was formed. Furthermore, the tensile yield stress and tensile stress at break gradually decreased up to UPP30 and then slightly increased for UPP40, while the elongation at break slightly decreased up to UPP30 and then dramatically decreased for UPP40 and UPP50. The reduction in tensile strength occurred through the weak interface interaction between UHMWPP and LMWPP, which result in uneven shear distribution within the blends, and the increase for UPP40 and UPP50 indicated that UHMWPP acts like a filler in LMWPP matrix due to the uniform dispersion of UHMWPP. It means that two phase of the blend occurred partial diffusion during the melting process. UHMWPP chains partly entangled and dispersed as various sized fillers in the LMWPP matrix like UPP40 and UPP50, which achieved to improve the tensile yield strength. The drastic changes in the % elongation for UPP40 and UPP50 are suggested to be because UHMWPP acted as stress concentration points, when the blends were subjected to tensile stress, the molecules that were less entangled with LMWPP easily became disentangled, which caused reduction in the % elongation. The chain formation of PP, which is semicrystalline polymer, in the crystalline regions has a significant effect on the mechanical properties. UHMWPP has many randomly entangled chains in amorphous regions, whereas UHMWPP chains in the crystalline regions are arranged regularly, which resulted in difficulty of slip chain or wind chain [22]. The specific mechanical properties of UHMWPP resulted from its long chains as well as random entanglement of chains in amorphous regions, and then it was disentangled by large amounts of energy, when subjecting to tensile stresses. The molecular chains of UHMWPP and LMWPP repulsed each other and made less entanglements while the content of LMWPP was more than UHMWPP in blend; As the viscosity mismatch between UHMWPP and LMWPP, the poor compatibility of blends was confirmed in a clearly phase separation(Fig 6). This could be explained that LMWPP, which has low molecular weight, acts as a plasticizer that reduces the melt viscosity of the polymers and results in slipping the UHMWPP chains during subjecting to tensile stresses and making the UHMWPP chains move softly.

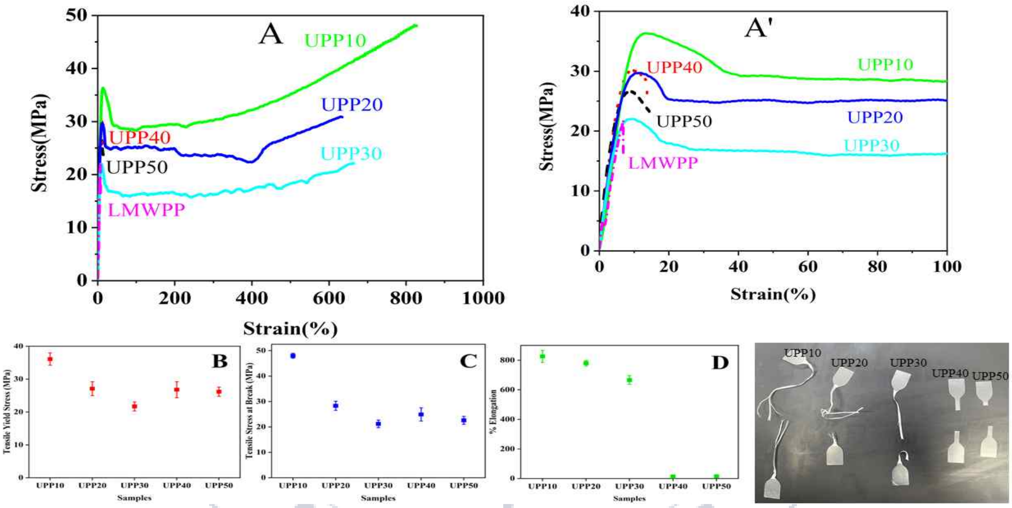

Figure 3. Mechanical properties of UHMWPP/LMWPP blends: (A) stress–strain curve behavior, (A) is the enlarged initial section of (A), (B) average tensile yield stress, (C) tensile stress at break, (D) % elongation at the break of the UHMWPP/LMWPP blends (E) Pictorial presentation of fractured blend samples after the tensile test.

Table 3. Mechanical properties of UHMWPP/LMWPP blends

Sample name	Tensile Yield Stress (MPa)	Elongationat Break (%)	Tensile Stress at Break (MPa)
LMWPP	23.0±80.8	7.2±20.7	21.1±10.6
UPP50	26.1±80.5	15±0.7	22.5±90.7
UPP40	26.8±3.0	14±0.9	24.9±4.7
UPP30	21.7±1.7	678±47	21.2±0.6
UPP20	27.1±2.6	780±23	28.3±2.2
UPP10	36.1±12.3	826±50	47.9±91.2

4.1.3. Thermal properties

The thermal properties of the UHMWPP/LMWPP blends are shown in Fig 4 and Table 4. The crystallization of a polymer depends on the initial nucleation and its growth. The long chains of UHMWPP entangled in melting phase and occurred homogeneous nucleation during the cooling, but it can freeze and manufacture nuclei at higher temperature than LMWPP [6]. The rate of chain movement results in the crystal growth rate, thus the longer the chain, the slower the movement rate. The long chains in the UHMWPP with many entanglements was occurred the reduction in the movement of UHMWPP chain segments during cooling crystallization; and then this means lower crystallinity due to low crystal growth [23]. We indicate that LMWPP had the same effect as a nucleating agent, forming seeds of nuclei for nucleation process and improving the crystallinity of blend, except the UPP50. The crystallinity of the UHMWPP/LMWPP gradually increased with the addition of LMWPP, that the content of LMWPP had an effect on the crystallization behavior of the blends. On the other side, the existence of UHMWPP as a heterogeneous nucleus was conducive to improving the crystallinity of the blends, although it decreased with increasing UHMWPP content. Also, all blends of UHMWPP/LMWPP were a single compound due to only one melting point peak.

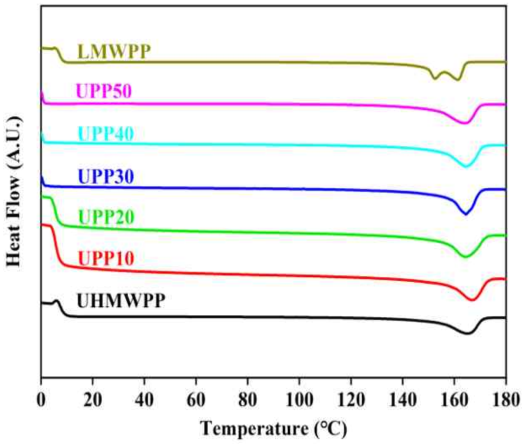

Figure 4. DSC curves of the UHMWPP/LMWPP blends during the first scan. (Heating rate of 10℃/min from 0℃ to 180℃)

Table 4. DSC data of UHMWPP, LMWPP and UHMWPP/LMWPP blends

Sample name	UHMWPP	UPP10	UPP20	UPP30	UPP40	UPP50	LMWPP
T_m(℃)	165	167	165	164	165	164	152,160
Crystallinity (%)	44.0	45.0	45.2	52.6	54.6	46.9	41.5

TGA analysis was performed to confirm the thermal degradation behavior of the blend and to determine the effect of the blend composition on thermal stability of the polymer. The all TGA curves were observed one-step degradation as shown in Fig 5. The initial thermal degradation, which is the most important in thermal degradation behavior of polymers, was determined at degradation temperatures up to 5%, 10% and 20%, and was referred to as T5%, T10% and T20%. UHMWPP's T5%, T10%, and T20% values appeared at 403 ℃, 419 ℃, and 436 ℃, respectively , while for LMWPP, the T5%, T10%, and T20% values appeared at 383 ℃, 409 ℃, and 427 ℃, respectively (Table 4). The thermal degradation behavior of the UHMWPP started at 300 ℃ and ended with a drastic weight loss at 400 ℃. Excluding T5% of UPP, all T5%, T10% and T20% of UHMWPP/LMWPP blends were measured higher than LMWPP and lower than UHMWPP, and there was no significant change in the thermal degradation behavior and temperature between UHMWPP/LMWPP blends.

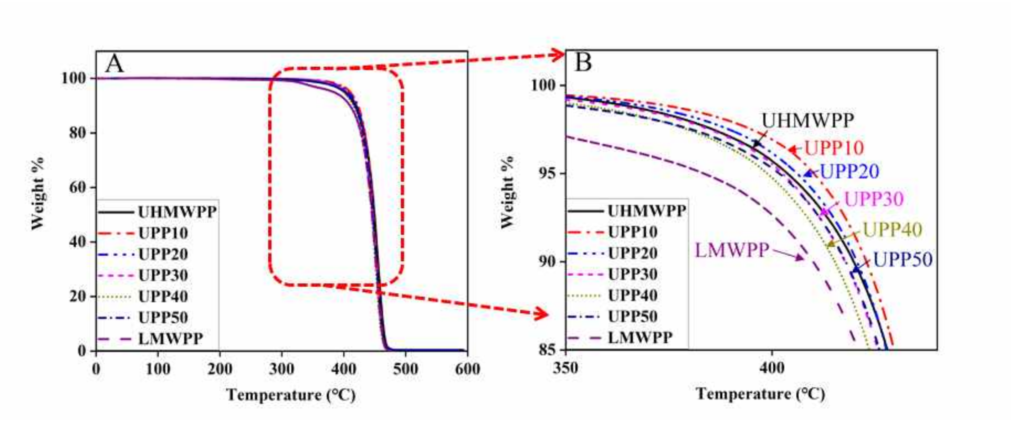

Figure 5. (A) TGA analysis of UHMWPP/LMWPP blends and (B) magnified TGA plot.

Table 5. TGA data of the UHMWPP, LMWPP and UHMWPP/LMWPP blends

Sample name	$T_{5\%}$(℃)	$T_{10\%}$(℃)	$T_{20\%}$(℃)	$T_{50\%}$(℃)
UHMWPP	403	419	436	449
UPP10	410	422	433	447
UPP20	398	414	428	444
UPP30	402	417	431	446
UPP40	406	420	432	447
UPP50	402	417	428	447
LMWPP	383	409	427	445

4.1.4. Morphology of fractured surface

As shown in Fig. 6, the SEM images of the tensile fractured surfaces of two blend samples are observed. The SEM images of the fractured surfaces were obtained next to the sample surfaces in the stress direction as shown in Fig. 6A and Fig 6B. The many UHMWPP fibers were observed on the UPP10 blend sample surface. For testing tensile stress on blend films, the lamellar structure of the samples will be restructured into an oriented fibril structure. A further tensile deformation will lead to a stretching of the structure of the formed fibrils, which in its turn will lead to a decrease in the thickness of the fibrils (micro and nanofibers) and a rupture of the highly oriented amorphous network, which was built up by the load-bearing inter-fibril tie chains, causing the formation of cavities. For UPP10 blend samples, the fractured surface was almost covered by the fiber bridges (marked by red dotted eclipses), attributed to the improved interfacial interaction and intermolecular entanglement of the UPP10 blend system (Fig. 6A). For cyro-fractured sample, the fracture surface was quite rough and many pulling-out UHMWPP fibrils (marked by red dotted arrows) with some fiber bridges (marked by red dotted eclipses) were observed on the fractured surface (Fig. 6C). In contrast, for the UPP50 blend, the tensile fractured sample surface and the cyro-fractured surface was rough, and spherical particles of UHMWPP were observed (marked by red arrows), due to the poor compatibility, with an apparent phase separation structure (Fig. 6B and Fig. 6D).

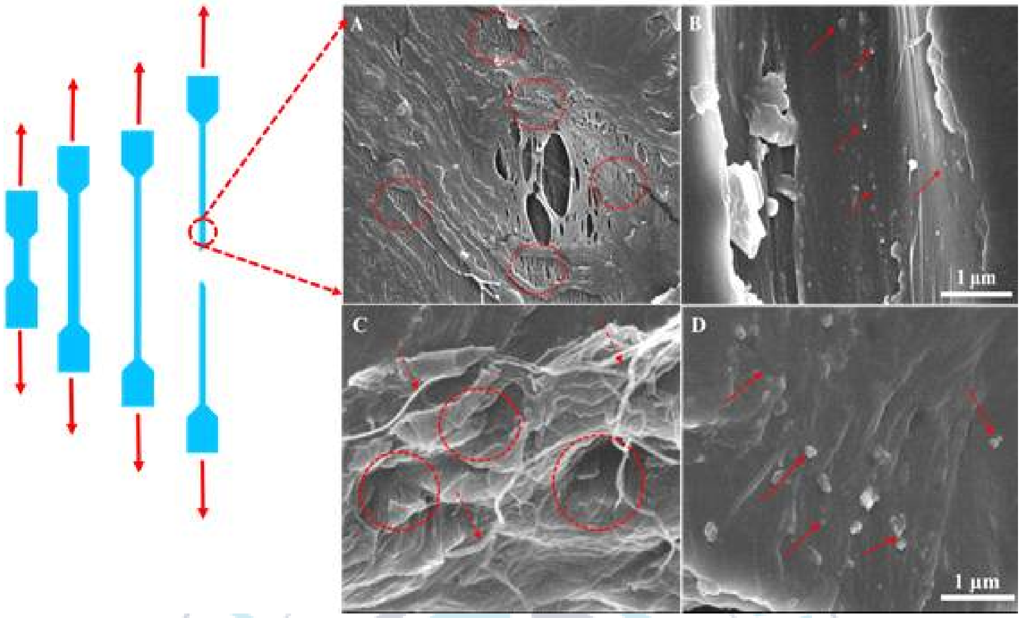

Figure 6. SEM images of tensile-fractured samples of A) UPP10 and B) UPP50 blend and cyro-fractured samples C) UPP10 and D) UPP50 blend.

4.2. Various PP/UHMWPP blends

4.2.1. Mechanical properties

The mechanical properties of the polymers such as viscosity, draw ability, toughness and diffusion coefficient are greatly influenced by molecular weight and its molecular weight distribution [9,10]. The UHMWPP did not melt completely for increasing in the processing temperature due to the high molecular weight and high melt viscosity. Therefore, the mechanical properties of UHMWPP were investigated through blending with various PP. The mechanical properties of UHMWPP/PP blends were especially observed by blending 10 wt% UHMWPP compared with the PPs. Block type PP (PP60 and PP90 with ethylene chains) was observed to decrease in Elongation at break than homo type PP (PP9), as shown in Figure 7A. The UHMWPP/PP blends with 10 wt% of UHMWPP were shown a dramatic change. The tensile yield stress of 90PP9 blends increased, but the % elongation decreased. However, the mechanical properties of PP60 and PP90 blends were shown contrarily, the tensile yield stress decreased while the % elongation increased, as shown in Figure 7B. Therefore, we select PP9 which is the most suitable candidate due to the high tensile yield stress of 90PP9.

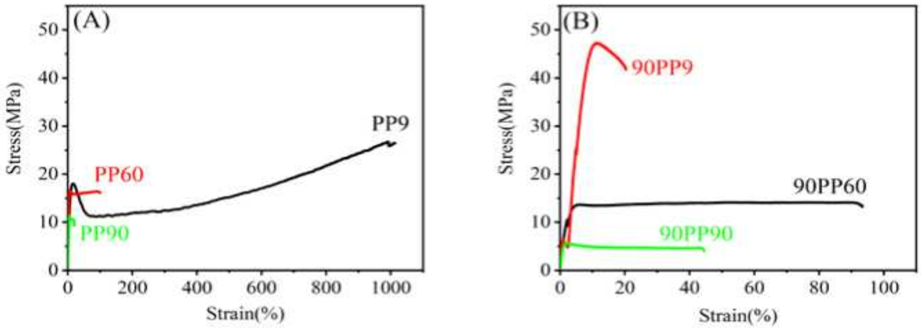

Figure 7. Examples of stress-strain curves of (a) neat PP as PP9, PP60, and PP90 and (B) UHMWPP/PP blends (10:90 by weight %).

The tensile stress-strain curves of UHMWPP/PP9 blends which blending various PP9 contents was shown in Figure 8. It was obtained that the stress-strain curves of 10PP9, 30PP9, 50PP9, and 70PP9 showed a behavior similar to stress-strain curve of PP9 such as strain hardening and stress yield. Table 2 presented all the mechanical properties of the blends with various contents of UHMWPP. The tensile yield strength and tensile strength at break gradually increased as increasing UHMWPP content up to 90 wt%. This is that UHMWPP contents act as fillers reinforced PP9 matrix due to a good miscibility of UHMWPP with PP9. The addition of 90 wt% UHMWPP caused that 47% and 48% increase in tensile yield strength and ultimate tensile yield strength compared with PP9, but decrease in % elongation is 21%. The 90PP10 blend indicates that UHMWPP chains were co-crystallized with PP9 chains, resulting in the tensile yield strength attributed to intrinsic load capacity and magnificent interfacial adhesion. The UHMWPP 10 wt% blend among the blend of UHMWPP and PP9 significantly increased the mechanical properties of PP9 as increase the tensile yield strength by 145% the expense of a decrease in the % elongation at break.

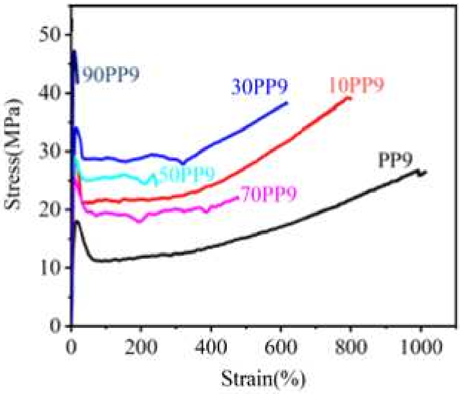

Figure 8. Stress-strain curves of PP9 and UHMWPP/PP9 blends.

Table 6. Mechanical properties of neat LMWPPs and UHMWPP/LMWPPs blends

Sample Code	Composition (by wt%)	Tensile Yield Stress (MPa)	Elongation at Break (%)	Tensile Stress at Break (MPa)
PP9	0/100	19.3±0.7	1013±.357	26.5±1.9
PP60	0/100	16.3±1.6	99.3±11.6	15.2±1.2
PP90	0/100	10.2±1.0	19.5±1.3	9.5±0.7
90PP9	10/90	47.3±2.9	18.3±2.0	41.6±0.9
90PP60	10/90	13.5±1.7	86.0±4.3	13.2±0.3
90PP90	10/90	5.7±0.8	43.1±1.0	4.7±0.2
70PP9	30/70	25.3±1.3	476.7±47.9	22.7±0.9
50PP9	50/50	28.7±0.7	812.0±21.7	39.1±0.3
30PP9	70/30	34.4±2.1	612.7±21.7	38.3±0.7
10PP9	90/10	28.4±3.1	793.4±39.3	39.2±1.7

4.2.2. Thermal properties

As shown in Figure 9, the melting temperature of UHMWPP and PP9 was obtained large difference, but their crystallinity was stable with negligible change. The crystallinity of UHMWPP/PP9 blends slowly increased to 90 wt% PP9 due to increasing UHMWPP content as shown in Table 7. Especially, the crystallinity of 90PP9 was the highest among the neat UHMWPP, neat PP9 and UHMWPP/PP9 blends. As the difference in the crystallization range of UHMWPP/PP9 blends was not found, it could be shown that co-crystallization of PP9 and UHMWPP occurred through the similar crystal structure between their chains. The growth rate of crystal depends on the chain segment movement; the longer chains show a lower movement rate due to entanglement of chain. During the crystallization time, UHMWPP, which had a long chain with plenty chain entanglement, decreased the chain movement, and thus the crystal growth, resulting in lower crystallinity of UHMWPP/PP9 blends as the content of UHMWPP increased. We suggested that UHMWPP chains act as a nuclei seed for crystallization process and increases the crystallinity of the blends.

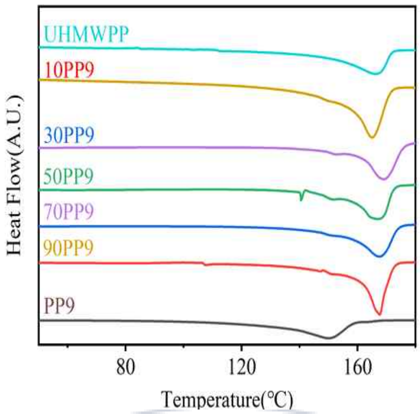

Figure 9. DSC analysis of UHMWPP/PP9 blends.

Table 7. Thermal properties of UHMWPP, PP9 and UHMWPP/PP9 blends

Sample name	UHMWPP	10PP9	30PP9	50PP9	70PP9	90PP9	PP9
T_m(℃)	166	164	168	167	167	167	150
Crystallinity (%)	45.59	45.23	47.02	47.90	48.25	56.92	40.12

4.2.3. Rheological properties

The melt index (MI) of the polymer is inversely proportional to the melt viscosity and molecular weight of polymer [24]. The MI of the UHMWPP/PP9 blends was characterized to investigate the effect on melting flow properties according to the amount of PP9. The melt viscosity of neat UHMWPP was obtained very high when MI was measured 0.87 g/min using a 21.6 kg load at 230 ℃, while the MI of PP9 was 9 g/min using a 2.16kg load at 230 ℃. The purpose of the blending of UHMWPP was to improve the processability of UHMWPP by maintaining the excellent mechanical properties of UHMWPP and the high processability of PP9 with relatively low melting viscosity. The MI of the blends increased in proportion to the content of PP. when the PP9 content was maximum (90%), the MI value of the blend was obtained as 79.2 g/min in Figure 10.

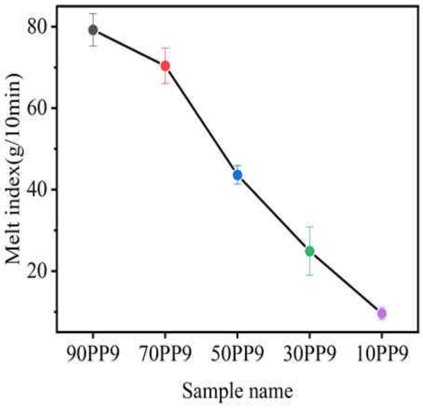

Figure 10. MI of UHMWPP/PP9 blends (2.16 kg rod, 230 ℃, Average of six time measurements).

The dynamic mechanical properties of UHMWPP/PP9 blends were shown in Figure 11. The E′ shows the elastic behavior of the polymer that characterized the properties of entropy elasticity in polymer chains [25-27]. Figure 11A showed that the chain entanglement of UHMWPP was relatively higher than that of PP9 chains and the chain relaxation time was longer because of the high molecular weight of UHMWPP, as the E′ of the UHMWPP/PP9 blend was higher than the E′ of the UHMWPP. The E″ of all samples, which is an indicator of dissipation energy, showed the similar behavior and there was no significant change. The tan δ, which is determined by network formation, indicated an increase in toughness of the blend as the UHMWPP content increased, resulting in a drastic drop in the tan δ value of the blend.

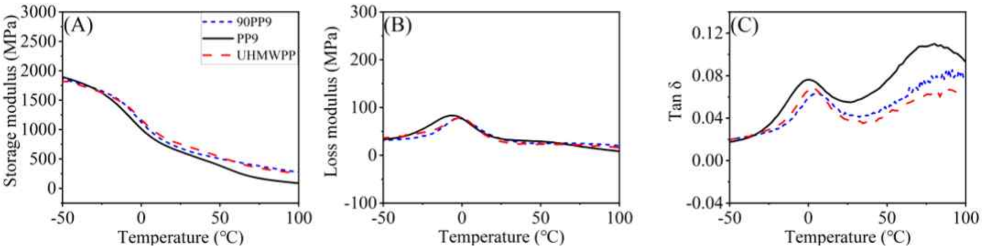

Figure 11. DMA curve of PP9, UHMWPP, and 90PP9 blend: (A) storage modulus (E ′), (B) loss modulus (E ″), and (C) damping factor (tan δ).

CHAPTER 5. Conclusions

The UHMWPP was melt blended with various LMWPPs, which had the melt index of 9, 60, 90, and 1500 by a kneader to improve a processability of UHMWPP. As LMWPP was added to UHMWPP, MI increased as the amount of LMWPP increased, resulting in increased the processability of UHMWPP. The most effective blend appeared to be UPP10, which maintained mechanical properties and showed a significant increase in crystallinity. This showed that the improvement of the processability of UHMWPP and the maintenance of mechanical properties can be solved through the blend. In addition, T5%, T10%, T20%, and T50% of UHMWPP/LMWPP blend was obtained between the UHMWPP and LMWPP, indicating that the thermal degradation properties are better than the LMWPP. Homo PP9 measured higher mechanical properties than other block type PPs. The addition of PP9 to UHMWPP increased the MI of the blend to improve processability, and the mechanical properties were UHMWPP/PP9 (10/90 wt%) at the expense of the elongation, which significantly improved the tensile yield strength by 145%. The storage modulus of the UHMWPP/PP9 blend increased slowly due to the high molecular weight of UHMWPP, which has a relatively longer relaxation time than PP9 as many chain entanglements.

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