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PROCESSABILITY AND THERMAL PROPERTIES OF ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE/ POLYPROPYLENE BLENDS

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ABSTRACT

Ultra-high molecular weight polyethylene (UHMWPE) is a polymer with superior mechanical properties. However, processing of UHMWPE has been a great challenge due to the extremely high viscosity of UHMWPE which limits its utility in applying it for some processing technology such as Fused Deposition Modeling (FDM) which receives raw material only in filament form. Recent processing technology highlighted that extrusion technology is the most economical way for producing filament. Thus, the aim of this work is to improve the processability of UHMWPE for extrusion process via blending with polypropylene (PP), with enhancing the mechanical properties of UHMWPE. The result shows that UHMWPE/PP blend at 80/20 ratio provides maximum melt flow rate. The highest thermal stability observed at 90/10 ratio of UHMWPE/PP blend. Thermal decomposition curves revealed that UHMWPE/PP blends and both pure UHMWPE and PP decomposed above 250 °C.

Keywords: polymer blends, UHMWPE, polypropylene, thermo gravimetric analysis, rheological.

INTRODUCTION

UHMWPE with its superior properties such as high impact strength, high resistance to stress cracking and wear, and extremely low embrittlement temperatures, is one of highly demand polymer specifically for medical applications *(Liu et al., 2004*, Diop *et al.*, 2014). These superior properties are due to the extremely high molecular weight of UHMWPE which leads to increase in chains entanglement density and hinder the chains mobility. Consequently, causes processing difficulties and limits the processing method by ram extrusion and compression moulding only (Xie et al., 2009, Huang *et al.*, 2014).

To overcome this challenge, many researchers focused on disentanglement the chain network to facilitate its movement (Xie and Li, 2007, Xin *et al.*, 2011). Some researchers used dissolution in appropriate solvent or utilizing irregular polymerization techniques. However, these approaches do not provide definitive solutions to the entanglements problem because disentangled chains can re-implicate during melt-state heating (Diop *et al.*, 2014). Alternative solution for chain entanglement have been conducted by several searchers, via blending UHMWPE with lower MW polyethylene (PE) or polypropylene (PP) (Liu *et al.*, 2004, Xu *et al.*, 2012, Chen *et al.*, 2013). These additives have a significant ability to penetrate to the spaces between UHMWPE molecules particularly under action of extruder pressure due to mixing process. Consequently, reducing it is apparent viscosity then enhancing material flow (Xie and Li, 2008). Conventional polyolefins (HDPE, LDPE, MMPE, ect) have similar structure and high compatibility to UHMWPE, so usually used as processing agents. However, Liu *et al* (2004) noticed significant difficulty in processing UHMWPE/HDPE compared to polypropylene (PP) instead of HDPE. They have observed that the die pressure is much greater in the case of HDPE than PP, and several blockings occur during extrusion UHMWPE/HDPE blend by single extruder. In addition, the best solution of HDPE blocking is to add small amount of PP.

It is worthy to review the role of PP in extruding of UHMWPE. Generally, the ideal situation for extruding melt materials based on maintaining maximum friction between the material and the barrel wall, and minimum friction between material and screw surface. In the case of extrusion pure UHMWPE, the coefficient of friction is very low, so the rotation of the extrusion screw cannot push it. However, after adding the PP and at the onset of the screw (feeding section) will concentrate at the skin of UHMWPE which will increase the friction with barrel wall, and thus make the movement of the blend forward is possible. Owing to the high degree chain entanglement of UHMWPE, the mixing process with PP is difficult. However, under the intense shearing and squeezing through the compression section, PP particles will penetrated into the gaps of UHMWPE towards the blend core. Thus the concentration of the PP at the core will be more than the skin. It is known that PP usually prefers to disperse in the amorphous zones (Xie and Li, 2007, Mourad, 2010), which decreases the entanglement density at these zones, and acts as heat-transfer agent which helps the UHMWPE chains to slippage and move easily.

PP role does not stop at improving the UHMWPE processability only, but it provides significantly enhancing the mechanical properties of the blend. Liu and Li (2003) demonstrated significant improvement in Izod Notched Impact Strength, Young's Modulus, and Yield Strength with adding PP, but these improvements do not occur at the same content (Liu and Li, 2003). As first stage the present work focuses on carrying out the best

UHMWPE/PP ratio based on monitoring both melt flow rate and thermal stability under impact of PP content.

EXPERIMENTAL

Materials

UHMWPE GUR 1020 (Ticona, Telford, UK), supplied in powder form with average molecular weight of 3.5×10^6 g/mol and density of 0.93 g/cm^3. Polypropylene impact copolymer (sm 240) was supplied by Lotte Chemical Titan Holding Sdn. Bhd with a high melt flow rate (MFR) of 25 g/10 min (ASTM-D 1238-13), and density 0.9g/cm^3.

Blending process parameters

Twin Roller mixing machine has been approved for mixing the polymer in order to primarily evaluate the UHMWPE/PP blend melt flow rate and specify the best blend composition which exhibit higher melt flow rate. It is worthy to note that the blending process based on controlling three parameters namely; blend materials content, process temperature, mixing speed. Firstly, the main goal of present wok is to improve the processability of UHMWPE without scarifying the mechanical properties of matrix material and a fortiori if can improve some of matrix material properties such as impact strength. Based on that, the researchers selected the additive material as mentioned previously with high melt flow rate and it would lead to improve key matrix material properties. This expectation based on several studies has been conducted on other types of the same additive (Liu et al., 2004, Xie and Li, 2007, Kuram *et al.*, 2014). PP content range 10% to 30% has been specified for this study due to the presence of evidence from previous studies indicate that this range provide enough improvement for UHMWPE process-ability.

Secondly, according to the melting temperature of UHMWPE and PP, 140^o C and 160^o C respectively, and to compensate the heating loss, so the blending temperature was set at 190^o C. *(Liu et al., 2004)*. Yang *et al* (1995) noted that the shear intensity (rpm) does not significantly improve the final dispersion in the immiscible binary blend (Yang *et al.*, 1995). Ghasemi (2009) demonstrated that the temperature and time of mixing have dominant impact among the mixing process parameters which have been studied in order to improve the dispersion of organoclay in styrene-butadiene rubber (I. Ghasemi*, 2009). Nevertheless, most of researches set mixing speed around and mixing time as 50 rpm and 20 min respectively (Vaidya and Bhattacharya, 1994, Marić and Macosko, 2001). So drawing on that, 40 rpm selected as shear intensity, and 15 min was the mixing time (Kalappa *et al.*, 2008, Xie *et al.*, 2009)for each sample to make sure the two materials are well mixed and in the same time prevent the blend from material burning of.

According to maximum capacity of mixing machine which can be calculated from the following equation, the samples were prepared from suggested materials.

$$Specimen\ weight = 55 \times d \times 0.4 \quad (1)$$

$$Where\ 55{:}\ \ maximum\ capacity; 0.4\ capacity\ factor$$
$$d(density) = d_{UHMWPE} + d_{PP}$$

After blending, all samples pass to crushing machine in order to be subject to melt flow rate test.

Measurements

Processability of UHMWPE/PP blends was examined through Melt Flow Rate (MFR) test to ASTM D1238 standard test method (190 °C, 5Kg). The MFR results are presented in Table-1.

Thermogravimetric analysis (TGA) was conducted to investigate the thermal stability of the blends.

Biocompatibility test has been conducted in order to exploit the polymers (UHMWPE/PP) in medical applications in future work. Before applying the bio-test samples must be cleaned by ethanol and sterile with Hank's Balanced Salt Solution (HBSS) to avoid any contamination. Ten samples for each blend ratio were placed in microtiter plate. Each sample was overlaid by both HaCaT cells and cell culture medium (Dulbecco's modified Eagle's medium) and left in incubator for 24 hours. Cells situation have been investigated under microscope, then the culture media has been removed and applied new one with (3-(4,5-dimethylthiazol-2-yl)2,5-diphenyl tetrazolium bromide) (MTT) salts for assessing cell metabolic activity. The samples have been incubated for another 4 hours and then checked again.

RESULTS AND DISCUSSIONS

Processability study

The Melt Flow Index (MFI) results shown in Table-1and Figure-1 indicate that the addition of PP range from 20% to 25% contributes to a significant improvement on the processability of UHMWPE. This result is approximately consistent with findings reported by (Liu *et al.*, 2004). However, the MFI value decreased drastically above 25% of PP. It is possibly due to the inhomogeneous mixing between polymers, pressure built up inside the barrel which consequently negatively affects the flowability of the blend.

Table-1. Melt flow index.

UHMWPE/PP	MFI(average)	SDV
90/10	**0.107**	**±0.345**
80/20	4.185	±0.570
75/25	4.019	±0.643
70/30	1.260	±0.152

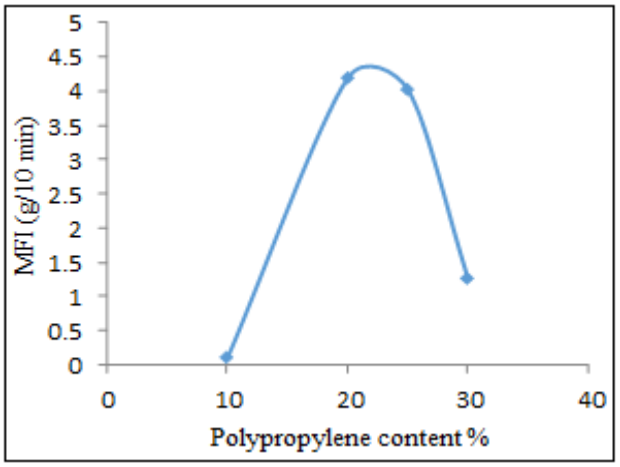

Figure-1. Melt flow index (MFI).

Thermal study

Thermo gravimetric analysis (TGA)

TGA of the pure UHMWPE, PP, and UHMWPE/PP blends was performed to evaluate the impact of PP content on the thermal stability of UHMWPE. TGA curves in
Figure-2 shows the degradation temperature of pure polymers and their blends.

It can be observed that all TGA curves are single-stage with continuous reduction in weight for virgin and blends of UHMWPE/PP. UHMWPE's $T_{10\%}$ temperature was 397.7° C, 83.9 °C higher than PP. This result indicates that the UHMWPE is more thermally stable than PP due to extremely high molecular weight of UHMWPE (Ahmad *et al*., 2013). Actually, the values of initial decomposition temperature for these polymers are different from that values which already carried out by Harutun *et al* (2003) and Mazatusziha *et al* (2013), attributed to the variation of materials grade (Karian, 2003, Ahmad *et al*., 2013).

Decomposition temperature of PP took place most rapidly compared to pure UHMWPE and blends. Whereas, it was obviously noticed that 90/10 blend showed highest thermal stability in whole blend and pure articles. The results are inconsistent with those reported by Mazatusziha (2013), where the value of blends decomposition temperature lies between virgin polymers

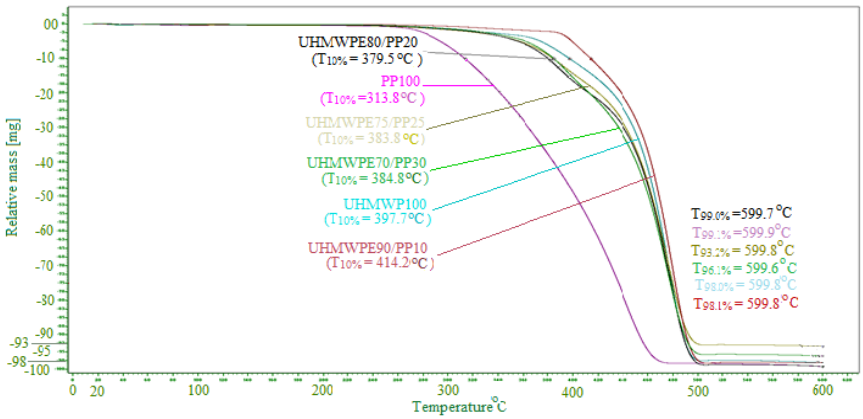

Figure-2. Thermo gravimetric analysis (temperature at 10% material degradation).

These results are significantly affected by blends ratio (Klarić *et al*., 2000). As presented in Table-2, blends with PP content range from 20 to 30 percent show a reduction in thermal decomposition temperature ranged between 379.5 °C and 384.8 °C.

From TGA curves, it can be clearly observed that the decomposition occur above 250 °C. This temperature is considered as a reference for processing temperature. However, it must not lose sight of that the polymer thermal behavior depends on temperature processing and exposure time too

Table-2. Decomposition temperatures of UHMWPE/PP.

UPE/PP	$T_{10\%}$ [°C]	T_P [°C]	$T_{99\%}$[°C]
100/00	**397.7**	**476.9**	**599.8**
90/10	414.2	479.1	599.8
80/20	379.5	476.3	599.7
75/25	383.8	475.6	599.8
70/30	384.8	475.9	599.6
00/100	313.8	442.8	599.9

UPE = UHMWPE; T10% = Initial decomposition temperature; TP = Peak of decomposition temperature; $T_{99\%}$ = Temperature at 99% weight loss.

Figure-3 shows the effect of PP content on the melting point of the blends. The highest melting point observed for UHMWPE/PP blend at composition of 90/10 which lies between the two pure polymers. Others were biased to the UHMWPE. This result is consistent with the previous results ($T_{10\%}$) and it assures that this blend was the most stable ratio.

Figure-4 presents temperatures of the tested samples at maximum rate of decomposition. It is clearly shown that the PP reach the maximum decomposition rate earlier (442.8 °C) than UHMWPE which makes sure that UHMWPE is more stable than PP, whereas 90/10 blend withstands up to 479.1 °C, which provides the same previous indication for this ratio blend. Residual blends segregated around 475 °C, more close to the UHMWPE decomposition temperature.

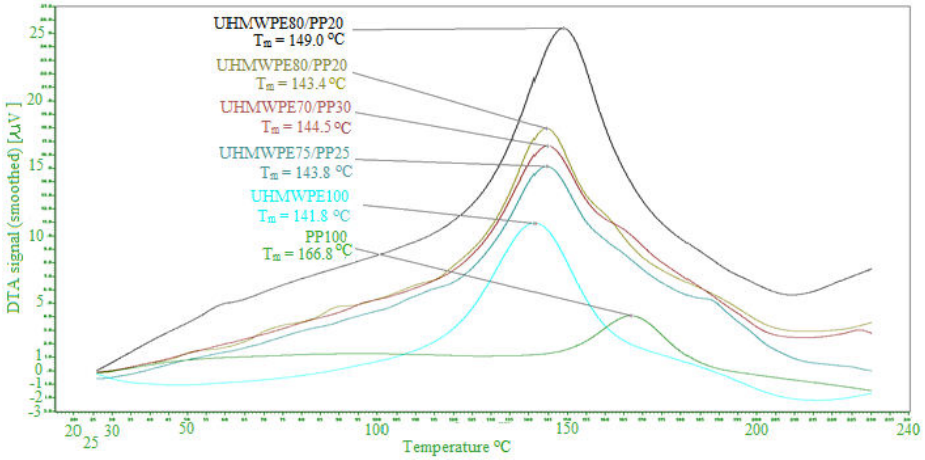

Figure-3. Impact PP content on blends melting point.

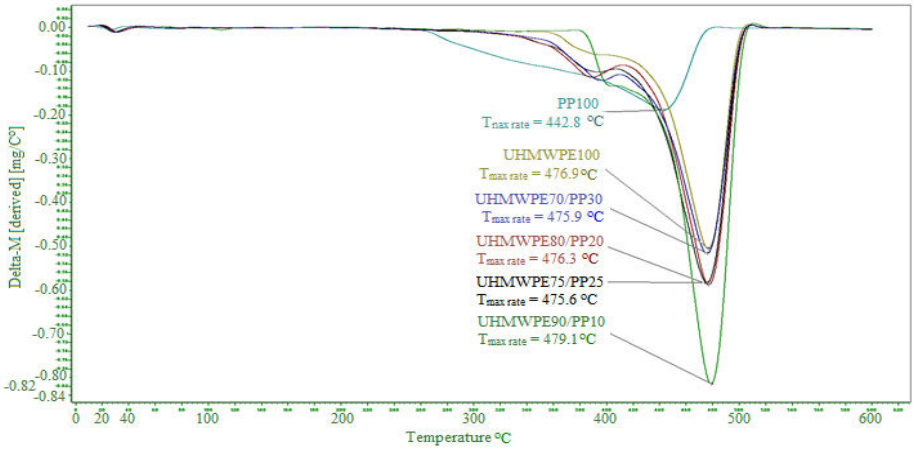

Figure-4. Impact of PP content on blend decomposition rate.

Biocompatibility study

Figure-5 presents the microscopic photo for one of random samples of biocompatibility test. It is clearly shown that the purple color, since this color is a direct evidence that the cells remained alive and practiced their metabolic activity. Consequently it can be considered that this material is compatible for human body environment.

CONCLUSIONS

The present work has been conducted as a base to achieve comprehensive study for the impact of PP content on the rheological, thermal, mechanical properties of UHMWPE in order to improve its processability without sacrificing the original characteristics or improve, at least, some of it. The strategic goal of this study and its future extensions is exploit these improved blend as alternative material for orthopedics application which proved as biocompatible material.

MFI test indicated a rise in UHMWPE flow-ability with an increase in PP content up to 20%, the peak point of the flow. Over this percentage continuous declination in blend process-ability occurs related to the increase PP content.

TGA results demonstrated, beyond any doubt, that 90/10 blend ratio was the most stable percentage in thermal test. Furthermore, thermal decomposition curves revealed that the UHMWPE, PP and UHMWPE/PP started decomposition after 250 °C, which should be considered as an upper limit for any thermal treatment for these polymers blend.

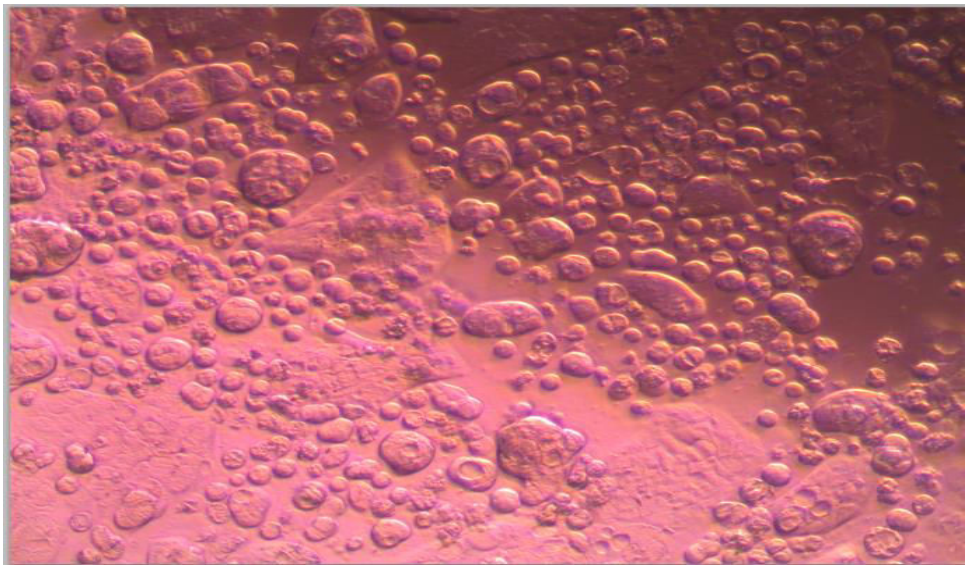

Figure-5. Microscopic photo of random sample for biocompatibility test.

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