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Mechanical Properties of Polypropylene/Recycled Rubber Blends

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ABSTRACT : Mechanical properties of polypropylene filled with recycled rubber dusts obtained from the buffing process in sport shoe sole manufacture were investigated. The use of these dusts eliminates the need for the size reduction process which is usually employed in rubber recycling. Two different waxes, polypropylene wax and ethylene vinyl acetate wax, were used in the PP/rubber dust compound. Two different processes, extrusion and injection moulding, were used to study the influence of the blends on the properties. The waxes gave significant improvement in the shaping of the extrudate. It was found that the impact strength of the injection moulded samples were higher than the extruded samples and the virgin PP. The tensile properties (yield stress and modulus) were dependent on the amount of rubber dust addition. An increase in the rubber dust loading gave lower yield stress and modulus.

Keywords : polypropylene, recycled rubber, blends, processability, toughening.

I. Introduction

Polypropylene is one of the high quantity used commodity thermoplastics for fabrication of various objects, due to its excellence in moulding processability and good mechanical properties.[1] It has been widely found in the form of moulded articles, films, fibres or sheets. However its poor impact property at low temperature, due to its high glass transition temperature and high crystallinity, limits its application to high performance materials. The tougheness of polypropylene (PP) can be enhanced while maintaining stiffness, strength and processability, by addition of some elastomers. A number of reports have indicated that melt blending of PP with different elastomers such as natural rubber (NR), butadiene rubber (BR), ethylene-propylene-diene terpolymer (EPDM), ethylene-vinyl acetate copolymer (EVA) and styrene-butadiene rubber(SBR) can be used to improve the impact strength of PP especially at low temperature.[2-8]

Blending of waste rubber into thermoplastics such as cryo-ground rubber blend with PP plays

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an important role in the modern polymer industry not only for the development of new materials but also for practical recycling purposes.[9] The major barrier of recycling discarded rubber is the high cost processes such as devulcanisation reaction, crumbing, cryogenic grinding and separation of contaminated rubber. Therefore utilisation of waste rubber ready in the form of dust particle would have much potential in commercial development. In Thailand, considerable amounts of vulcanised rubber dusts are generated during the sport shoe sole manufacture. The use of these dusts as an impact modifier in PVC has been successfully applied.[10-12] Preliminary work on the toughening of PP with these dusts has been carried out and it has been reported that the reuse of the dust improved the impact strength of the PP compound and resulted in volume cost saving and better appearance.[13] This work investigated the mechanical properties of PP filled with different types and loading of recycled rubber dust. The PP compounds were prepared by two different processing methods, extrusion and reprocessing by injection moulding. The effect of waxes on processability by extrusion was also studied.

II. Experimental

1. Materials

Extrusion grade homopolymer polypropylene (Profax 6631 from HMC Co., Ltd., Thailand) was used in this study. Three types of recycled rubber were scrap rubber dusts from sport shoe sole manufacture, midsole (M, vulcanised EVA foam), outsole (O, vulcanised rubber blend of NR, BR and SBR) and laminate (L, mixture of midsole and outsole) supplied by Piyavat Rubber Industry Co., Ltd., Thailand. Two types of polymer wax used; polypropylene wax (PP wax) and ethylene vinyl acetate wax (EVA wax) were Hoechst wax PP230 and BASF products respectively. Ultranox 626 (GE Speciality Chemicals) was used as an antioxidant.

2. Masterbatch Preparation

Three types of masterbatch were prepared ; no-wax addition, addition of PP-wax, and addition of EVA-wax (represented by the codes MB#1, MB #2 and MB#3 respectively), with an internal mixer (Chang Tong 1655). The formulations and internal mixer conditions are shown in Table 1. The mixed materials were sheeted on a 2-roll mill, and then granulated with a granulator.

3. Blending Method

Three blend ratios of PP with masterbatch containing 10, 20, 30 weight of rubber dust together with 1 phr antioxidant were melt blended in a single screw extruder (Betol 3225 J with a screw diameter 32 mm) connected with a self driven cavi-

Table 1. Masterbatch forMulation and Internal Mixer Conditions

Type of masterbatch	% PP	% dust	% wax	AO (phr)	Speed of rotor (rpm)	Set temperature (℃)	Mixing time (min.)
MB #1	20	80	–	1	70	175	20
MB #2	17	80	3	1	70	175	20
MB #3	17	80	3	1	70	175	20

ty transfer mixer (Iddon SD-CTM with a screw diameter 30 mm). All ingredients were randomly mixed by shaking in a plastic bag to give a random distribution before blending in the extruder. In this study, two types of die were used to produce two different profiles (pre-form of impact and tensile specimens). The temperature profile of the single screw extruder was 190/195/200/205℃ and the temperature profile of the SD-CTM was 195/200℃. The screw speed of the extruder and the SD-CTM were 40 and 80 rpm respectively. The extrudate was drawn from the die and then cooled in a water bath, with the aid of a haul-off unit to give a constant profile cross section. The long profile of the extrudate was cut and shaped to the size of the impact and tensile specimens. The residual extrudate were granulated and moulded into impact and tensile bars by using an injection moulding machine (Dr. Boy 22 S with a screw diameter of 24 mm).

4. Charpy Notched Impact Testing

The size of the impact specimens obtained from the extrudate profile and injection moulding was prepared according to ASTM D256. Impact strength testing was conducted using a 2-joule hammer of the Charpy impact tester (Ceast model 6545 100). The average value and the standard deviation of the impact properties were calculated from twenty samples.

5. Tensile Testing

The long profile extrudate was cut and shaped into tensile specimen by using a tensile cutting machine (Yasuda, No. 189 PF, Japan) with the forming holder ASTM D 638 type I. The tensile specimens obtained from injection moulding was according to ISO 527 type B. Tensile testing was conducted using an Instron mechanical tester (model 4301). The average value and the standard deviation of the tensile properties were calculated from twenty samples.

6. Particle Size and Particle Size Distribution

The particle size and particle size distribution of the rubber dust from the impact specimen were analysed by an optical microscope (Olympus BH2-UHA Japan), mounted with CCD camera (Hitachi KP-M1E/E, Japan) with common light and 20x objective lens. The particle size and particle size distribution of the recycled rubber were evaluated by using an image analysis software (Omniment 4, Buehler, USA.).

Ⅲ. Results and Discussion

1. Effect of Waxes and Rubber Dust Type on the Blends Processability by Extrusion

In this study, three different types of PP masterbatch were prepared; MB#1 without wax, MB#2 with PP wax and MB#3 with EVA wax. The comparison of the processability of PP filled with different types and loadings of rubber dusts were investigated together with the different types of masterbatches. Table 2 shows that not every composition of rubber dust and masterbatch type of the blends were able to be extruded to a controlled shape. For the impact profile extrudate, the PP/midsole blend showed the best processing characteristics, followed by PP/laminate and PP/out-

Table 2. Processability of Extruded Samples; (+) Controlled Shape of Profile, (-) Uncontrolled Shape of Profile

Scrap dust	Type of MB*	% Scrap dust	Impact bar	Tensile strip
Midsole (EVA)	MB#1 (no wax)	10	+	+
		20	-	+
		30	-	+
	MB#2 (PP wax)	10	+	+
		20	+	+
		30	+	+
	MB#3 (EVA wax)	10	+	+
		20	+	+
		30	+	+
Outsole (NR, BR, SBR)	MB#1 (no wax)	10	-	-
		20	-	-
		30	-	-
	MB#2 (PP wax)	10	-	-
		20	-	-
		30	-	-
	MB#3 (EVA wax)	10	-	-
		20	-	-
		30	-	-
Laminate	MB#1 (no wax)	10	+	-
		20	-	-
		30	-	-
	MB#2 (PP wax)	10	+	-
		20	-	-
		30	-	-
	MB#3 (EVA wax)	10	+	-
		20	-	-
		30	-	-

*MB=masterbatch

sole blends. The blends containing lower content of midsole scrap dust (10%) could be shaped for both impact and tensile profiles for all types of masterbatches while at higher percentage of rubber only the masterbatches including wax could be shaped.

For the PP filled with outsole rubber dusts, it was found that at every composition of rubber dust and masterbatch type, the blends were unable to be extruded to a controlled shape. The laminate dust/PP blends could be shaped only at the lower percent concentration of scrap dust (10%) for all the masterbatches i.e. including waxes or without wax. The results showed that waxes have a significant effect on processing particularly in PP/midsole blends, by functioning as a lubricant in the blend, which decreased the resistance to movement of molecular chains of the blends, resulting in enhancement of the flow. In addition, the midsole dust (EVA) which has similar structure to the PP and EVA waxes as well as the PP matrix would result in better compatibility to PP. While the outsole dust which was composed of various types of crosslinked elastomer (NR, SBR and BR) was not compatible with either of the two waxes, resulting in masterbatches incompatible with the PP.

The laminate dust which is a mixture of the outsole and midsole dusts had intermediate processability of the blends. For the tensile profile extrudate, it was also found that the midsole scrap rubber dust lead to better processability than the outsole and the laminate dusts.

2. Effect of Rubber Dust Type and Processing Methods on Impact Strength of the PP Blends

It has been reported in various publications that impact strength of PP can be improved by physical blending with various rubbers. However, the characteristics of the rubber additive are of critical importance in determining the toughness of the final products. Among these, the size of the rubber particles, the phase structure within the rubber particles the glass transition of the rubber

Table 3. Impact Strength (I.S.) of Extruded Samples

Batch	Midsole			Outsole			Laminate		
	I.S.(kJ/m²)	SD	% variation	I.S.(kJ/m²)	SD	% variation	I.S.(kJ/m²)	SD	% variation
PP	4.06	0.349	8.6						
#1-10	4.46	0.498	11.2	-	-	-	4.4	0.689	15.6
#1-20	-	-		-	-	-	-	-	-
#1-20	-	-		-	-	-	-	-	-
#2-10	4.28	0.356	8.3	-	-	-	4.14	0.435	10.5
#2-20	5.17	0.438	8.5	-	-	-	-	-	-
#2-30	4.91	0.394	8.0	-	-	-	-	-	-
#3-10	4.7	0.571	12.2	-	-	-	4.34	0.578	13.3
#3-20	4.41	0.425	9.6	-	-	-	-	-	-
#3-30	4.45	0.286	6.4	-	-	-	-	-	-

Table 4. Impact Strength (I.S.) of Injection Moulded Samples

Batch	Midsole			Outsole			Laminate		
	I.S.(kJ/m²)	SD	% variation	I.S.(kJ/m²)	SD	% variation	I.S.(kJ/m²)	SD	% variation
PP	4.22	0.544	12.9	-	-	-			
#1-10	6.38	0.208	3.3	6.19	0.370	6.0	6.40	0.275	4.3
#1-20	6.61	0.294	4.5	6.94	0.579	8.3	6.59	0.231	3.5
#1-20	7.06	0.462	6.5	7.62	0.694	9.1	6.79	0.494	7.3
#2-10	6.59	0.234	3.6	6.31	0.357	5.7	6.66	0.323	4.9
#2-20	7.56	0.295	3.9	6.57	0.332	5.1	6.56	0.260	4.0
#2-30	7.86	0.663	8.4	6.82	0.489	7.2	6.36	0.359	5.6
#3-10	6.72	0.413	6.1	6.6	0.278	4.2	6.55	0.263	4.0
#3-20	6.99	0.471	6.7	6.78	0.424	6.3	6.41	0.248	3.9
#3-30	7.40	0.302	4.1	7.22	0.056	7.8	6.57	0.376	5.7

and the adhesion between the rubber and the matrix are of particular importance. The rubber droplets must be at least as large as the crack they are trying to stop. It has been reported the optimum rubber particle size for toughening of pseudoductile polymers was about 0.1-0.5 micron.[14]

Results of impact strength of extruded samples (midsole and laminate blends) in Table 3 show that the increase of scrap dust loading had a little effect on the impact strength of the blends and the impact strengths of all the blends were similar to pure PP but lower than the injection moulded samples (shown in Table 4). Addition of the rubber dust to PP gave higher impact strengths of the injection moulded blends than were acheived with the unfilled PP. Similar results were obtained for all of rubber dust types and masterbatch types. The rubber particles could play an important role in improving the impact strength of the injection moulded samples by functioning as stress concentrators under deformation. The increasing percentage of loading of midsole and outsole scrap dust gave an impact strength shift to slightly higher values while the impact strength for laminate

Table 5. Particle Size and Particle Size Distribution of Extruded Samples

Masterbatch type	Scrap dust content (%)	Midsole		Outsole		Laminate	
		Diameter(μm)	Range(μm)	Diameter(μm)	Range(μm)	Diameter(μm)	Range(μm)
MB#1	10	2.09	0.612-47	-	-	-	-
	20	-	-	-	-	-	-
	30	-	-	-	-	-	-
MB#2	10	1.63	0.612-29	-	-	-	-
	20	2.28	0.612-51	-	-	-	-
	30	2.26	0.612-33	-	-	-	-
MB#3	10	2.20	0.612-19	-	-	-	-
	20	2.36	0.612-35	-	-	-	-
	30	1.51	0.612-39	-	-	-	-

Table 6. Particle Size and Particle Size Distribution of Injection Moulded Samples

Masterbatch type	Scrap dust content (%)	Midsole		Outsole		Laminate	
		Diameter(μm)	Range(μm)	Diameter(μm)	Range(μm)	Diameter(μm)	Range(μm)
MB#1	10	2.02	0.612-77	3.76	0.612- 38	2.72	0.612-33
	20	1.97	0.612-51	3.40	0.612- 67	2.10	0.612-38
	30	1.23	0.612-35	3.59	0.612- 43	1.83	0.612-62
MB#2	10	1.98	0.612-50	2.70	0.612- 39	2.53	0.612-55
	20	1.70	0.612-48	3.00	0.612- 81	1.99	0.612-42
	30	1.54	0.612-82	3.04	0.612- 83	1.85	0.612-70
MB#3	10	1.81	0.612-49	3.45	0.612- 42	2.66	0.612-36
	20	1.66	0.612-50	3.26	0.612- 57	2.01	0.612-41
	30	1.37	0.612-41	2.89	0.612-112	1.93	0.612-39

scrap dust was similar to the PP resin.

It has been reported that the impact strength is better with smaller rubber particle sizes in an EPDM modified PP system.[15] In this study, the results of the particle size and the particle size distribution of rubber dust shown in Table 5 and 6 revealed that smaller particle size of the rubber were obtained from the injection moulded samples than the extruded samples, resulting in higher impact strength of the injection moulded samples. The injection moulded samples also have narrow particle size distributions. This may come from the second processing step of the injection moulding processed samples having experienced more shear action and increased homogenization times of the blends resulting in the dispersion of agglomerates to smaller size.

3. Effect of Rubber Dust Type on Tensile Properties of PP Blends

3.1 Analysis of Tensile Properties

In this study, the ultimate tensile strength and elongation at break results were invalid as the injected tensile samples were stretched over the maximum machine strain point (500%) without breakage. Results of yield stress, yield strain and modulus of the extruded samples (only PP/midsole blends) and injection moulded samples are shown in Table 7 and 8 respectively. In general, the tensile properties of PP filled with rubber decreased because of the poor adhesion or the incompatibility between the PP and the rubber phases. In this study, it was also found that all blends had tensile properties lower than the pure PP. Addition of rubber dust into the PP led to an unstable flow which caused premature rupture of the specimens. The increase in the loading of scrap dust results in a consistent decrease in the yield stress and modulus. The yield stress of the extruded samples were lower than the injected samples. This was due to the occurrence of many voids, probably at the PP/scrap dust interface, in the extruded samples that act as defects in the blends reducing the ability of the blends to resist loading. It may also be due to the poor adhesion between the scrap dust and PP, so that the interface between the scrap dust and PP act as flaws in the PP.

The rubber particle size and size distribution also influenced the tensile properties of the blend. The results in Table 5 and 6 show that the particle size of injection moulded samples were smaller and of narrower particle size distribution than the extruded samples. The smaller particle size of dust in the injection moulded samples may be from a more thorough mixing during the amorphous melt phase of PP giving the more homogeneous particle size and resulting in the better tensile properties of the injection moulded samples.[16]

Table 7. Tensile Properties of Extruded Samples (Midsole Blended)

Sample	Yield stress (MPa)	Yield strain (%)	Modulus (MPa)
PP	29.86	10.48	760.83
M (#1-10)	25.58	10.35	686.14
M (#1-20)	18.80	10.89	500.57
M (#1-30)	15.52	8.63	438.80
M (#2-10)	26.55	9.53	725.74
M (#2-20)	21.52	11.01	559.94
M (#2-30)	16.44	10.73	447.76
M (#3-10)	25.94	10.26	694.74
M (#3-20)	19.4	10.47	515.57
M (#3-30)	11.68	8.78	299.51

Table 8. Tensile Properties of inj ection Moulded Samples

Batch	Midsole			Outsole			Laminate		
	Yield stress (MPa)	Yield strain (%)	Modulus (MPa)	Yield stress (MPa)	Yield strain (%)	Modulus (MPa)	Yield stress (MPa)	Yield strain (%)	Modulus (MPa)
PP	31.80	10.88	816.45	31.80	10.88	816.45	31.80	10.88	816.45
#1-10	29.16	9.42	808.07	28.67	9.31	712.51	26.69	9.82	781.77
#1-20	25.98	9.28	718.51	23.31	9.14	587.28	22.88	9.26	675.92
#1-30	23.00	10.17	639.28	19.94	10.54	487.00	24.40	8.83	643.37
#2-10	28.38	9.45	784.41	28.89	11.89	641.21	28.62	8.74	757.13
#2-20	25.98	8.80	709.43	24.92	12.53	558.30	25.77	9.08	681.13
#2-30	22.72	10.13	609.74	20.90	13.66	495.95	22.40	9.39	597.58
#3-10	29.20	9.17	758.80	20.09	10.14	709.14	29.74	8.76	805.06
#3-20	27.59	10.01	668.11	23.35	9.64	589.51	26.19	9.05	692.40
#3-30	22.30	10.90	568.44	18.80	11.37	475.14	23.29	9.99	606.91

3.2 Analysis of Stress Concentration Parameters

Analysis of mechanical properties of the two-phase blends (or composites) can be carried out by using the "first power" law and "two-thirds power" law, stated below:[17]

$$\sigma B = \sigma P(1-\phi) \quad (1)$$

$$\sigma B = \sigma P(1-\phi^{2/3}) \quad (2)$$

Where σB and σP denote the mechanical properties of the blend and matrix, respectively. Where ϕ is the volume fraction of the dispersed phase. For a completely random distribution of the dispersed phase, the first power law relationship is applied and for the case of spherical inclusion the two-thirds power law with an appropriate weighting factor is considered.

Gupta and Purwar introduced a stress concentration parameter (S) to the "first power" law while Nielsen incorporated stress concentration parameter (S′) to the "two-thirds power" law, shown in equation 3 and 4 respectively.

$$\sigma B = \sigma P(1-\phi)S \quad (3)$$

$$\sigma B = \sigma P(1-\phi^{2/3})S' \quad (4)$$

The parameter S accounts for the weakness in the structure introduced through discontinuity in stress transfer or formation of stress concentration points at the filler-polymer interphase, in analogy to the parameter S′. When the value S (or S′) is unity "no stress concentration effect" is indicated, the lower the value of S (or S′) the greaterthe "stress concentration effect". The results of S and S′ of extruded samples and injection moulded samples were presented in Table 9 and 10. The stress concentration parameters of the extruded samples increased when the volume fraction of the rubber dust increased. This indicated the weakness or discontinuities present in the structure of the blends. The S and S′ of the injection moulded samples for every blend composition were close to unity. This indicated that there was little stress concentration effect on the blends. The results correlated to the lower tensile properties of the extruded samples than the injection moulded samples.

Table 9. Stress Concentration Parameters of Extruded Samples

Type of masterbatch	% Scrap dust in blend	S			S′		
		Midsole	Outsole	Laminate	Midsole	Outsole	Laminate
MB#1	10%	0.95	-	-	1.09	-	-
	20%	0.79	-	-	0.96	-	-
	30%	0.74	-	-	0.94	-	-
MB#2	10%	0.99	-	-	1.13	-	-
	20%	0.90	-	-	1.10	-	-
	30%	0.79	-	-	1.00	-	-
MB#3	10%	0.97	-	-	1.11	-	-
	20%	0.81	-	-	0.97	-	-
	30%	0.56	-	-	0.77	-	-

Table 10. Stress Concentration Parameters of Injection Moulded Samples

Type of masterbatch	% Scrap dust in blend	S			S′		
		Midsole	Outsole	Laminate	Midsole	Outsole	Laminate
MB♯1	10%	1.02	1.00	0.93	1.17	1.15	1.07
	20%	1.02	0.92	0.90	1.24	1.11	1.09
	30%	1.03	0.90	1.10	1.31	1.14	1.39
MB♯2	10%	1.00	1.01	1.00	1.15	1.16	1.15
	20%	1.02	0.98	1.01	1.24	1.19	1.23
	30%	1.02	0.94	1.01	1.29	1.19	1.28
MB♯3	10%	1.02	1.02	1.04	1.17	1.17	1.19
	20%	1.08	0.92	1.03	1.32	1.12	1.25
	30%	1.00	0.84	1.05	1.27	1.07	1.33

IV. Conclusions

Mechanical properties of PP filled with recycled rubber dusts can vary significantly with rubber dust types and processing methods. By using the recycled rubber, we have produced PP blends with higher impact strengths than unfilled PP depending on type and amount of the rubbers. The impact strengths of the compounds prepared by extrusion were lower than those prepared by reprocessing in injection moulding. The rubber particle size influenced the impact strength, the smaller particle size enhanced the impact strength because of more effective energy absorption that occurred than with the larger particle dust. Incorporation of recycled rubber dust into PP resulted in a decrease in the yield stress and modulus. It was due to poor adhesion between the scrap dust and the PP. The analysis of stress concentration parameters also confirmed the effect of rubber dust on the mechanical properties of the blends.

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