COMPOSITES FROM GROUND TYRE RUBBER. EFFECT OF SURFACE MODIFIED BY WETTING ADDITIVES

J. Cañavate, P. Casas, F. Nogués, F. Carrillo and X. Colom

Department of Chemical Engineering, Technical University of Catalonia,
Colom 1, 08222 Terrassa, Barcelona, Spain
xavier.colom@upc.edu

ABSTRACT

The concern about the amounts of used tyres that end in landfills and the environmental problems that they produce have lead to the research of alternative ways to use these residues in common applications. An adopted practice in the recovering procedures starts by grinding the tyres in order to obtain a powder known as Ground Tyre Rubber (GTR). In this paper, GTR was used as filler in a matrix of HDPE. The incompatibility between the two phases, the already crosslinked rubber particles and the thermoplastic (HDPE), leads to a difficult mixture of both materials and a decrease of the mechanical properties, comparatively with 100% HDPE. The effect of some waxes and wetting additives added to the HDPE/GTR mixture was investigated in order to improve adhesion between the two phases. The influence of these additives was determined by mechanical properties, DSC analysis and SEM. An acidic wetting additive and a non polar polyethylene wax gave the best results regarding mechanical properties, dispersion of the GTR particles and adhesion.

1. INTRODUCTION

From July 2006 the EU Landfill Directive has been banned the disposal of tyres (whole and shredded). The ban applies to almost all tyres including car, commercial, motorbike, aircraft, and industrial (including solid tyres). In Europe around 250 million tyres are withdrawn from use every year. Tyre rubber, due to its crosslinked structure and presence of stabilizers and other additives needs a very long time for natural degradation. This enormous amount of tyres wasted every year requires the development of strategies directed to its recovery or reuse. Around 60% of this amount is used as an energy source in some way via incineration [1], as mixtures with asphalt or concrete [2], combinations with natural rubber [3] or in toughened polymers like epoxy resins [4]. During the last years a great amount of efforts has been devoted to finding new fields of application for ground tyre rubber (GTR). The incorporation of GTR into a polymer matrix has some limitations due the poor matrix-GTR adhesion, and the lacks of reactive site on the particle surface are one of the most important factors that affected the mechanical properties.
In this study, GTR has been used as filler in a matrix of HDPE. The incompatibility between the two phases, the already crosslinked rubber particles and the thermoplastic (HDPE), leads to a difficult mixture of both materials and a decrease of the mechanical properties. The effect of some waxes and wetting additives added to the HDPE/GTR mixture has been investigated in order to improve adhesion between the two phases. The influence of these additives has been determined by mechanical properties, DSC analysis and SEM.

2. EXPERIMENTS

High-density polyethylene (HDPE) with a melt flow index of 1.35 g/min and density of 960 kg/m^3 was used. Commercial ground reused tyres were obtained from industrial rubber recycle plant, already micronized with a particle size average of 400-600 µm. This material was supplied by Alfredo Mesalles (Spain) in the usual form that industrial clients require. No further processes were applied. The additives were supplied by two different companies: wetting additives were provided by BYK GmbH (Wesel, Germany) and waxes were from Clariant Ibérica S.A. (Barcelona, Spain).

The mixing process was carried out in a two roll mill heated at 150-155ºC. The first minute only the HDPE matrix was melted and then, the mixture reused tyre plus additive (previously mixed) was added and mixed for another 10 minutes. Composite sheets (150 x 150 x 2 mm) were prepared by hot press moulding at 100kN and 170ºC for 10 minutes. After this step, the sample sheets were cooled for 5 min under pressure in the same press, refrigerated by water. The materials were then shaped mechanically in testing specimens. The different compositions prepared in that way are shown in table 1.

Table 1.- Composition of the mixtures 80%HDPE/20%GTR/Additive

HDPE/GTR Mixture	Additive Code	%wt HDPE	%wt GRT	% wt * Additive	%wt * Additive
HDPE/GTR		80	20	-	-
HDPE/GTR/Disperbyk-108	2,5%DB108	80	20	2,5	-
HDPE/GTR/Disperbyk-108/Byk Synergist-2100	2,5%DB108/2%BS2100	80	20	2,5	2
HDPE/GTR/Byk-9077	5%B9077	80	20	5	-
HDPE/GTR/Byk-9077/Byk Synergist-2100	5%B9077/2%BS2100	80	20	5	2
HDPE/GTR/Byk-P 105	3%BP105	80	20	3	-
HDPE/GTR/Licowax PE520	5%LPE520	80	20	5	-
HDPE/GTR/Licocene PP1502	5%LCPP1502	80	20	5	-
HDPE/GTR/Ceridust 5551	2,5%BP105	80	20	2,5	-

(*) % on GTR

Tensile test was carried out to determine the evolution of Young's modulus, tensile strength, elongation at break and toughness on mixtures of HDPE/GTR without additives and HDPE/GTR + additives. For this purpose, the ASTM D-638 was applied using an Instron 3366 universal machine. The testing speed was 20 mm/min and the samples cross-sections were 6.1·2.0 mm. The measures were taken as indicated in the aforementioned standard, at a temperature of 23ºC ± 2ºC and a relative humidity of 50 ± 5%. Five replicate samples were analyzed, and average and standard deviation percentages were calculated.

The dynamic thermal behavior of the samples was analyzed using heat flow DSC. The measurements were made with a Mettler TA4000 termoanalyser coupled with a DSC 30 apparatus. Samples were heated from 40 to 200ºC at a heating rate of 10 K/min and using synthetic air as purging gas at a flow rate of 40 ml/min.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

The mechanical properties of different dosages of GTR added to the HDPE matrix are shown in table 2. It can see that the most affected properties are elongation at break and toughness. According to previous studies [5], the mixture 20%GTR/80%HDPE is a good compromise between GTR quantity (which interest is as much as possible) and mechanical properties (- 18% of Young Modulus, -17% of Tensile Strength, -67% of Elongation at break and -70% of Toughness, compared to neat HDPE). Samples with higher amount of GTR are more difficult to process and show a decrease too important in Young's Modulus and tensile strength. This composition (20%) was then used to compare the effect of additives.

Table 2: Young Modulus, tensile strength, elongation at break and toughness vs. different GTR %

GTR%	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Toughness (J)
0	920	17,2	39	3,92
5	1115	17,8	25	2,31
10	890	16,4	17,7	1,62
20	775	14,2	13,3	1,19
40	365	8,9	13,1	0,82

At low dosages of GTR (5%) the material improves stiffness and tensile strength but when around 10% of GTR is added then all the properties drop down. The same result was observed by Colom *et al* [5]. A possible explanation for this could be that at low dosages of none uniformly distributed GTR particles, those act as stress concentrating flaws. GTR particles at higher dosages can undergo deformation and relieve a portion of the applied stress due to the more uniformly distribution in the HDPE matrix.
In order to evaluate the previous effect of the additive in the HDPE matrix, different percentage of both components has been tested. The following results can be observed: (1) Young Modulus increases in all the mixtures HDPE/Additive when comparing with neat HDPE, (2) additives reduce Elongation at Break and Toughness as well, (3) tensile strength increase with some of the additives, although other additives like BP105, polyethylene and polypropylene waxes slightly decrease the tensile strength.

Figure 1 shows the mechanical properties of the mixture 20%GTR/80%HDPE with different wetting additives and waxes compared to the reference sample without additives.

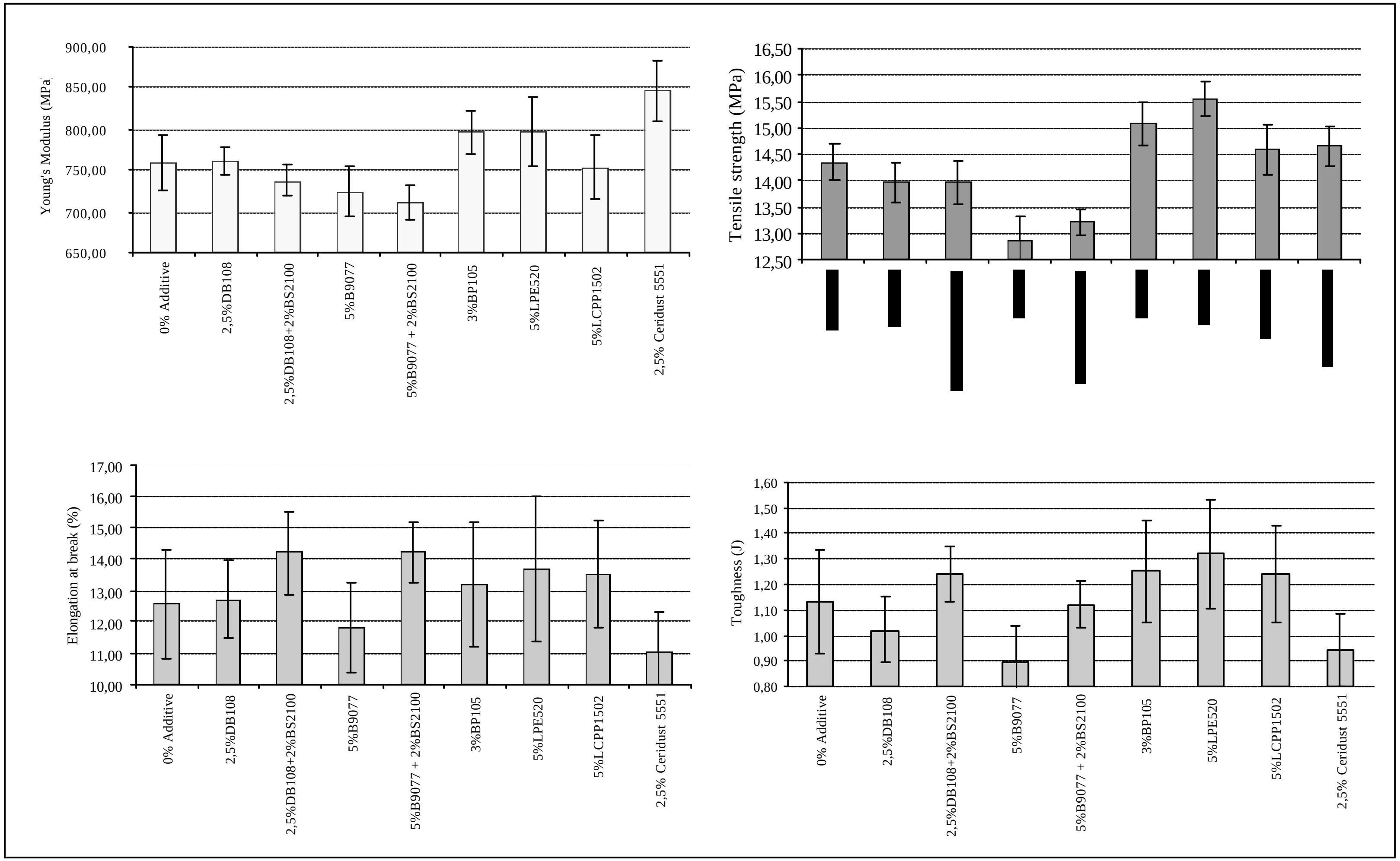


Figure 1: Young's Modulus, tensile strength, elongation at break and toughness vs. the mixture 80%HDPE/20%GTR plus the following percentages of additives on GTR: 2,5% DB108, 2,5%DB108 + 2%BS2100, 5%B9077, 5%B9077 + 2%BS2100, 3%BP105, 5%LPE520, 5% LCPP1502 and 2,5%Ceridust 5551.

The main results obtained are: (1) basic additives as DB108 and B9077 do not improve any of the properties in the mixture. Only when they are mixed with the synergist additive BS2100 their elongation at break and toughness (only DB108) are slightly increased. The synergist additive has a few acidic groups which some could react with the basic additives (synergist effect) and some others with basic groups on the GTR surface, (2) ester wax Ceridust 5551 seems to have an important influence on the resin following the same behavior than when is mixed only with the matrix. Although Young's Modulus and tensile strength increase, the effect is not positively on elongation and toughness, (3) mixtures with better properties are those including BP105P, LPE520 and LCPP1502. Despite behavior between the two polyolefin waxes is very similar, LPE520 gives a better improvement of the properties and (4) acidic groups of BP105P may interact with the basic ones of the carbon black contained on the GTR surface. There is an improvement of wetting via decreasing the interfacial energy between the two phases and a dispersing effect with the polar part of the additive anchored on the GTR surface and the non polar part extended in the HDPE matrix. The effect of LPE520 on the mechanical properties can be attributed at: a) existence of non polar additives like zinc stearate present into the GTR's particles that migrates to the surface. Once there, it could be solubilised onto the HDPE matrix helped by the temperature and low viscosity provided by the wax. With the achievement of a "cleaner" GTR surface, the wetting of the particles by the mixture HDPE/wax is improved. b) LPE520 is a polyethylene wax which reduces the viscosity of the matrix and helps to penetrate at the GTR particle porous (helping adhesion). There is an improvement of the ability of the matrix to flow into the cracks and pores present in the particles of rubber, obtaining in that way a better mechanical adhesion.

Once studied the effect of the additives in the mixture 20%GTR/80%HDPE. The best additives, DB108+BS2100, BP105, LPE520 and LCPP1502, have been used to analyze the mechanical properties of different GTR/HDPE compositions. Table 3 shows all the results obtained. Considering the global behavior, the effect on studied properties and compositions, the additive BP105 gives the best performance, followed by LPE520, LCPP1502, the combination of DB108 + BS2100 and the samples without additives. Properties are generally improved with the use of additives. Young modulus increase in all GTR compositions when additives are incorporated, tensile strength increase slightly, elongation at break only increase with the GTR dosages of 20 and 40% and toughness, only increases with a 20% of GTR.

In the case of the mixture 20%GTR/80%HDPE properties increase with the use of additives, specially with BP105 and LPE520 where young modulus is increased 4,84% and 4,93%, tensile strength 5,1% and 8,44%, elongation at break 5,09% and 9%, and finally, toughness 10% and 16,8% respectively.

Table 3: Young's Modulus, tensile strength, elongation at break and toughness vs. different percentages of GTR and the following additives dosages: 2,5%DB108 + 2%BS2100, 3%BP105, 5%LPE520 and 5% LCPP1502.

GTR %	Additives	Young Modulus (MPa)	Tensile Strenght (MPa)	Elongation at break (%)	Toughness (J)
0	without	930	17,50	39,00	3,85
	2.5%DB108+2%BS2100	1080	20,25	29,00	2,98
	3%BP105	1060	16,50	36,00	3,60
	5%LPE520	1085	17,00	31,00	3,45
	5%LCPP1502	1055	16,60	36,50	3,70
5	without	1015	17,85	25,00	2,40
	2.5%DB108+2%BS2100	935	17,50	27,00	2,50
	3%BP105	1050	18,50	20,00	1,85
	5%LPE520	1010	18,30	20,50	2,00
	5%LCPP1502	1070	18,80	19,50	1,95
10	without	880	16,50	17,50	1,60
	2.5%DB108+2%BS2100	840	16,00	15,00	1,40
	3%BP105	910	17,00	18,00	1,70
	5%LPE520	925	17,20	14,50	1,60
	5%LCPP1502	900	16,50	18,00	1,45
20	without	750	14,50	12,50	1,00
	2.5%DB108+2%BS2100	730	14,00	12,00	1,20
	3%BP105	800	15,00	13,20	1,25
	5%LPE520	795	15,50	13,50	1,30
	5%LCPP1502	745	14,60	13,30	1,20
40	without	375	8,80	12,00	0,90
	2.5%DB108+2%BS2100	360	6,70	13,00	0,85
	3%BP105	425	8,50	14,00	0,90
	5%LPE520	410	9,00	15,00	0,95
	5%LCPP1502	405	8,40	11,00	0,60

3.2. DSC analysis

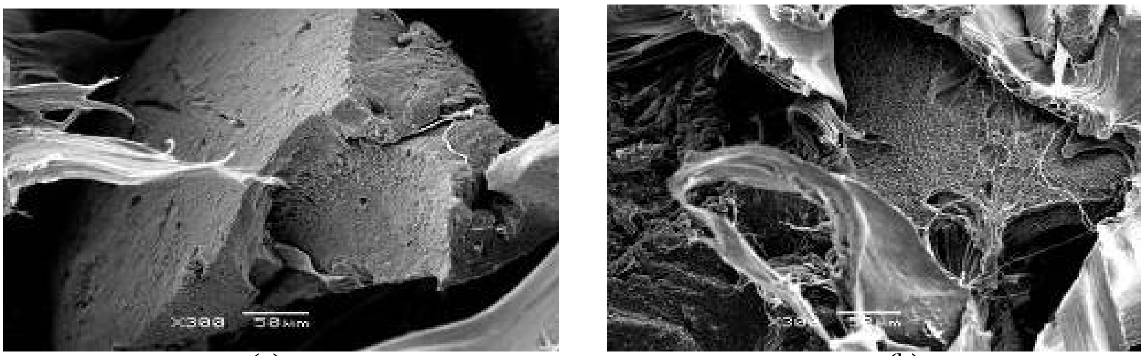
In order to study the thermal behavior of the chosen additives with the HDPE matrix, a DSC analysis was performed. Obtained results are shown at table 4. From the values may be deduced that all additives, even when added in small proportion to the HDPE, produce a displacement of the melting temperature (Tonset) of HDPE and a change in the enthalpy of melting. The DSC curves (not reproduced here) show only the HDPE melting point with no indication of other melting point. This is probably due to the incorporation of the additive to the crystal lamellae of HDPE. Results obtained in case of the wax LPE520 agree with those obtained by other researchers [6,7] which deeply studied other HDPE/wax blends and attributed this effect to cocrystallization. The increase of the amount of wax tends to decrease the enthalpy of the blend, as a result of the smaller value of enthalpy of the wax when compared to the pure HDPE.

Table 4.- DSC analysis of the HDPE blended with additives. The % is referred to the amount of additives included in the 80/20 blend.

Sample	**?Hm (Jg^{-1})**	**T_{onset} (ºC)**	**T_{peak} (ºC)**
neat HDPE	182,51	121,41	131,21
2,5%DB108	161,16	119,80	131,61
2%BS2100	182,42	121,30	130,77
3%BP105	175,24	118,43	131,15
5%LPE520	175,08	119,41	131,09
5%LCPP1502	177,45	120,78	131,20
2.5%Ceridust5551	177,43	118,81	132,19
5%B9077	175,43	119,58	130,64
5%B9077-2.5%2100	168,34	120,42	131,22

3.3. Scanning electronic microscopy

Fracture surfaces of the blends containing additives that gave better mechanical properties were examined by SEM. Figure 2 contains SEM images of mixture 20%GTR/80%HDPE a) sample control without additives and with 5%LPE520. In picture a) the GTR particles do not display any signs of HDPE adhesion. Instead photograph b) corresponding to the composite with LPE520, shows good adhesion between the two phases. The existence of some filaments protruding from the GTR particles indicates a sound interaction within the particle. As mentioned before, the polyethylene wax mixed with the HDPE, reduces viscosity and favors the polymer interlocking in the interstices of the GTR particles.



(a) (b)

Figure 2: SEM Microphotographs of the mixtures 20%GTR/80%HDPE plus the following additives: a) no additives (control), and b) 5% LPE520

4. CONCLUSIONS

From the study of mechanical properties of the composites prepared, the following conclusions can be drawn: i) the mechanical properties (especially toughness and elongation at break) decrease with the amount of GTR, being the mixture 20%GTR/80%HDPE a balanced compromise between amount of GTR and good mechanical properties ii) when applied to the mixture 20GTR/80HDPE, the best performance was obtained with the wetting agent BP105 and the polyethylene wax LPE520 iii) additives increase the Young's modulus and the tensile strength due to a possible cocrystallization effect with the HDPE matrix and vi) when used in blends containing different amounts of GTR, BP105 and LPE520 gave always the best results.

The DSC data support the existence of cocrystallization of the additives with HDPE, since there appears only a melting point related to HDPE and there is a variation of enthalpy and melting temperature of HDPE when blended with the studied additives. In case of LDE520, the variation is greater to higher content of additive.

SEM microphotographs show that LPE520 acts adequately promoting adhesion. Fracture surface reveals figments of HDPE attached to the particles. BP105 images show particles better embedded in resin than any other additives studied.

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