RESEARCH ARTICLE

The development of rubber-thermoplastic blends from ground tyre rubber and waste polypropylene**

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Abstract: Ground Tyre Rubber (GTR) from scrap automotive and truck tyres was blended with Waste Polypropylene (WPP) from injection moulded products to prepare GTR/WPP blends. The blends were prepared in a Haake Rheocord PolyLab System, operating at 180 °C and 30 rpm for 8 minutes. The degree of crystallinity of the WPP in the GTR/WPP blend was found to be unchanged up to a GTR level of 60 % by weight. Crystalline melting point and re-crystallization temperature showed a significant decrease with GTR content. Optical micrograph of the blends containing up to 60 wt% GTR showed a similar morphology, in which the GTR was dispersed in a continuous WPP phase. The GTR dispersed phase grew in size with GTR content until at 70 wt%, it changed to a continuous phase. However, all blends showed a mixture of cohesive, adhesive and ductile failures. The response to tensile loading ranged from a ductile plastic response with WPP-rich blends to a high extension–rubbery response with GTR-rich blends. Under impact loads, brittle fracture occurred in blends containing up to 40 wt% GTR, with ductile fracture thereafter. Hardness, tensile strength, secant modulus at 7% strain and tear resistance decreased with increase in GTR content, while % elongation at break and impact failure energy increased.

Keywords: Ground tyre rubber, mechanical properties, rubber thermoplastic blends, waste polypropylene

INTRODUCTION

Polymer waste accounts for a major share of all waste materials collected in the world today. With the rapid development of the automobile industry, waste tyres contribute significantly to the increased polymer waste volume. Similarly, the volume of thermoplastic waste also appears to have increased significantly over the years since the increase in use of commodity thermoplastics, such as polyethylene (PE), polyvinyl chloride (PVC), and polypropylene (PP), over conventional materials in domestic applications. Polymer waste can be either disposed of in a safe manner or be recycled and reused[1, 2]. Alternatively these materials can be utilised to generate energy or to recover fuels[3, 4] and valuable chemicals, which are feedstock for other industries[5, 6].

Polymer waste can also be blended with virgin materials to produce polymer blends having desired properties. The blending of two polymer waste materials will reduce the price of the end product.

A polymer blend such as rubber-thermoplastic blends when rubber-rich, produces soft thermoplastic elastomers, while plastic-rich blends produce rubber toughened thermoplastic[7]. Rubber toughened thermoplastics which exhibit flexible and high impact properties can be used as economical alternatives for ordinary plastic materials. The market for such materials has grown dramatically because of the ability to recycle and reprocess them using conventional thermoplastic machinery [8-11]. However, literature reveals that the additions of rubber to a thermoplastic matrix results in a significant overall deterioration in mechanical properties[8, 9, 12, 13].

The properties of rubber-thermoplastic blends are reported to be dependent on the type of rubber/thermoplastic used, the composition and adhesion between the phases[10]. Further, the adhesion between the materials depends on the melt viscosity of the matrix phase, the shape and size of the dispersed phase, and the processing conditions. In addition, blend properties also vary with the moulding techniques used to make test specimens[14].

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The use of polypropylene (PP) is quite significant in the world today, as products made out of PP are used for both indoor and outdoor and certain engineering applications due to its low cost, low density, high rigidity and hardness, high softening temperature and excellent electrical and chemical resistance at higher temperatures[15,16]. The availability of large quantities of recycled rubber (RR), and the advantages of PP, blends based on RR/PP has led to many studies and reports[10,12,17-19]. It has been found that RR/PP blends, when compared to NR (Natural Rubber)/PP blends prepared with the same rubber content, showed slightly higher tensile strength and Young's modulus but with lower elongation at breaks[12, 17]. RR in ground form was used in these studies.

This paper presents the preliminary work on the processing and development of blends containing waste materials from the polymer industry for use in products such as roof slates, sports surfaces and industrial belts. The initial work was focused on the preparation of simple rubber-thermoplastic blends from ground tyre rubber and waste polypropylene, studies of their morphologies, physical property variations with composition and finally the identification of suitable blends for commercial applications.

METHODS AND MATERIALS

The waste poly propylene (WPP) used in this study was of injection moulding grade and was supplied by Plastic Reclamation Limited, UK. The ground tyre rubber (GTR), a recycled product from ambient ground scrap automotive and truck tyres, was supplied by Alruba Rubber Company, UK and had a 40 mesh size.

Compound processing and characterisation: Blends from GTR and WPP were prepared by melt mixing in a Haake Rheocord Polylab System at a rotor speed of 30 rpm and a temperature of 180 °C, for 8 min. Both GTR and WPP were added to the mixer at the same time. The weight percentages of each material were varied from 0% to 100 % in 10% intervals.

Maximum torque, steady state torque and time taken to reach steady state were obtained from the torque-time plots. Steady state was defined as the state when the torque was at 110% of the value recorded after 8 min. Torque reduction rate and the specific energy requirement were calculated according to Equation 1 and Equation 2, respectively.

Torque Reduction Rate = $\dfrac{(T_{max} - T_{ss})}{(t_{ss} - t_{max})}$ (1)

Where, T_{max} = maximum torque in Nm
t_{max} = time taken to reach maximum torque in min
T_{ss} = steady state torque, where, $T_{ss}=1.1*T_{min}$
T_{min} = torque at 8 min in Nm
t_{ss} = time taken to reach steady state in min

Specific Energy, $W = \dfrac{2\,\pi\,n \int_{t_1}^{t_2} M\,d}{m}$ (2)

Where, n = rotor speed in rpm
M = torque in Nm
$t_1 (= 0)$ = initial time in min
$t_2 (= t_{ss})$ = time at the end of processing (=time to reach steady state) in min
m = weight of the material processed in grams

Moulding of test specimens: Sheets, which were used to cut test specimens, were prepared by compression moulding in an electrically heated hydraulic press. The small pieces of blends from the Haake mixer were initially compressed under a 500 kN/m² pressure at 200 °C for 4 min, and then the pressure was slowly increased to 1000 kN/m² for another 4 min. The blends were subsequently cooled for 2 min under a 1000 kN/m² pressure in a cooling press.

Mechanical properties: Hardness tests were performed using a Wallace Dead Load Hardness tester according to BS EN ISO 868:2003 test standards.

Tensile tests were performed according to BS EN ISO 527-2: 1993 standard using a Lloyd Tensometer L10000, with a 500 N load-cell and crosshead speed of 50 mm/min. Elongation was determined using the crosshead displacement, and the secant modulus was calculated at 7% strain.

Tear tests were performed according to BS EN ISO 6383-1:2004 using a Lloyd Tensometer L10000 with a 500 N load-cell. Trouser test specimens were used.

Impact tests were performed, according to BS EN ISO 6603-2:2002, using a Rosand Falling Dart Impact tester. The impact test was conducted at a velocity of 3 m/s under 4 kg impact load. Impact properties were normalized by dividing by the thickness of each specimen. All these mechanical tests were carried out at a temperature of 22±2 °C.

Differential Scanning Calorimetry (DSC): Thermal properties such as melting temperature (T_m), peak crystallization temperature (T_{cp}), onset crystallization temperature (T_{co}) and heat of fusion (ΔH_f) were determined using a DSC 2010 Thermal Analyser. The thermograms were produced over a temperature range of 20ºC to 210ºC at a heating/cooling rate of 10ºC/min. The readings of T_{cp} and T_{co} were taken during the first thermal cycle and those of T_m and ΔH_f were taken during the second heating cycle. The degree of crystallinity of a blend was calculated using Equation 3.

$$\text{\% Crystallinity of the blend} = \frac{\Delta H_f}{\left(\Delta H_f\right)_c} \times 100 \qquad (3)$$

Where, ΔH_f = enthalpy of fusion of the blend

$\Delta H_{f\,c}$ = enthalpy of fusion of pure crystalline polypropylene and is taken from literature[20] as 209 J/g.
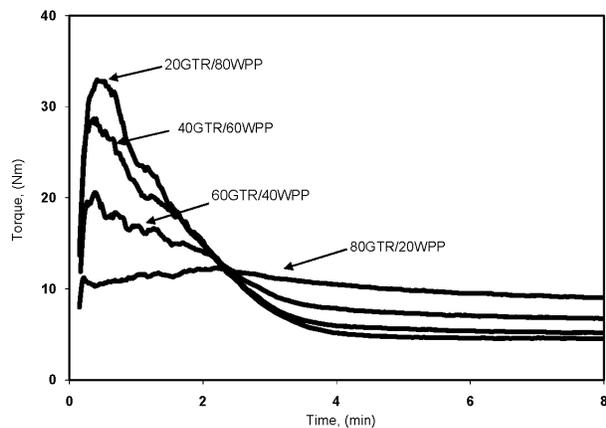
Morphological observations: The morphology of the blends was studied by optical and scanning electron microscopy. Microtomed films were examined using a bright field illumination technique on a Reichert MEF-3 microscope and the micrographs were obtained using ×10 magnification. A scanning electron microscope (SEM), Leica Cambridge Steroscan 360, was used to obtain SEM micrographs of the tensile fracture surfaces of the blends. The fractured ends of the specimens were mounted on aluminium stubs. The specimens were sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

RESULTS

The melt mixing behaviour of WPP, GTR and the blends of these two materials were studied. Figure 1 shows typical torque-time curves for blends of different compositions. The variations of maximum torque and steady state torque with GTR content are shown in Figure 2, while
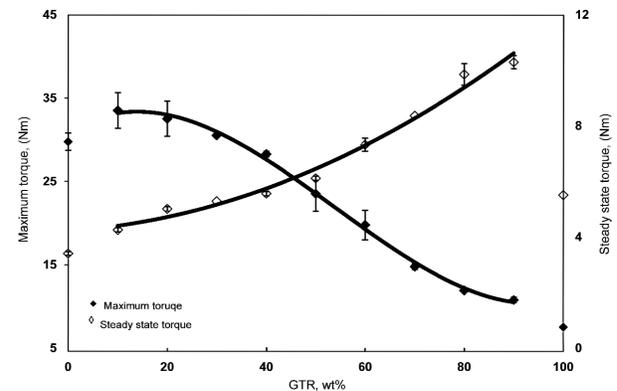

Figure 1: Torque development for GTR, WPP and the 50/50 blend

Figure 2: Maximum and steady state torque vs. GTR content
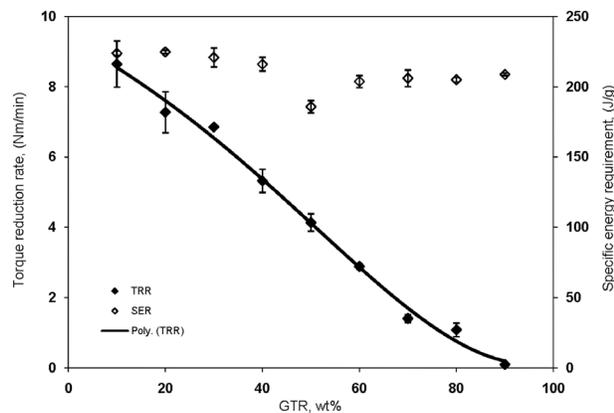
Figure 3: Torque reduction rate and specific energy requirement vs. GTR content
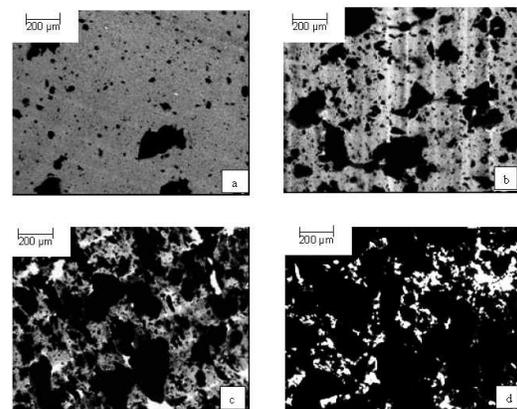

Figure 4: Optical Micrographs (×10)
    (a) 10GTR/90WPP   (b) 30GTR/ 70WPP
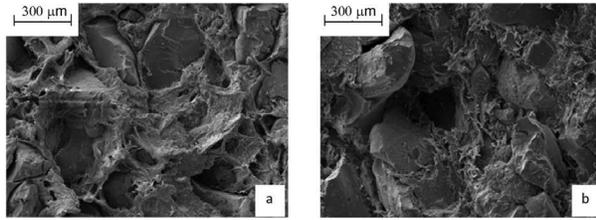   (c) 50GTR/50WPP   (d) 70GTR/30WPP

Figure 5: Scanning electron micrographs of tensile fracture
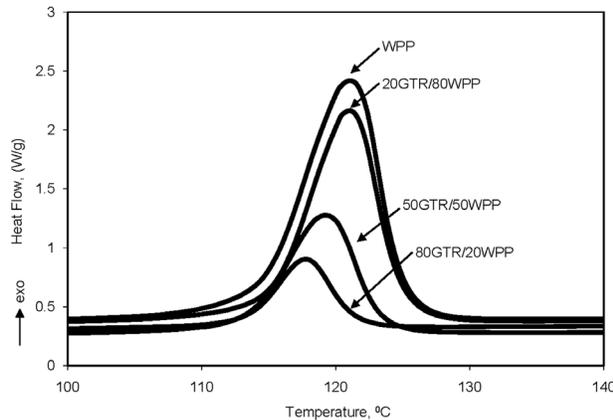surfaces   (a) 20GTR/80WPP   (b) 80GTR/20WPP

Figure 7: Re-crystallization exotherms for WPP and selected blend**s**

Figure 6: Melting endotherms for WPP and selected blends

showed knotty behaviour during tearing. Tear tests could
not be conducted for blends containing low GTR levels
due to the high stiffness of the specimens.

DISCUSSION

Processing characteristics

Torque-time curves in Figure 1 show an increase in
torque due to the mechanical resistance exerted on the
rotors when loading with un-molten materials. The torque
decreases with softening and melting of the WPP when
it is subjected to thermal and mechanical stresses, and
stabilises upon completion of the melt mixing process.

Compared to the WPP, GTR is softer at loading, but
viscous at higher processing temperatures. As a result,
the maximum torque decreases with increase in GTR
content, while the steady state torque increases. The
steady state torque is an indicator of the viscosity of
the mix and is used to assess its processability. Hence,
an increased difficulty in processability with increase
in GTR content is evident. An increase in steady state
torque with increase in recycled rubber content in virgin
polypropylene-recycled rubber blends has been reported.
However, the increase exhibited was linear[17]. Compared
to virgin PP, WPP has a higher tendency to undergo
structural modifications, and hence, the variations noticed
between the studies were probably due to the forms of
polypropylene used.

The difference between maximum torque and steady
state toque, generated during the melt mixing process,
decreased with increase in GTR content (Figure 2). The
time taken to reach steady state was almost the same for
all blends (Figure 1). Because of that, the torque reduction
rate decreases with increase in GTR content (Figure 3).

the variations in torque reduction rate and specific energy
requirement with GTR content are shown in Figure 3.

Optical micrographs of a few selected blends are
given in Figure 4. In these micrographs the GTR is
black and is easily distinguishable. Scanning electron
microscopy was used to study the failure modes of the
tensile specimens. The tensile fractographs for two
blends, one with high WPP content and the other with
high GTR content, are given in Figures 5a and 5b,
respectively.

The melting endotherms and the re-crystallization
exotherms for WPP and selected blends are shown
in Figure 6 and Figure 7. Table 1 gives the degree of
crystallinity of the blend and the degree of crystallinity
of the WPP phase for all blends.

Tensile properties, such as tensile strength,
% elongation at break, secant modulus at 7% strain and
tensile fracture energy of the blends are given in Table 2.
Tensile fracture energy is the energy absorbed by the
specimen in the process of breaking, and was calculated
by the area beneath the stress vs. strain curve. This is
also called the modulus of toughness. Table 3 gives the
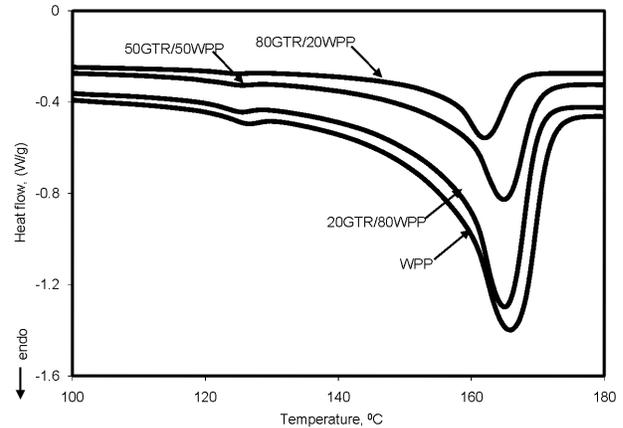hardness and the tear resistances of the blends. All blends

The WPP-rich blends consumed more energy at the early stages of mixing and lower energy in the later stage. In contrast, GTR-rich blends consumed less energy at the early stage and more energy at the later stage. Hence, the resultant specific energy requirement is more or less similar. The 50/50 blend shows the minimum specific energy requirement.

Blend morphology

The micrographs for blends containing 10 to 50 wt% GTR show a dispersed phase of GTR in the continuous WPP matrix phase (Figure 4). Further, the micrographs show that the concentration of larger GTR particles increases with increase in GTR content. This suggests that the GTR particles agglomerate or coalesce during processing, and the agglomeration effect is more at higher GTR contents. This is evident in the blend containing 70 wt% GTR, which shows a co-continuous phase morphology. The occurrence of coalescence and the formation of co-continuous phase morphology at higher rubber concentrations have been previously reported for virgin rubber-thermoplastic blends[21, 22]. Even though a change in phase morphology was observed with the blends containing 70 wt% GTR or more (Figure 4), all blends exhibited a similar fracture under tensile loading (Figure 5). The fracture was a combination of three different failure modes; ductile failure in the WPP phase, cohesive failure in the GTR phase and adhesive failure between phases.

Differential Scanning Calorimetry (DSC)

It is clear from melting endotherms and re-crystallization exotherms (Figure 6 and Figure 7 respectively) that the melting point, the onset crystallization temperature, and the peak crystallization temperature, of the blends decreases slightly (3 - 4 °C) with the increase in GTR

content. Further, the transitions associated with both melting and re-crystallization become narrower with increase in GTR content and this is attributed to the decrease of crystallinity content of the blends.

Percentage crystallinity of the blends decreases with increase in GTR content (Table 1). Further, % crystallinity of WPP remains unchanged up to 60 wt% GTR, and shows a slight increase thereafter. However, all these blends showed similar super cooling eg. temperature difference between onset crystallization and melting, indicating that no positive or negative nucleation effect occurred with the increase in GTR content. Therefore, it can be concluded that the increase in crystallinity of WPP at higher GTR contents was due to the occurrence of strain induced crystallization influenced by the GTR continuous phase. The decrease in blend crystallinity with the increase in rubber content is a common observation in rubber-thermoplastic blends, irrespective of whether the rubber used was virgin or recycled[19, 23].

Mechanical properties

The WPP has the highest tensile strength and secant modulus (Table 2). The tensile strength and modulus, decrease with increase in GTR content and this is attributed to the replacement of WPP with GTR. This is also in agreement with the fall in crystallinity of the blends with increase in GTR content. However, due to the physical entrapment of GTR particles in the WPP continuous phase at low GTR contents (up to 30 wt%), the variation in tensile properties shows a relatively slow decline. With the increase in GTR agglomerant size, with increase in GTR content (Figure 4) and with poor interfacial adhesions between phases (Figure 5), the tensile properties exhibit a more rapid decline. This could also be due to improper homogenisation of the

Table 1: Crystallinity of blends

GTR:WPP	Crystallinity of blend (%)	Crystallinity of WPP phase (%)
0:100	44 (0)	44(0)
10:90	417(1)	45(1)
20:80	37(0)	46(1)
30:70	31(0)	45(2)
40:60	26(1)	44(2)
50:50	22(1)	44(2)
60:40	17(1)	43(3)
70:30	14(0)	47(1)
80:20	10(0)	48(0)
90:10	5(1)	48(1)

Table 2: Tensile properties of blends

GTR, wt%	Tensile strength (MPa)	Elongation at break (%)	Secant modulus (MPa)	Tensile fracture energy (MJ/m³)
0	28.6(1.2)	16.5(1.3)	331(4)	2.33(0.11)
10	18.6 (2.0)	14.9(0.6)	236(2)	1.63(0.09)
20	17.4(1.3)	14.4(1.1)	234(8)	1.55(0.07)
30	16.1(0.8)	15.0(0.8)	200(7)	1.39(0.05)
40	12.7(0.7)	14.7(1.3)	153(9)	1.25(0.03)
50	11.1(1.2)	16.5(1.5)	104(5)	0.75(0.07)
60	7.0(0.7)	16.7(1.4)	72(8)	0.5(0.04)
70	4.9(0.3)	20.5(0.8)	41(6)	0.48(0.03)
80	3.1(0.3)	24.1(0.9)	26(8)	0.44(0.03)
90	3.2(0.2)	27.5(1.1)	22(3)	0.43(0.04)

Table 3: Hardness and tear resistances of blends

GTR, wt%	Hardness (IRHD)	Tear resistance (N/mm)
0	86 (1)	-
10	85 (1)	-
20	84 (1)	-
30	82 (1)	9.4(0.4)
40	81 (1)	8.0(0.4)
50	76 (1)	6.2(0.4)
60	75 (1)	4.3(0.3)
70	70 (1)	2.9(0.2)
80	61 (1)	1.9(0.1)
90	56 (1)	1.4(0.1)
100	19 (1)	-

GTR at higher concentrations. Due to the strain induced crystallisation associated with co-continuous phase morphology, the blends containing above 70 wt% GTR showed a slow variation again. The decrease in tensile strength and modulus with increase in recycled rubber content is a common observation in many studies [9, 24]. The % elongation at break of WPP is fairly low. Even though the GTR content in the blend increased, the elongation at break did not show a significant increase up to 60 wt% GTR. This is again due to the poor interfacial adhesion between phases. However, with the change in phase morphology, blends containing 70 wt% GTR and above showed rubbery properties and hence a gradual increase in elongation at break with increase in GTR content. As a result of the decrease in tensile stress with increase in GTR content, and a constant elongation up to 60 wt% GTR, the tensile fracture energy initially decreases with increase in GTR content (Table 2). Although the tensile stress is further decreased, due to the increase in elongation with GTR content above 60 wt%, the tensile fracture energy does not show a decrease thereafter. This is again associated with the change of phase morphology of the blends.

The variation in hardness with GTR content shows a similar trend to that of modulus variations (Table 3). However, the results obtained show a decrease in tear resistance with increase in GTR content (Table 3). This is due to failure in load transfer between phases associated with poor adhesion between phases. This was evident in the scanning electron micrographs (Figure 5).

The mechanical properties of the blends studied in the present work remained mainly constant up to 30 wt% GTR, but varied rapidly with further increases. Overall, the best physical properties were obtained when the GTR contents were between 50 wt% and 70 wt%. However, the overall properties expected from the blends of GTR and WPP were generally inadequate for high performance

applications. As such, use of a suitable compatibilizer to improve adhesion between the phases would be an essential requirement to be able to produce commercially viable rubber toughened thermoplastic materials from these polymers.

Acknowledgement

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