J. Rubb. Res., **12(1)**, 12–26

Assessing Effects of Thermoset Polyester Resin Waste Powder on the Processing and Mechanical Properties of Natural Rubber

A. ANSARIFAR[*#], L. WANG[*], M. OSMANI[**] AND A. PAPPU[**]

Products made of glass fibre reinforced polymers are often disposed off in landfills, incinerated or processed into waste powders at the end of their service life. Waste powders can be recycled as fillers for use in virgin polymers. The effects of up to 50 parts per hundred rubber by weight thermoset polyester resin waste powder on the viscosity, cure and mechanical properties of a sulphur-cured natural rubber compound were studied. The powder had resin polymer particles and glass fibre fragments ranging from approximately a few microns to 700 microns in size. The viscosity remained unchanged and the cure properties deteriorated when the powder was added to the rubber. The hardness, Young's modulus and tensile modulus increased whereas, the tensile strength, elongation at break, stored energy density at break and tearing energy decreased. There was also evidence of poor adhesion between the powder and rubber. The waste powder could be recycled as an extender filler to replace a portion of the raw rubber in the compound.

Key words: natural rubber; sulphur cure; glass reinforced thermoset polyester resin waste powder; processing properties; mechanical properties; recycling

Polymer materials are thermoplastics and thermosets. Thermosets consist of lightly crosslinked polymers such as natural rubber and styrene-butadiene rubber vulcanisates, and highly crosslinked polymers for example epoxies and polyesters[1]. The latter polymers are used in a wide range of industrial applications including automotive, electrical and aerospace[2], and are often reinforced with glass fibres to improve their mechanical properties[3,4]. Polyester resins reinforced with short glass fibres and low cost fillers to produce moulding compounds are used for applications where high mechanical properties are not required[2]. The automotive sector is among the largest users of composites. At the end of their service life, thermoset composite materials produce a high volume of waste which must be disposed off. For example, the recently implemented European Union (EU) Directive on end-of-life vehicles states that vehicles must have a minimal impact on the environment at the end of their useable life[5]. End-of-life vehicles generate around 9 million tonnes of waste each year so reuse, recover and recycling are important issues[5]. Moreover,

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vehicle manufacturers are responsible for the waste itself, but also for risk assessment and for possible damage to humans and the environment[6].

Waste management is a major area of concern within the European Union and there are numerous routes to achieve waste reduction. The alternative waste management routes are to reuse products, recycle materials, incinerate waste and landfills[2]. For many years, waste has been disposed off in landfills, however a recent EU Directive on Landfill of Waste (Directive 99/31/EC) will result in a reduction in the amount of organic material landfilled[2]. Cost effective recycling solutions are increasingly important in waste management.

Mechanical recycling has reached industrial applications[7]. This method is based on granulation and fragmentation of the composite material and often followed by a sieving process. The resulting powder and fibre can be used for many applications. For example, fine powders (less than 300–400 μm) can be used as fillers in thermoset compounds, long fibres (longer than 10 mm) in civil engineering materials[8,9] and fibres about 1 mm in size in thermoplastics[10,11].

Raw rubbers such as natural rubber often possess poor mechanical properties which must be improved with fillers. Fillers with surface areas ranging from 150 to 400 m^2/g offer reinforcement including improved tensile strength, tear strength, hardness, Young's modulus and tensile modulus[12-13]. There are also non-reinforcing or extender fillers for example talc and calcium carbonate ($CaCO_3$), which in small amounts have no major effect on the rubber properties, but can replace a portion of the raw rubber in compounds and reduce costs because they are significantly cheaper than raw rubbers.

This study examined the effect of up to 50 parts per hundred rubber by weight (p.h.r.) thermoset polyester resin waste powder on the viscosity, cure properties, hardness, tensile strength, elongation at break, stored energy density at break, tearing energy, Young's modulus and tensile modulus of a sulphur-cured natural rubber vulcanisate. The overall aim was to determine whether the powder could act as a reinforcing material or an extender filler for the rubber, and explore a new recycling route for the waste. It is anticipated that this new route could help to divert polymer composite waste from landfill and incineration to more useful applications in industrial rubber compounds.

EXPERIMENTAL

Materials

The raw rubber used was standard Malaysian natural rubber grade L (SMR L). The filler used was a thermoset polyester resin waste powder, referred to as GRP powder. The GRP powder was produced by grinding a glass fibre reinforced polymer composite solid waste and supplied by Hambleside Danelaw Rooflights and Cladding Limited, United Kingdom, in bags of 100 kg, and contained 95wt% resin powder and 5wt% glass fibre.

In addition to the raw rubber and filler, the other ingredients were N-t-butyl-2-benzothiazole sulphenamide (Santocure CBS, Flexsys, USA), zinc oxide (Harcros Durham Chemicals, UK), stearic acid (Anchor Chemical Ltd, UK), elemental sulphur (Solvay Barium Strontium, Hannover, Germany), N-(1,3-dimethylbutyl)-N'-phenyl-*p*-phenylenediamine (Santoflex 13, Flexsys, USA). In total, four compounds were made for this study.

Characterisation of the GRP powder

The GRP powder contained large chunks of loose glass fibre when it was originally supplied, which were not suitable for mixing with rubber and were separated from the powder by a 200 µm size sieve and discarded. 0.5 g of the remaining powder containing resin polymer particles and glass fibre fragments was placed on the sticky side of a sellotape and coated with gold, examined and photographed in a LEO 1530 VP Field emission gun scanning electron microscope (SEM) (Carl Zeiss SMT, Ltd., Cambridge, UK) to determine the size, size distribution and shape of the particles. In addition, the GRP powder was tested in a low angle laser light scattering Malvern Mastersizer 2000 Ver. 5. particle size analyser with a range of 0.02 microns to 2000 microns (Malvern Instruments Ltd, UK). Initially, 20 mg of the powder was mixed with distilled water in the bath of the machine and stirred to produce a good mixture. The machine was then switched on and the mixture was exposed to laser scattering. The data was collected and processed by Malvern Mastersizer 2000 Software to produce a range of particle sizes and a particle size distribution profile by plotting the volume fraction of the particles against particle size for the sample.

Mixing

The compounds 1-4 (*Table 1*) were prepared in a Haake Polylab System/Haake Rheomix (Berlin, Germany), a small-size laboratory mixer with counter rotating Banbury rotors. In these experiments, the Banbury rotors and the mixing chamber were maintained at 24ºC and the rotor speed was 45 r.p.m. The volume of the mixing chamber was 78 cm^3, and it was 60% full. A Polylab Monitor computer software was used for controlling the mixing conditions and storing data. To prepare the compounds, the rubber and the GRP powder were placed into the mixing chamber and the rotors started. Mixing continued for 6 min and then the rotors were stopped and the rubber compound was cooled down to about 40–45ºC to avoid scorch before the curing chemicals were incorporated in the rubber. The rotors were started and CBS, zinc oxide, stearic acid, sulphur and antidegradant were added and mixed for an extra 6 min. The total mixing time for the compounds was 12 min.

Finally, when the mixing ended the rubber was recovered from the mixer and milled to a thickness of about 6 mm for further work. The compounds were kept at ambient temperature (~22ºC) for at least 24 h before their viscosity and cure properties were measured.

Assessment of the Dispersion of the GRP Powder in the Rubber

The dispersion of the GRP powder (particles of resin polymer and glass fibre fragments) in the rubber was assessed in the Scanning Electron Microscope (SEM). Small pieces of the uncured rubbers were placed in liquid nitrogen for 3 min and then fractured to create two fresh surfaces. The samples, 40 mm^2 in area and 4 mm thick, were coated with gold, and then examined and photographed with the SEM. The degree of dispersion of the GRP particles in the rubber was subsequently studied from the SEM photographs.

Viscosity and Cure Properties of the Rubber Compounds

The viscosity of the rubber compounds was measured at 100ºC in a single-speed rotational Mooney viscometer (Wallace Instruments, Surrey, UK) according to the British Standard[14]. The results were expressed in Mooney Units (MU). The scorch time,

TABLE 1. RECIPES, VISCOSITY, CURE AND MECHANICAL PROPERTIES OF THE RUBBER COMPOUNDS

Formulation (p.h.r.)	Compound number 1*	 2	 3	 4
Natural rubber (SMR L)	100	100	100	100
GRP powder	0	5	25	50
Sulphur	2.5	2.5	2.5	2.5
Stearic acid	2	2	2	2
Zinc oxide	5	5	5	5
CBS[a]	1	1	1	1
Santoflex 13[b] (antidegradant)	1	1	1	1
Mooney viscosity, ML(1+4, 100ºC)	35	32	34	36
	ODR Results			
Scorch time, t_{s2} (min)	7	9	9	10
Optimum cure time, t_{95} (min)	14	17	18	25
Cure rate index (min^{-1})	14	13	11	7
	Mechanical properties			
Hardness (Shore A)	45	46	45	51
Tensile strength (MPa)	25	19	19.4	12
Elongation at break (%)	1393	1399	1237	946
Stored energy density at break (MJ/m^3)	87	73	81	44
Tearing energy (kJ/m^2)	14	11	14	7.5
Range of values (kJ/m^2)	11–20	10–16	13–18	7–10
Young’s modulus (MPa)	1.2	1.2	1.4	1.8
Modulus at different strain amplitudes (MPa)				
50%	0.55	0.54	0.78	0.96
100%	0.42	0.41	0.68	0.77
200%	0.35	0.36	0.62	0.67
300%	0.35	0.32	0.62	0.70

1* Control or Unfilled compound
a N-cyclohexyl-2-benzothiazole sulphenamide (CBS)
b N-(1,3-dimethylbutyl)-N'-phenyl-*p*-phenylenediamine

which is the time for the onset of cure, and the optimum cure time, which is the time for the completion of cure, were determined from the cure traces generated at 140 ± 2ºC by an oscillating disc rheometer curemeter (ODR, Monsanto, Swindon, UK) at an angular displacement of ± 3º and a test frequency of 1.7 Hz[15]. The cure rate index, which is a measure of the rate of cure in the rubber, was calculated using the method described in the British Standard[16]. The rheometer tests ran for up to one hour. Results from these experiments are summarised in *Table 1*.

Test Pieces and Test Procedure

After these measurements were completed, the rubber compounds were cured in a compression mould at 140ºC with a pressure of 11 MPa. Pieces of rubber, each approximately 130 g in weight, were cut from the milled sheet. Each piece was placed in the centre of the mould to enable it to flow in all directions when pressure was applied. This prevented anisotropy from forming in the cured rubber. For determining the mechanical properties of the rubbers, sheets 23 cm × 23 cm by approximately 2.6 mm thick were used, from which various samples for further tests were cut.

Hardness

For measuring the hardness of the rubbers, cylindrical samples 12 mm thick and 28 mm in diameter, were used. The samples were placed in a Shore A durometer hardness tester (The Shore Instrument & MFG, Co., New York) and the hardness of the rubber was measured at 22.5ºC over a 15-second interval after which a reading was taken. This was repeated at three different positions on the sample, and median of the three readings were calculated[17].

Cohesive Tear Strength

Rectangular strips, 80 mm long and 30 mm wide, were cut from the cured sheets of rubber and a sharp crack, approximately 35 mm in length, was introduced into the strips half way along the width and parallel to the length of the strip, to form the trouser test pieces for the tear experiments. The tear tests were performed at an angle of 180º, at ambient temperature (22.5ºC) and at a constant cross-head speed of 50 mm/min[18] in a Lloyd mechanical testing machine (Lloyd Instruments, UK). The tears produced in the rubber after the test pieces were fractured were 28 mm to 75 mm in length. In each experiment, the tearing force was recorded to produce traces from which an average force was measured. For each rubber, five test pieces were used. After these measurements were completed, and following the procedure described previously[19] the force values were placed in *Equation 1*.

$$T = 2F/t \qquad \ldots 1$$

where F is the force, and t the thickness of the test piece, to calculate tearing energies, T, for the rubbers. The median values of the tearing energies were subsequently noted.

Tensile Properties

The tensile stress, elongation at break, and stored energy density at break of the rubbers were determined in uniaxial tension in a Lloyd mechanical testing machine, using dumbbell test pieces 75 mm long with a central neck 25 mm long and 3.6 mm wide. The test pieces were die-stamped from the sheets of cured rubber. The tests were performed at 22.5ºC and at a cross-head speed of 50 mm/min[20]. Lloyd DAPMAT computer software was used for storing and processing the data. Typical stress versus strain traces from the tensile tests are shown in *Figures 1a–1d*.

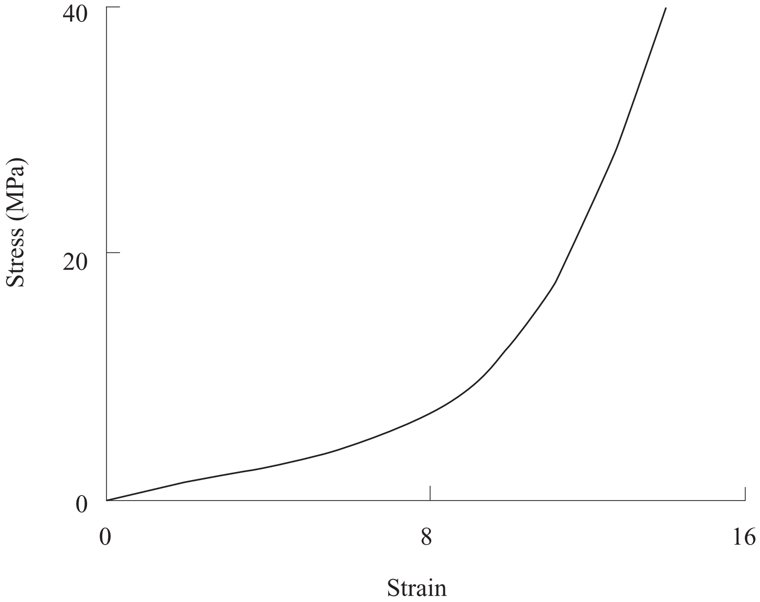

Figure 1a. Typical stress versus strain data for the rubber with no GRP powder.

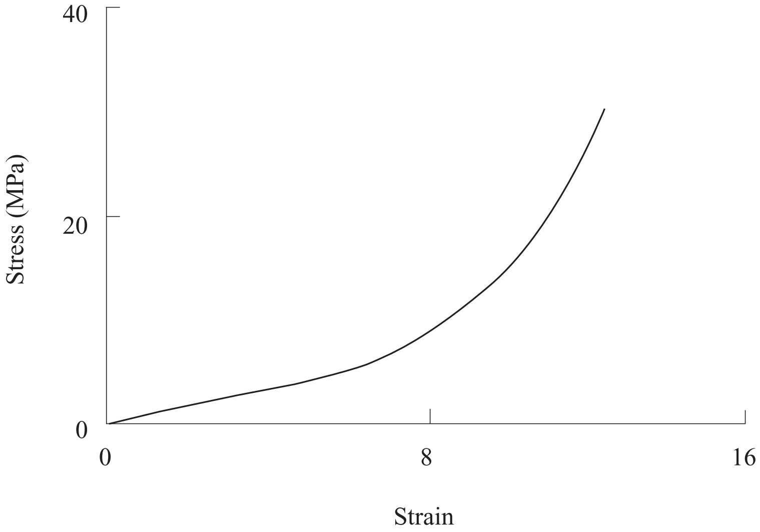

Figure 1b. Typical stress versus strain data for the rubber with 5 p.h.r. GRP powder.

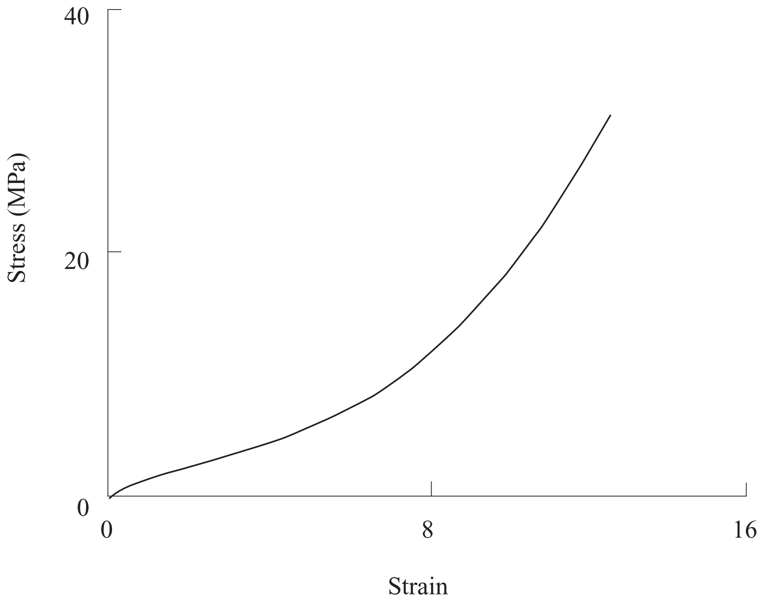

Figure 1c. Typical stress versus strain data for the rubber with 25 p.h.r. GRP powder.

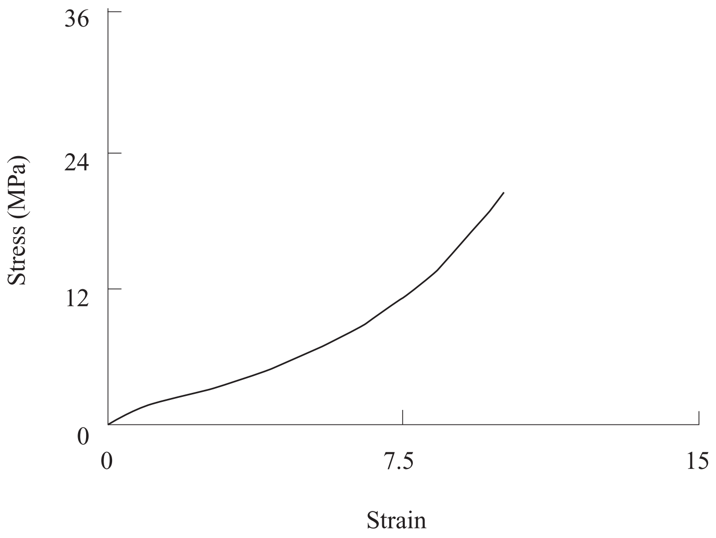

Figure 1d. Typical stress versus strain data for the rubber with 50 p.h.r. GRP powder.

Loss Tangent (tan δ)

Tan δ is the ratio between loss modulus and elastic modulus. The loss modulus represents the viscous component of modulus and includes all the energy dissipation processes during a dynamic strain. The tan δ was measured in a dynamic mechanical analyser DMAQ800 (TA Instruments, USA), using Universal Analysis 2000 Software Version 4.3A. Test pieces 34 mm long, 12 mm wide and approximately 2.7 mm thick were used. The tests were performed at 1 Hz frequency. The samples were deflected by 256 μm (nominal peak to peak displacement) during the test, and the sample temperature was raised from 24ºC to 100ºC at 3ºC/min steps.

Tensile Modulus at Different Strain Amplitudes

The tensile modulus of the vulcanisates at 50%, 100%, 200% and 300% strain amplitudes and Young's modulus were measured in uniaxial tension, using dumbbell test-pieces. The tests were carried out at approximately 28ºC at a cross-head speed of 50 mm/min[20] in a HT Hounsfield mechanical testing machine (Hounsfield, Surrey, UK). QMAT-DONGLE version 2003 computer software was used to process the data.

RESULTS AND DISCUSSION

Properties of the GRP powder

When the SEM photographs were examined, it was evident that the GRP powder was made of particles and glass fibre fragments of different sizes and shapes. The particles had irregular shapes (*Figure 2a*) and their sizes ranged from 0.5 micron to 200 microns (*Figure 2b*), whereas the glass fibre fragments were approximately from 25 microns to 600 microns in length (*Figure 2a*). The results from the particle size analyser indicated that the powder had particles from 1 micron to 700 microns in size, which indicated a wide particle size distribution profile (*Figure 3*). This was similar to the SEM results. However, it should be noted that particles of less than 0.02 micron could not be measured, and this method did not differentiate between glass fibre fragments and particles. Moreover, no information about the shape of particles could be attained from the results in *Figure 3*. It was therefore concluded that SEM was a more useful method for measuring the minimum particle size and determining the particle shape of the powder. SEM also differentiated between particles and glass fibre fragments in the powder whereas, the particle size analyser did not.

Dispersion of the GRP powder in the Rubber

Figure 4 shows dispersion of the GRP powder in the rubber after freeze-fracture. There were cavities present in the rubber matrix after the glass fibre fragments were pulled out during the freeze-fracture tests. This indicated poor adhesion between the rubber and glass fibre. The fibre/rubber adhesion can be significantly enhanced by the treatment of the fibre surfaces with adhesives[21]. Normally, glass fibres are treated with silane coupling agent to form strong adhesion with rubber. However, no such treatment was considered for the GRP powder before it was added to the rubber, and therefore resulting in poor adhesion between the glass fibre fragments and rubber.

Effect of the GRP powder on the Viscosity and Cure Properties of the Rubber

The viscosity of the unfilled rubber was 35 MU and it hardly changed when up to 50 p.h.r.

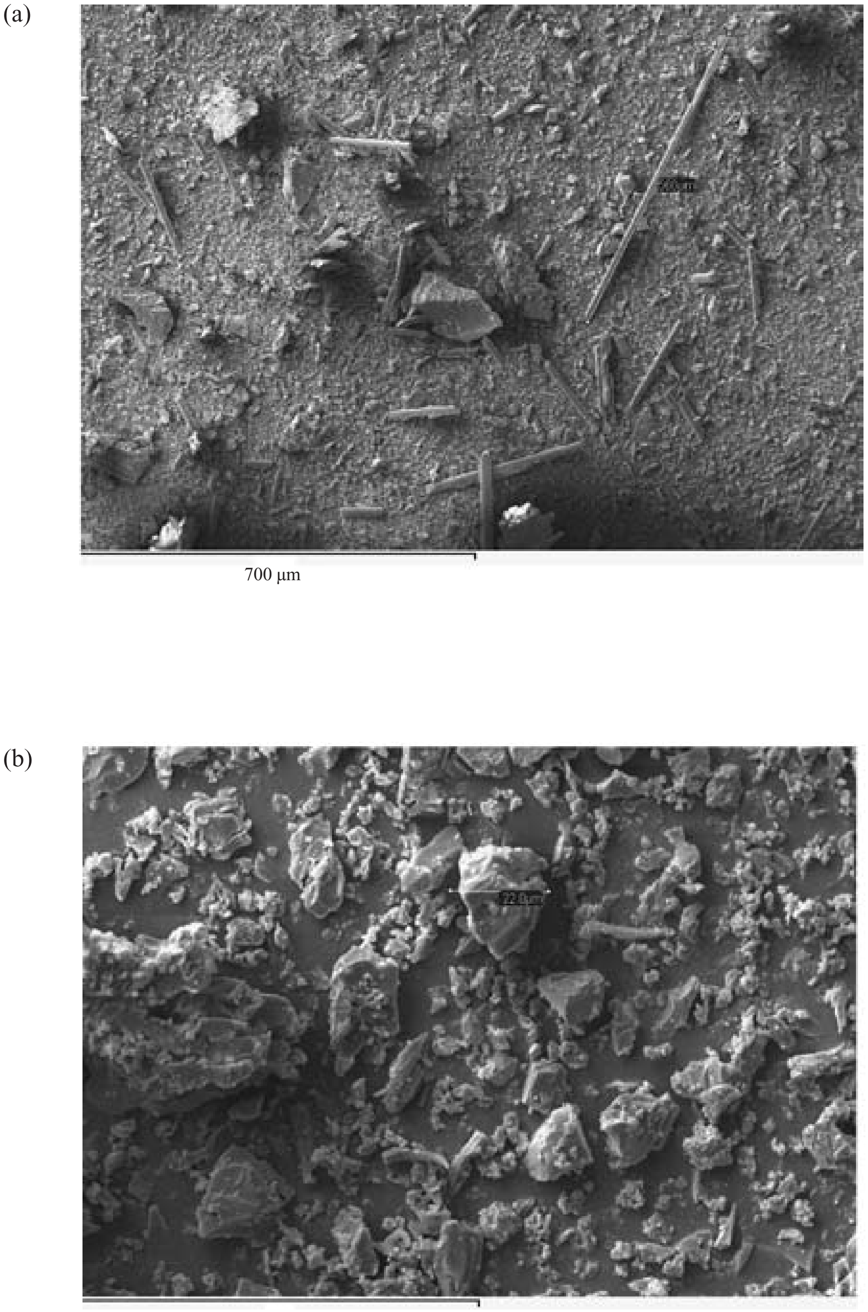

Figure 2. SEM photographs showing the GRP powder containing resin polymer particles and glass fibre fragments (a), and GRP particles (resin polymer particles) at a higher magnification (b).

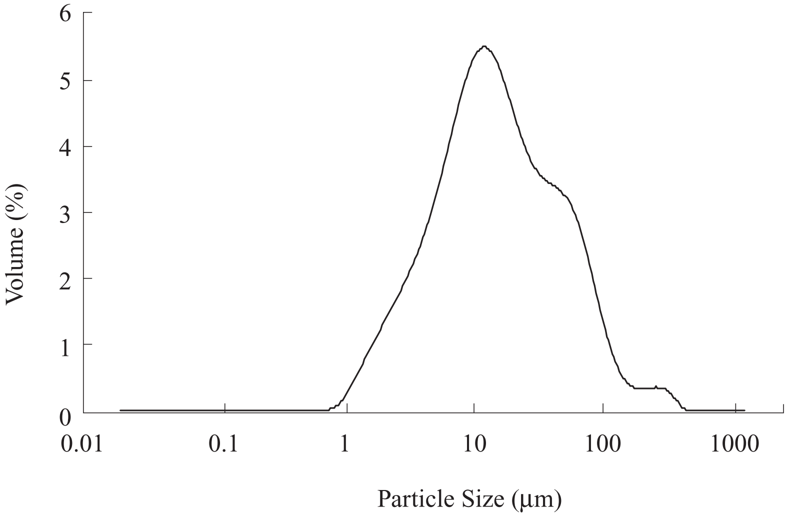

Figure 3. Volume percentage versus particle size distribution profile of GRP powder. Data produced with Particle Size Analyser.

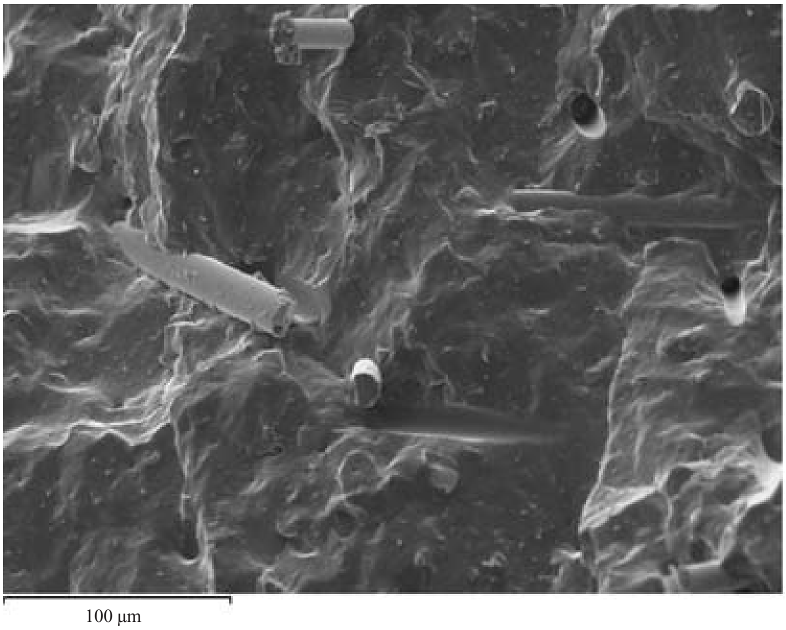

Figure 4. SEM photograph showing dispersion of the GRP powder in the rubber after freeze-fracture. Cavities (top right hand side) were produced after glass fibres were pulled out of the rubber. Data for compound 4.

GRP powder was added, though the rubber with 5 p.h.r. GRP powder had the lowest viscosity of 32 MU (*Table 1*). Normally, when reinforcing fillers such as carbon blacks or silicas are added, the rubber viscosity increases[12,22]. This is attributed to strong rubber/filler interaction[23] and presence of rubber/filler network, which increases stiffness, strength and viscosity of the rubber[22,24]. Notably, the rubber viscosity remained unchanged as the loading of the GRP powder was raised to 50 p.h.r. It was therefore concluded that the GRP powder was not a reinforcing filler.

The scorch and optimum cure times increased from 7 min to 10 min and 14 min to 25 min, respectively. The cure rate index decreased from 14 min^{-1} to 7 min^{-1}. Evidently, the addition of the GRP powder to the rubber had a detrimental effect on the curing properties of the compound. Some fillers are known to interfere with the curing mechanism of sulphur in rubbers. For example, significant cure retardation in sulphur-cured rubbers filled with silica nanofiller has been reported[25]. This was attributed to the adsorption of the curing chemicals on the filler surfaces and the interference of the filler with the reaction mechanism of sulphur in the rubber. It is likely that some of the curing chemicals in the rubber adsorbed on the surfaces of the GRP powder and never reacted during the curing process. This was exacerbated by increases in the content of GRP powder and hence, the deterioration in the cure properties of the rubber compounds.

Effect of the GRP powder on the Mechanical Properties of the Cured Rubber

The mechanical properties of the rubber vulcanisate, as shown in *Table 1*, were affected differently by the inclusion of the GRP powder in the rubber. The hardness was unchanged at 45–46 Shore A when up to 25 p.h.r. GRP powder was added, and it increased to 51 Shore A as the loading of the GRP powder was raised to 50 p.h.r. Similarly, the Young's modulus rose from 1.2 MPa to 1.8 MPa when the full loading of the GRP powder was incorporated in the rubber. It then continued to rise when more GRP powder was added. For example, at 50% strain amplitude, the modulus increased by 75% when the loading of the GRP powder reached 50 p.h.r. However, at a constant loading of the GRP powder, for instance at 50 p.h.r., the modulus decreased by 27% as the strain amplitude was raised to 300% (*Table 1*). Evidently, the modulus benefited from increases in the loading of the GRP powder, irrespective of the level of strain on the rubber, but was adversely affected by increases in the level of strain on the rubber at a given loading of the GRP powder.

The properties related to fracture deteriorated noticeably when the GRP powder was added to the rubber. The tensile strength decreased from 25 MPa to 12 MPa, elongation at break from 1393% to 946% and stored energy density at break from 87 $\mathrm{MJ/m^3}$ to 44 $\mathrm{MJ/m^3}$. The tearing energy decreased from 14 $\mathrm{kJ/m^2}$ to approximately 8 $\mathrm{kJ/m^2}$ when the loading of the GRP powder was raised to 50 p.h.r.

SEM Examination of the Fracture Surfaces after the Tensile Tests

When the fracture surfaces were examined after the tensile tests, there were extensive cavitation and localised tearing on the rubber surfaces (*Figure 5a*). It seemed that the particles and glass fibre fragments were pulled out of the rubber matrix, leaving large cavities behind. This indicated poor adhesion between the particles, glass fibre fragments and the rubber (*Figure 5b*), which weakened the rubber and adversely affected its properties such as tensile strength and tearing energy. This was further exacerbated by increases in the loading of the GRP powder in the rubber.

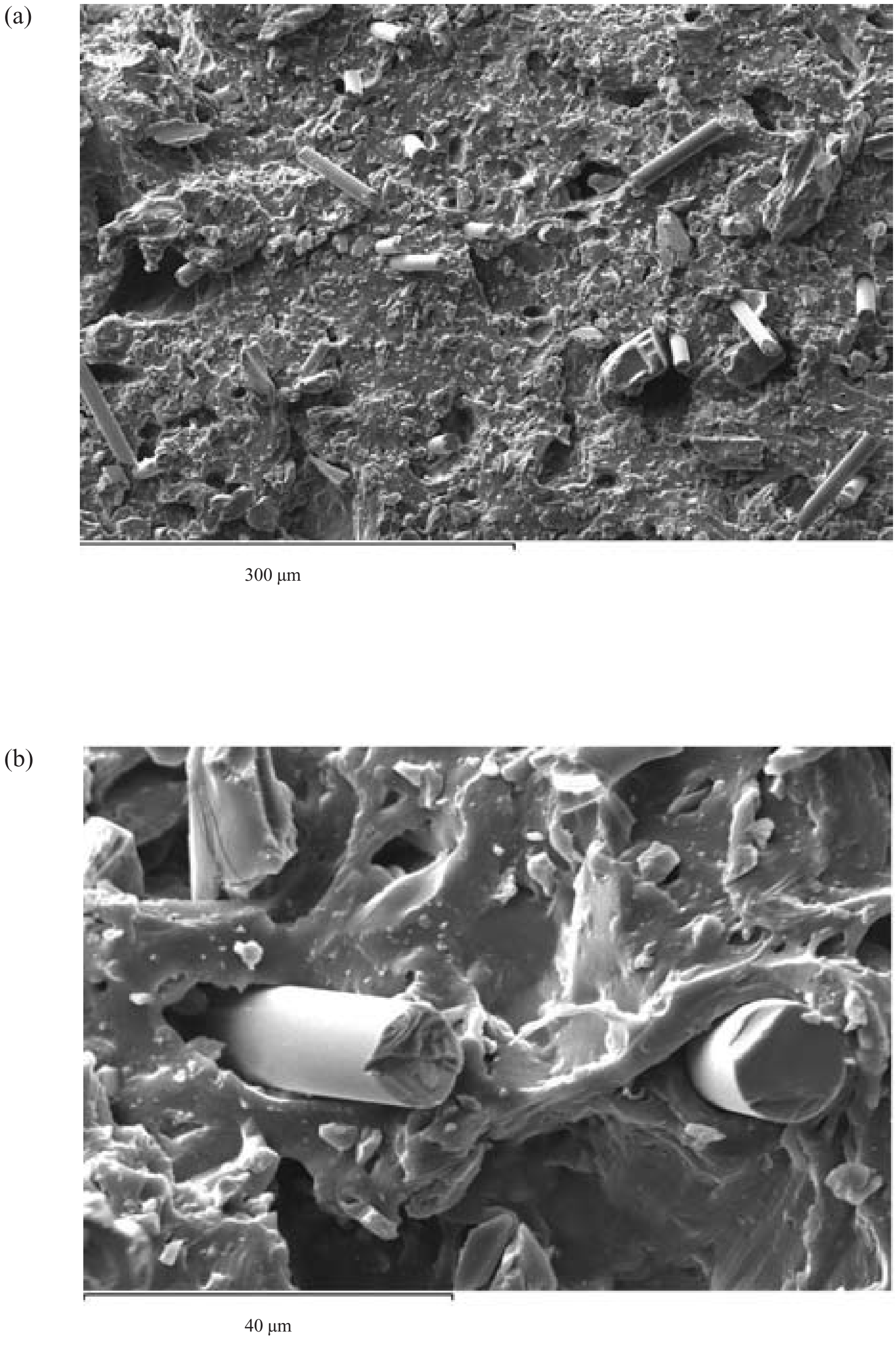

Figure 5. SEM photographs showing typical fracture surfaces after tensile testing. There are localised tearing and cavities in the rubber. Data for compound 4.

Effect of the GRP powder on the tan δ of the Rubber

The tan δ was also affected by the loading of the GRP powder in the rubber. For the rubbers with 0 and 5 p.h.r. GRP powder, tan δ decreased slowly from 0.030 to 0.016 and 0.048 to 0.028, respectively as temperature was increased to 95ºC (*Figure 6*). Interestingly, for the rubber with 25 p.h.r. GRP powder, tan δ increased from 0.083 to 0.095 and then decreased sharply to 0.029, almost equalling the values measured for the rubber with 5 phr GRP powder. Similarly, the tan δ of the rubber with 50 p.h.r. GRP powder rose rapidly from, 0.13 to 0.16 and then decreased to 0.045 as a function of temperature. It is worth mentioning that the largest tan δ values were recorded for the rubbers with 25 p.h.r. and 50 p.h.r. GRP powder at temperatures between 30ºC–45ºC. Evidently, the increased addition of GRP powder raised the energy dissipation processes in the rubber, and this was essentially temperature dependent.

The results suggest that there are potential applications for recycling the GRP powder as an extender filler in industrial rubber compounds. For example, the rubber industry manufactures a wide range of articles for the construction and building industry including carpet underlay, bearing pads, bridge and concrete expansion joints and insulation pads[26]. These articles often require a certain stiffness, which is determined by the hardness and modulus of the rubber. As the results

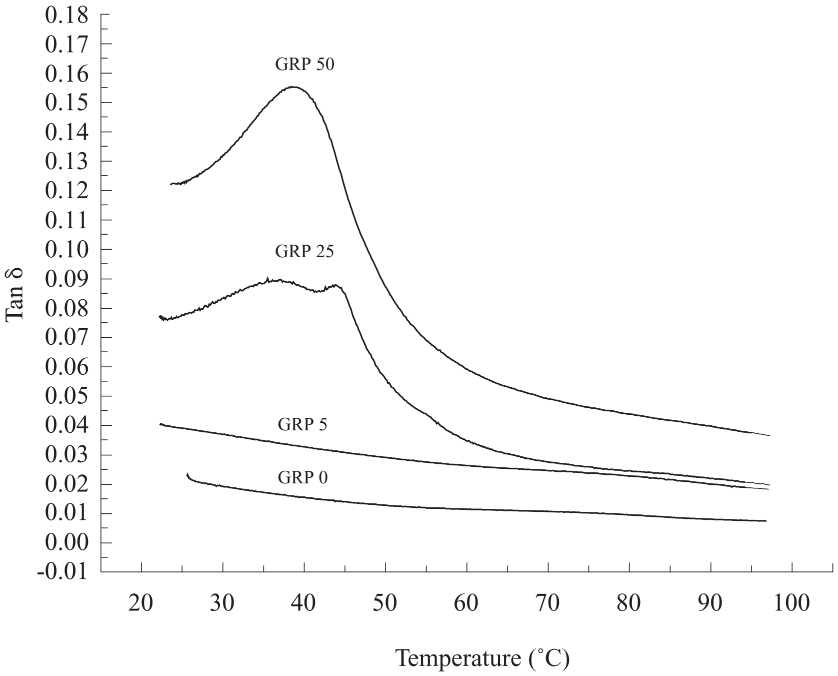

Figure 6. Tan δ versus temperature for compounds 1– 4.

have shown, the addition of the GRP powder increased both of these properties and made the GRP waste powder an ideal choice for these applications.

CONCLUSIONS

From this study, it was concluded that:

- When up to 50 p.h.r. GRP powder was added to natural rubber, the viscosity was unchanged, but the scorch and optimum cure times and the rate of cure decreased.
- The hardness, Young's modulus and tensile modulus increased, and the tensile strength, elongation at break, stored energy density at break and tearing energy decreased substantially. The deterioration in the properties related to fracture was due to poor adhesion between the GRP powder and rubber. This caused extensive cavitation when the rubber was strained during mechanical testing and consequently weakened the rubber.
- The tan δ of the rubber increased when the GRP powder was added. The increase was more substantial at 30ºC–45ºC for the rubbers containing 25 p.h.r. and 50 p.h.r. GRP powder.

In summary, the GRP powder can be re-used as an extender filler in natural rubber. This offers a potentially new recycling route for thermoset polyester resin wastes, hence avoiding disposal to landfill and incineration.

ACKNOWLEDGMENTS

The authors thank Loughborough Materials Characterisation Centre for carrying out the scanning electron microscopy of our samples. The authors are also grateful to Hambleside Danelaw Rooflights and Cladding Limited, UK for preparing and supplying the GRP waste powder. The work was carried out under the heading of Built Environment Action on Waste Awareness and Resource Efficiency (BeAware). The programme was funded by industry and the department of trade and industry (DTI), UK.

Date of receipt: June 2008
Date of acceptance: October 2008

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