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Compatibilizing thermoplastic/ground tyre rubber powder blends: Efficiency and limits

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A B S T R A C T

This paper deals with the compatibilization between recycled HDPE matrix and ground tyre rubber powder, through a free radical mechanism, by adding a peroxide. Mechanical tests show competition between the crosslinking of HDPE and the formation of interfacial bonding. The addition of more than 1 %wt of peroxide results in a strong improvement of interfacial adhesion and elongation at break. The performance is also compared to that resulting from gamma irradiation of the same blends.

In the second part of this article, experimental tests and simulation by finite elements analysis were performed and showed the non-possibility of obtaining a “thermoplastic elastomer” by blending and compatibilizing HDPE and ground tyre rubber powder, since perfect interfacial adhesion still results in decohesion between matrix and particles.

Keywords:

Compatibilization

HDPE

Tyre rubber

Finite element analysis

1. Introduction

The management of end-of-life tyres is a great environmental challenge. In France, 270,000 tons of scrap tyres are generated each year [1]. Recent European regulations forbid the burning and landfilling of tyres and set recycling objectives.

Mechanical recycling, i.e. the grinding of tyres and separation of metal and rubber components, is one of the most interesting waste management approaches. Various research articles and patents showed the possibility of recycling ground tyre rubber (GTR) powders as functional fillers in host polymers. Nevertheless, while some applications already exist in the case of thermosets (athletic tracks, pavements, playgrounds) [2], no effective applications were found for thermoplastic/GTR blends due to the very poor mechanical properties of such composite materials [3,4], which were attributed to the lack of interfacial adhesion between the rubber particles and the thermoplastic matrix.

Various research articles focus on solutions to compatibilize these two phases, the ultimate objective being to obtain a “thermoplastic elastomer”-like behaviour by combining rubber elasticity and thermoplastic matrix properties. Many processes have been carried out to improve the mechanical behaviour, such as the control of GTR particle morphology, mean particle size or specific surface area [5–7], the oxidation or chlorination of GTR particle surface [8–10], the de-vulcanization of GTR particles using various physical, chemical or biological processes [11,12] or the addition of a third polymer or reactive molecules (as maleic anhydride or methyl methacrylate) [7,13,14]. This last approach led to better results in terms of mechanical properties. However, the approach which gave the best results consisted in performing co-crosslinking radical reactions at the interface between rubber particles and host thermoplastic matrix. Such reactions are initiated by free radicals obtained either by the decomposition of a peroxide during melt blending, or by gamma irradiation of the blend [15–17]: Wiessner et al. compatibilized PP matrix and GTR particles using 2 %wt of dicumyl peroxide (DCP) [15]. Elongation at break and impact energy increased significantly. Nevertheless, the authors did not study the influence of the DCP content.

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In a recent article, we promoted interfacial adhesion between recycled HDPE and GTR particles by gamma irradiation at moderate doses (less than 100 kGy) [17]. However, it appeared that the mechanical properties of the blends were always lower than these of the virgin matrix, even in the case of effective compatibilizing treatments, showing the limited interest of the recycled materials obtained which did not show the expected “elastomer” behaviour.

In the present article we would like to first make a comparison between these two co-crosslinking methods in the case of GTR/recycled HDPE blends. The irradiation approach will be the same as described in our previous article [17]. For the peroxide approach, we will take into account the influence of the DCP content and the processing conditions.

Secondly, we would like to evaluate the true influence of the adhesion level at the interface on the mechanical properties. We will show that the “thermoplastic-elastomer”-like behaviour actually cannot be obtained independently of the quality of interfacial adhesion between GTR particles and host thermoplastic.

2. Experimental

2.1. Materials

The HDPE used is a recycled material supplied by Valco SAS (France). It contains a small amount of polypropylene impurities. Two ground tyre rubbers were used in this study. The first was purchased from Granuband BV (concerning irradiated blends). The second was supplied by Transeco (corresponding to blends compatibilized by peroxide). Both powders have a mean particle diameter between 400 and 500 μm and a specific surface area less than 0.1 m^2/g . Dicumyl peroxide was supplied by ACROS Organics.

2.2. Processing

In the case of compatibilization by a peroxide, 50/50 HDPE/GTR blends were prepared using two different processes:

- Process 1: HDPE and GTR were melt blended using an internal mixer Haake Rheomix 3000. HDPE was first melted and GTR powder was added after 4 min. DCP was introduced after 2 min and the blending continued for 4 min (process 1). The speed of rotors was fixed at 60 rpm. The initial temperature was 145 $^{\circ}\text{C}$ but it increased during blending, allowing the decomposition of the peroxide.
- Process 2: Prior to melt blending, GTR powder was immersed in a cyclohexane/DCP solution which was stirred for 4 h. After evaporating cyclohexane, DCP was present at the surface of GTR particles (as was verified by DSC measurements). Using this process, DCP was found at the rubber–matrix interface, which promoted interfacial co-crosslinking. Then GTR was added in the Haake mixer according to process 1.

For both processes, various DCP weight contents were used. After blending, the blends were ground into shredded particles using an Alpine Rotoplex cutting mill.

In the case of compatibilization by gamma irradiation, 50/50 HDPE/GTR blends were compounded using a twin screw extruder (Clextral BC 21, 180 $^{\circ}\text{C}$, 250 rpm) and pelletized. Gamma irradiation (from 0 to 100 kGy) of these pellets were performed by Ionisos SA (France), using a 2×10^6 Ci ^{60}Co source, under air atmosphere.

Standard ISO 527-2 type 1A tensile test specimens were injection-moulded (95 tons Sandretto AT press, 170 $^{\circ}\text{C}$) from all compositions.

2.3. Thermal analysis

The melting temperature and crystallinity content of samples were measured by differential scanning calorimetry (DSC Setaram 92, 5 K/min, under air). Crystallinity content was calculated considering a melting enthalpy of 295 J/g for a 100% crystalline polyethylene.

2.4. Mechanical testing

Tensile properties and Charpy impact strength were determined at least 3 days after injection moulding. Ten samples were tested for each formulation. Tensile tests were carried out using a ZWICK 2010 apparatus at 1 mm/min for the determination of Young’s modulus, and at 100 mm/min for the determination of yield stress and elongation at break. Charpy impact strength was measured on un-notched ISO 179 standard specimens using a ZWICK 5101 pendulum (4 J or 7.5 J for samples which did not break with the lightest pendulum).

Tensile tests were also performed according to the following procedure: standard specimens were elongated to a controlled value (6, 10 or 15%), then the stress was removed (zero stress).

2.5. In situ scanning electron microscopy observations

Interfacial adhesion between GTR particles and the surrounding HDPE matrix in both untreated and compatibilized blends was investigated by in situ Scanning Electron Microscopy observations under tensile strain: A Quanta 200 FEG environmental Scanning Electron Microscope (FEI), equipped with a micro tensile test module (Microtest 5000, Gatan) was used. This device allows performing tensile tests on samples (size $4 \times 10 \times 10 \text{ mm}^3$) at 0.5 mm/min and to observe the behaviour of a particle during the test. The samples were notched before testing in order to promote the propagation of a crack. The SEM beam was focused around a GTR particle, on the crack propagation direction, in order to observe the behaviour of the particle during the tensile test. Micrographs are taken using retro-diffused electrons in order to avoid the influence of topography.

Photomechanical analysis was performed to study qualitatively the debonding at the polyethylene–rubber interface. The axial and transverse deformation profile of two zones (the first in the particle, the second in the matrix, near the interface, as seen in Fig. 1) was measured using the

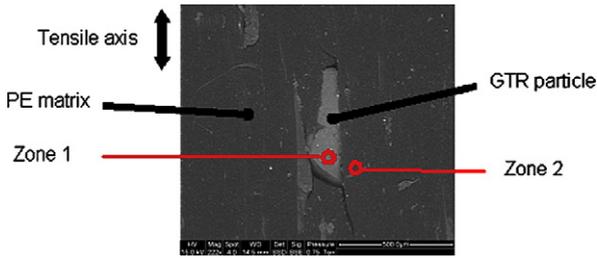


Fig. 1. Principles of photomechanical analysis.

software cinEMA (developed by Ecole des Mines d'Alès) during the tensile test (1 image every 10 s).

2.6. Finite element analysis

Finite elements analysis was performed using Zebulon software from Ecole des Mines de Paris [18]. The quartered Representative Elementary Volume was constituted by 570 prismatic elements (triangular base). It contains 9 cylinder particles (fillers) homogeneously distributed in a HDPE matrix, as seen in Fig. 2, corresponding to a rubber content equal to 50%. The constitutive behaviour of the materials is described by Hooke's law. A panel of material parameters can be found in Table 1 for both materials in order to test the sensitivity of the simulation.

A tensile stress is applied in the fibre direction (30 MPa) while symmetrical conditions are considered on areas S_1 , S_2 and S_3 . Two cases of interface between filler and matrix are considered: in the first perfect adhesion is considered and in the second no adhesion is assumed.

The aim of this study is to compare the equivalent Von Mises stress σ_{eq} and its in plane (\vec{x}_1 , \vec{x}_2) counterpart $\sigma_{eq-transverse}$ along the \vec{x}_1 axis (for $0 \leq x_1 \leq 100 \mu\text{m}$, the origin was taken at the centre of a particle).

3. Results and discussion

3.1. Compatibilization using DCP

3.1.1. Mechanical performance of HDPE

Fig. 3 shows the mechanical properties of HDPE according to the DCP/HDPE ratio. At very low ratio, impact energy, maximum tensile stress and Young's modulus

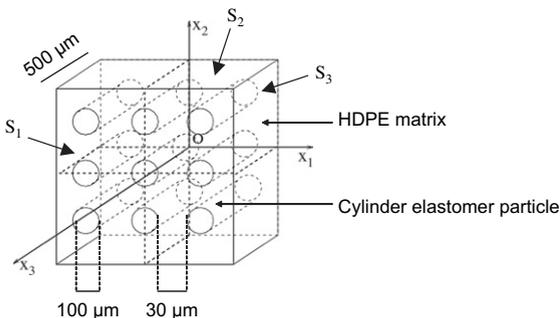


Fig. 2. Representative elementary volume.

increase while elongation at break decreases, but at higher ratio (more than 0.001), all properties decrease. For 2 %wt of DCP, HDPE is too crosslinked to be injection-moulded. The former behaviour corresponds to the crosslinking of HDPE which becomes stiffer. However, at the same time, the crystallinity content of HDPE tends to decrease because of the formation of intermolecular bonding (Fig. 4). In addition, the breaking of macromolecular chains could also be caused by free radicals. Consequently, for a definite DCP content, these two last phenomena are expected to impair mechanical performance. Moreover, other researchers have noticed the same evolution [19,20].

3.1.2. Mechanical properties of 50/50 HDPE/GTR blends

Young's modulus and maximum tensile stress of 50/50 HDPE/GTR blends compatibilized by DCP (Fig. 5) show the same evolution of properties as HDPE with DCP. However, elongation at break and impact energy behave differently. At low DCP/HDPE ratio, a decrease is noticed in comparison with no DCP, but at higher DCP content (0.5–1 %wt, for a DCP/HDPE ratio equal to 0.01–0.02), the values rise significantly. This evolution is ascribed to the co-crosslinking at the rubber–polyethylene interface by grafting of HDPE macromolecular chains onto the particle surface, as was reported by Weissner in the case of PP/GTR blends [15].

3.1.3. Consumption of free radicals

It is interesting to note that the crystallinity content of the matrix in the HDPE/GTR blends decreases only for a DCP/HDPE ratio higher than 0.01, while crystallinity content of virgin HDPE decreases at lower DCP/HDPE ratio (Fig. 4). We could observe also that the highest maximum stress is observed for a DCP/HDPE ratio equal to 0.001 in the case of virgin HDPE, against 0.01 for 50/50 HDPE/GTR blends. However, the maximum stress value depends only on the crosslink state of the matrix and not on the interfacial adhesion (as we will see later). Hence, these observations show that only 10% of free radicals are involved in the HDPE crosslinking for the 50/50 HDPE/GTR blend. Consequently, it is suggested that 90% of free radicals are involved in other reactions, as interfacial co-crosslinking or "secondary" reactions consuming free radicals.

3.1.4. Comparison of different processes

Fig. 6 shows mechanical properties of 4 blends: untreated 50/50 HDPE/GTR, 50/50 HDPE/GTR compatibilized by 2 %wt of DCP according to processes 1 and 2, respectively, irradiated (50 kGy) 50/50 HDPE/GTR.

Table 1
Finite elements analysis: tests and parameters

Simulation no.	Matrix		Filler	
	E (MPa)	ν	E (MPa)	ν
1	1000	0.4	5	0.499
2	800	0.4	5	0.499
3	1000	0.499	5	0.499
4	1000	0.4	20	0.499
5	1000	0.2	5	0.499
6	1000	0.4	0.2	0.499

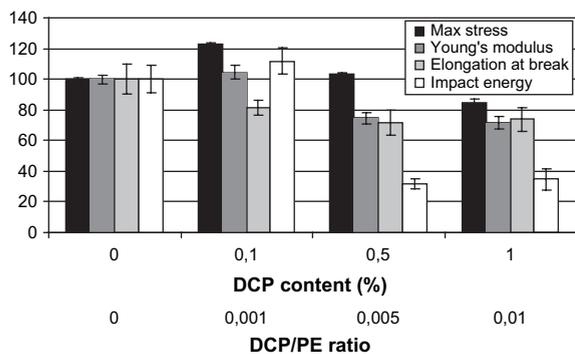


Fig. 3. Mechanical properties of HDPE treated with DCP.

It can be seen that process 2 is more efficient than process 1 because the free radicals, caused by the breakdown of DCP, are directly located at the rubber-matrix interface. Hence, interfacial co-crosslinking is promoted and, conversely, HDPE crosslinking would be restricted. Elongation at break of the irradiated blend is lower than the two previous blends. However, a relatively high maximal stress and elongation at break can be achieved together only by irradiation.

Moreover, in irradiated blends, HDPE crosslinking and interfacial co-crosslinking can be considered as two independent phenomena. On the contrary, with peroxide compatibilization, the consumption of free radicals is shared between these two reactions (and possibly others).

3.2. Limits of compatibilization

We have just presented some efficient processes to compatibilize HDPE/GTR blends. These processes promote an interfacial co-crosslinking between polyethylene and rubber particles. Nevertheless, the best combination of mechanical properties achieved is still lower than those of virgin HDPE. Hence, it is important to determine if compatibilization could really provide innovative materials with interesting properties or if it is not possible to obtain better performance than that of the virgin polymer.

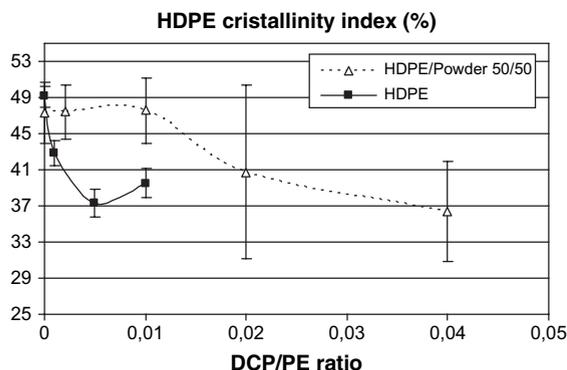


Fig. 4. Crystallinity content of HDPE and 50/50 HDPE/GTR blends.

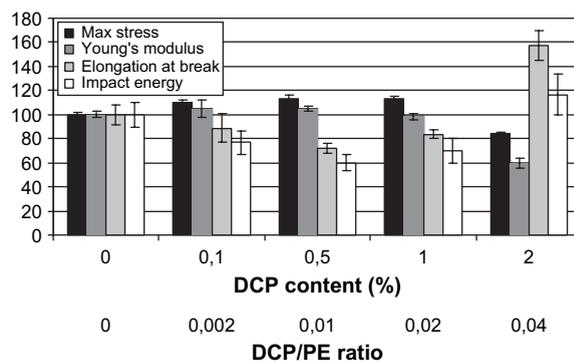


Fig. 5. Mechanical properties of 50/50 HDPE/GTR blends treated with DCP.

3.2.1. SEM observations under tensile tests

Fig. 7 shows a HDPE/GTR standard specimen (non-compatibilized) under tensile tests. A decohesion phenomenon occurs quickly (at an elongation of 6%), followed by the breaking of the material (at 8%). Moreover, numerous particles are located along the crack. The poor elongation at break is caused by the presence of particles and to the lack of rubber-polyethylene interfacial adhesion.

Tensile tests described previously were instrumented by an optical method based on Digital Image Correlation. This technique provides full field displacement and strain measurements on the surface of the material with a wide range of measurement sensitivity and spatial resolution [21]. Results obtained by photomechanical analysis are given in Fig. 8. Transverse and axial local strains are plotted versus the macroscopic strain imposed on the specimen. The elongation and breaking of materials could be divided in three steps. In the first step, only the particle (zone 1) is strained in the tensile axis. Polyethylene is not strained because of its stiffness (Young's modulus of PE is equal to 1000 MPa against a few MPa for rubber). Along the transverse axis, the section of a particle decreases because rubber volume remains constant (isochoric behaviour is generally observed for these materials). The matrix is constrained by the particle due to the interfacial adhesion. However, for a given elongation, the stress at the interface is too high and debonding occurs (vertical line, step 2). After the debonding, the elongation of polyethylene

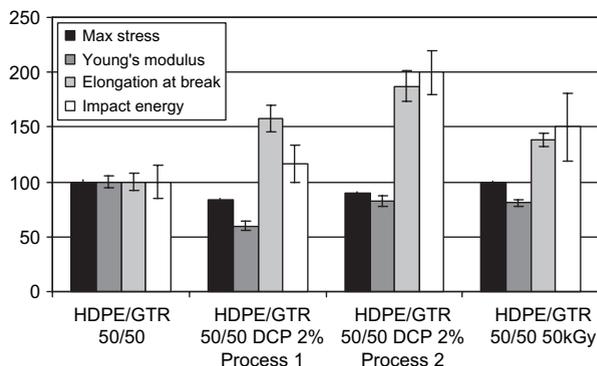


Fig. 6. Comparison of different processes.

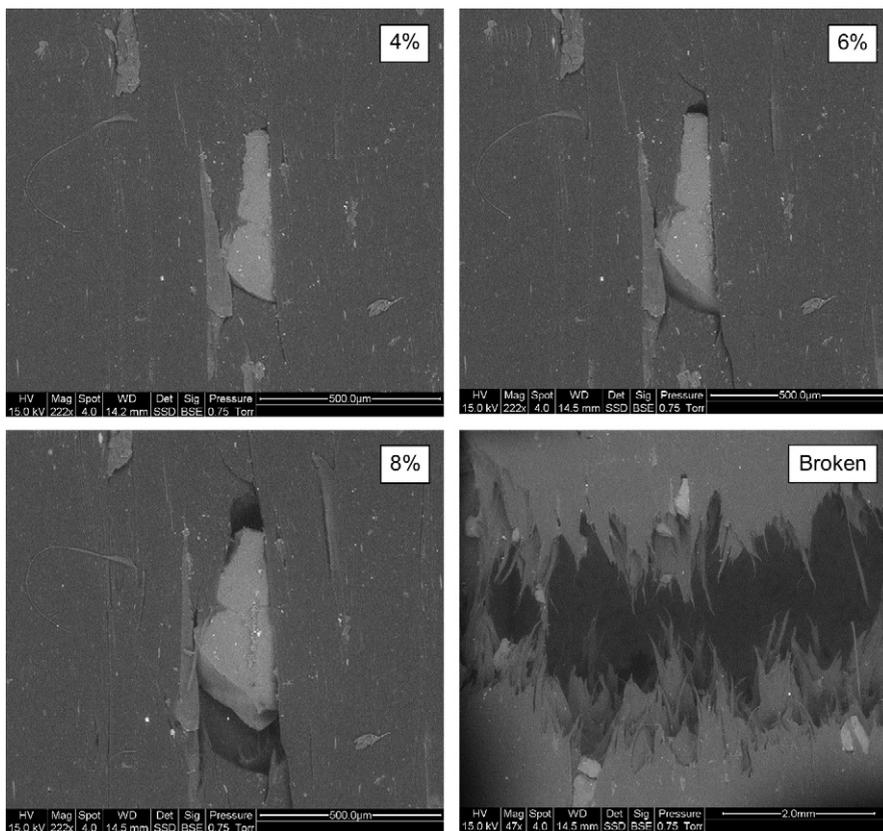


Fig. 7. HDPE/GTR blends under tensile tests.

increases very quickly along the tensile axis, up to the breaking of the material. Consequently, an improvement of interfacial adhesion could allow debonding and material rupture to be delayed.

3.2.2. Elasticity

Two materials – irradiated (50 kGy) and untreated 50/50 HDPE/GTR – underwent elongation up to a given value (6, 10 and 15%). Then the stress was reduced to zero. The difference between the maximal elongation and the residual elongation is the reversible elastic deformation.

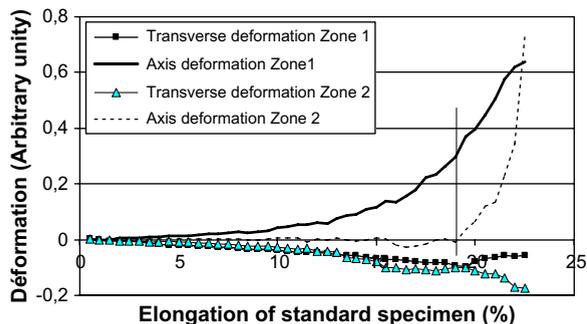


Fig. 8. Example of photomechanical results.

According to Fig. 9, it is obvious that elastic deformation is not improved by irradiation. This means that compatibilization, which increases elongation at break by promoting interfacial adhesion and delaying debonding, does not lead to a more elastic material (and hence to a “thermoplastic elastomer” material).

3.2.3. Finite elements analysis

3.2.3.1. Influence of adhesion. The finite elements analysis (presented in Experimental Part) run with variable

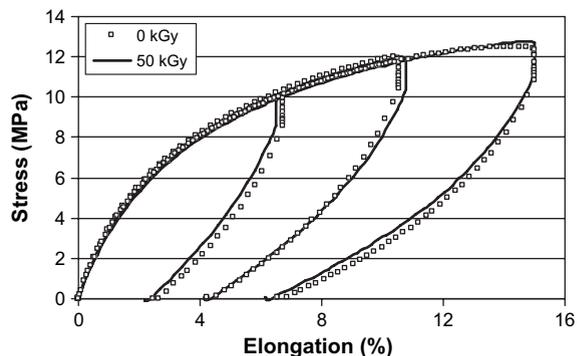


Fig. 9. Mechanical behaviour of two materials under tensile tests.

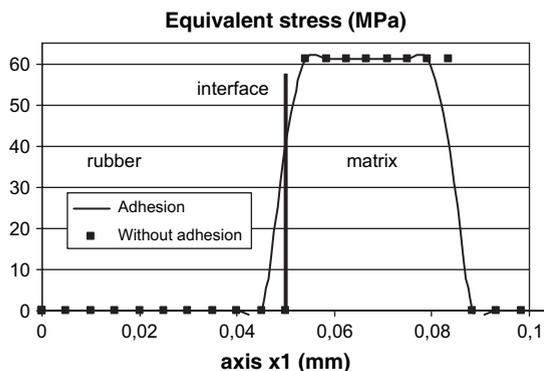


Fig. 10. Effect of adhesion on equivalent stress.

adhesion between filler and matrix was used to study the influence of interfacial adhesion on the distribution of a given stress in the blend. Fig. 10 shows the results concerning the equivalent stress. We can note that equivalent stress is nearly equal to zero in the particle. Only polyethylene undergoes the applied stress and the interfacial gradient is very high. The stress in the matrix is similar in the two cases (perfect adhesion and without adhesion).

Hence, we could assume that interfacial adhesion could not improve maximal stress of the blend.

3.2.3.2. *Influence of Young's modulus.* Tests no. 1, 2, 4 and 6 (see Table 1) are compared in Figs. 11 and 12. All these tests correspond to realistic blends with a matrix stiffer than the particle. Nevertheless, it is interesting to evaluate the effect of the difference between Young's modulus of polyethylene and rubber on the stress into the material. Firstly, transverse stresses are much weaker than equivalent stresses. Secondly, equivalent stresses are similar in all cases.

So, the distribution of stress is very limited in the material because Young's modulus of the matrix is very high compared to Young's modulus of rubber. The maximal stress of the blend could not be improved significantly.

4. Conclusions

A treatment of compatibilization using peroxide and based on free radicals mechanisms has been presented. The resulting blends exhibit better elongation at break and

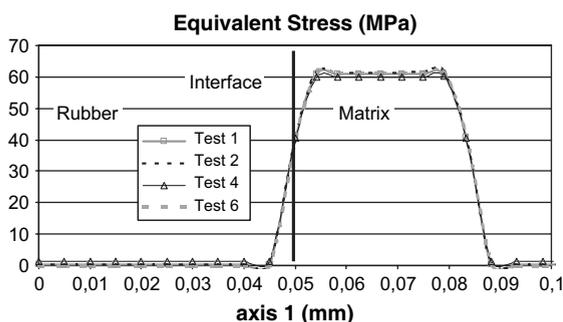


Fig. 11. Effect of Young's moduli on equivalent stress.

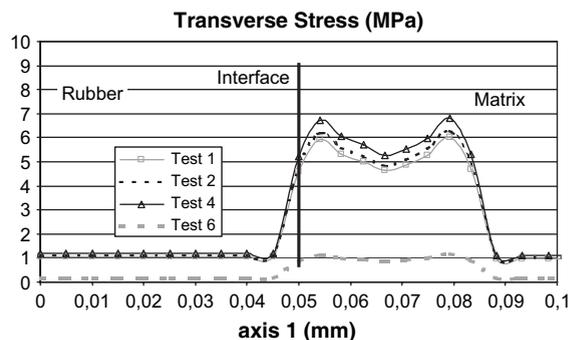


Fig. 12. Effect of Young's moduli on transverse stress.

impact energy than uncompatibilized blend. This is due to a co-crosslinking phenomenon which creates interfacial adhesion between polyethylene and rubber. Crosslinking of the matrix occurs also, consuming free radicals and degrading mechanical performance from a given DCP content. The presence of these radicals at the interface promotes compatibilization and so the mechanical properties.

Nevertheless, it was also shown that such a treatment of compatibilization could not lead to a "thermoplastic elastomer". Experimental tests and finite elements analysis showed that neither elasticity nor maximal stress was improved by interfacial adhesion. The only effect of the compatibilization was to delay the debonding and so the breaking of the material.

Taking into account these limitations in relation to expected mechanical properties, the recycling of end-life tyres by grinding and incorporating powder into a thermoplastic matrix appears not very promising as a new route for waste management.

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