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ORIGINAL PAPER

Evaluation of the Role of Devulcanized Rubber on the Thermo-mechanical Properties of Polystyrene

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Abstract

In this paper, different amounts of both devulcanized rubber (DR) and non-devulcanized rubber (NDR) were melt compounded and compression moulded with a brittle thermoplastic matrix such as polystyrene (PS). Scanning electron microscopy observations of the prepared blends showed that the PS/rubber interfacial adhesion, although rather limited, was improved in the case of DR, and that DR domains within the PS matrix had a lower size than NDR particles. Thermogravimetric analysis highlighted that the onset degradation temperature decreased upon the addition of rubber, and the maximum mass loss rate temperature increased. Differential scanning calorimetry tests showed that the glass transition temperature slightly decreased upon addition of DR and NDR. This increase also enhanced the maximum service temperature determined by measuring the Vicat grade. The surface hardness, the tensile modulus and stress at break were negatively affected when recycled rubber was added, because of the limited compatibility between PS and rubber particles and the relatively large size of the rubber domains. A notable increase in material ductility, with an enhancement of the tensile strain at break and of the impact resistance, was detected at elevated rubber amounts. Quite interestingly, mechanical properties of the blends with DR were systematically higher than those of the corresponding blends with NDR.

Keywords Rubber · Devulcanization · Recycling · Polystyrene · Blends · Mechanical properties

Introduction

Rubber is a material with unique properties, difficult to be replaced and with a significant economic and social impact in Europe, especially in the transportation field. According to the International Rubber Study Group (IRSG), in 2018 the worldwide consumption of rubber has been 29.2 Mton and it is estimated that almost 70% of this quantity has been used in the tyre industry [1]. During the manufacturing operations of a tyre, the different constituents are vulcanized together in order to form a crosslinked structure with good mechanical properties and dimensional stability [2, 3]. The crosslinked nature of vulcanized rubber and the presence of additives such as stabilizers, antioxidants, antiozonants can explain why tyres are extremely resistant to biodegradation, photochemical and thermal degradation [4, 5]. According to the European Tyre and Rubber Manufacturers Association (ETRMA) statistical booklet of 2017 and of the European Synthetic Turfs Organisation (ESTO) report of 2016, it is estimated at the European level that the overall reuse rate within the rubber industry of the rubber coming from End of Life Tyres (ELT) is as low as 16.5%, decreasing to 1.5% for in-compound applications. The remaining rubber content is lost during usage through wear (7.5%), energy recovery (56.8%), material recovery through non-rubber applications (12.8%), and landfill disposal (6.5%). The extremely low recycling rate of rubber products, coupled with the high degree of dependency of Europe's industry on natural rubber supplies from non-EU countries, forced in September 2017 the inclusion of natural rubber in the list of Critical Raw Materials for EU [6].

It is estimated that around 800 million tyres are discarded worldwide every year, although in the European Union the landfill of end of life tyres is forbidden since 1999 [1, 7]. However, recovered waste tyres can be source of valuable raw materials. In fact, part of the worn tyres is still suitable

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for the on-road use and can be therefore reused. From the economical point of view, retreading is the most viable way of waste tyres usage since it requires only 30% of energy and 25% of raw materials used to manufacture a new tyre [8]. Other end of life options for tyres, are represented by recycling [9] reclamation [10, 11], devulcanization [12], energy recovery [13, 14] and pyrolysis [15, 16]. Waste tyres, after their shredding into crumbs, can be used for the production of playground surfaces, athletic tracks, artificial reefs, crash barriers and flotation devices [5, 16, 17].

The recycling of rubber generally starts by grinding the post consumed rubber through dry, wet or cryogenic processes [18]. Cryogenic milling allows to obtain particles of small dimensions, but the costs of this operation can make the process not economically [19]. In most rubber recycling processes, the destruction of the carbon–carbon (C–C) bonds and a consequent decrease of the molecular weight and of the physical properties of the resulting compounds is occurring [20–22]. In the ideal case, the recycling process of rubber should consist in the breakage of the sulphur–carbon (C–S) or the sulphur–sulphur (S–S) linkages between the different polymer chains in order to obtain a rubber compound that can be processed and vulcanized similarly to virgin rubber [23]. This process is generally called devulcanization. Devulcanization is a process of cleaving the C–S–C and C–S–S–C bonds of vulcanized rubber in order to breakdown the three dimensional structure formed during the vulcanization [20, 24]. Devulcanization can be a chemical, ultrasonic, microwaves-based or a thermo-mechanical process [25]. Chemical devulcanization involves the use of chemicals such as disulphides, thiol-amine reagents, hydroxide or chlorinated hydrocarbons in order to break the C–S or the S–S bonds [1]. It is important to underline that during chemical devulcanization process also a partial degradation of the rubber macromolecules takes place [1]. The drawback of this method is the toxicity of the involved chemical agents [26].

The use of devulcanized rubber (DR) in polymer blends could represent an interesting way of using recycled rubber. Considering that the worldwide plastics production has reached 380 million tons in 2015 [27], even the addition of a small percentage of DR in virgin plastics could lead to a noticeable consumption of DR [22]. In this way, it is possible to obtain materials with different properties in comparison to the pristine matrices, to lower the cost of the resulting compounds and to save considerable amounts of raw materials. Therefore, devulcanized rubber has been recently compounded with virgin rubber, and it was demonstrated that the addition of DR can strongly affect the processability and the tensile properties of the resulting materials, leading also to a substantial cost reduction [19, 28–31]. Some attempts have been also made in blending DR with thermoplastics, such as polyethylene [31] and polypropylene [30]. For instance, Hassan et al. introduced waste rubber powder in a two-roll mill in the presence of various ratios of curatives to develop sheets of devulcanized rubber and a thermoplastic elastomer (TPE) was then prepared by blending the obtained devulcanizate with high density polyethylene (HDPE) at different concentrations. A remarkable enhancement in tensile strength and hardness by increasing HDPE feed ratio and dose was detected, while elongation at break was adversely affected by addition of DR [31]. According to the authors opinion, it could be also interesting to evaluate the potential of DR on the physical properties of brittle thermoplastic polymers, such as polystyrene (PS). In fact, PS is a synthetic aromatic hydrocarbon polymer and it is also one of the most widely used plastics, the scale of its production being several million tonnes per year. General purpose PS is clear, hard, and rather brittle. Its diffusion in the last decades was favoured by its relatively low price. It has a rather poor barrier to oxygen and water vapour, and has a relatively low softening point (of around 90 °C). Polystyrene can be naturally transparent, but it can be coloured with colourants. In order to overcome the problems related to the brittleness and the limited impact resistance of PS, high impact polystyrene (HIPS) and styrene-acrylonitrile copolymers were developed. It is also therefore clear that in order to use PS for some specific applications, it is necessary to prepare PS blends with toughening agents. In the case of rubber, several references regarding the use of ground-tyre-rubber (GTR) as a toughening additive of PS can be found in the open literature [22, 32–36]. For instance, Pittolo et al. showed that the toughness of the PS was found to increase with increasing rubber-to-matrix adhesion and rubber decreasing particle size. It has also found that the main contribution to the improvement of the fracture toughness is related to a crack bridging mechanism, with the rupture of the rubber particles during the crack propagation [25].

Despite the possible advantages deriving from blending devulcanized rubber with polystyrene in terms of increased fracture toughness, cost reduction and increased environmental sustainability, only few papers can be found in the open literature on this topic. For instance, rheological properties and the morphology of blends of devulcanized styrene-butadiene rubber (dSBR) with PS were investigated by Scuracchio et al. [19]. In this work, it was concluded that in order to achieve a toughening of PS by the addition of dSBR, their particle size should be further reduced by changing the devulcanization process conditions. However, a comprehensive investigation about the thermo-mechanical behaviour of PS/DR blends has never been reported in literature. Therefore, this work investigates in a systematic way the most significant microstructural, thermal and mechanical properties of polystyrene blended with different amounts of DR, in order to verify the potential of the use of devulcanized rubber as toughening agent in a brittle thermoplastic matrix such as PS. The physical properties of the resulting compounds were compared with the corresponding blends prepared with non devulcanized rubber (NDR). In the present paper, recycled rubber coming from a rather new devulcanization technology is considered.

Experimental Part

Materials

Polystyrene granules (Edistir ICES900) with density of 1.04 g cm^{-3} and Melt Flow Index of 2.5 g/10′ (200 °C, 5 kg) were provided by Versalis spa (Milano, Italy) and used as polymer matrix. Both devulcanized rubber (DR) and non-devulcanized rubber (NDR), kindly provided by Rubber Conversion srl (Verona, Italy), were used for the preparation of PS/rubber blends. NDR consisted of ground-tyre-rubber coming from truck tyres, and it was constituted by a mixture of natural rubber (NR) and styrene-butadiene rubber (SBR). DR was produced starting from the corresponding NDR through a patented chemical devulcanization process performed by a chemical-modifier and activated by the mechanical shear induced by refining rollers. The process is performed at ambient pressure and temperature and the rubber never exceeds 90 °C, well below the threshold temperature for rubber degradation. The process has no air or water emissions hence it is environmentally friendly, and the chemical modifier is patented and specifically engineered [37].

Both DR and NDR were provided in form of fluffy material with irregular size and heterogenous dimensional distribution, with a mean dimension lower than 1 mm. While polystyrene granules were used as received, both DR and NDR were cryo-milled using liquid nitrogen and consequently sieved with a 300 μm mesh size. A picture of the DR provided by Rubber Conversion is shown in Fig. 1. The properties of the devulcanized rubber provided by the producer are reported in Table 1.

Fig. 1 Devulcanized rubber provided by the producer

Table 1 Technical data sheet of de-vulcanized rubber

Property	Unit	Method	Value
Total polymer content	%	UNI EN ISO 9924	55–68
Carbon black	%	UNI EN ISO 9924	27–34
Ash	%	UNI EN ISO 9924	6 max
Acetone extract	%	ASTM D 297	6 max
Density	g cm^{-3}	ASTM D6226	1.18
Tensile strength (15′/145 °C)	MPa	ASTM D 412	8 min
Elongation at break (15′/145 °C)	%	ASTM D 412	400
Hardness (IRHD)	IRHD	ISO 48	53–63

Samples Preparation

PS/rubber blends were obtained by mixing polystyrene granules and rubber by using a Thermo Haake melt compounder (Thermo Fischer Scientific, USA) operating at 130 °C, 40 rpm for 15 min. The mixing was proceeded by firstly plasticizing PS in the internal mixer for 3 min and subsequently adding weighted rubber directly inside mixer chamber: compounding was then carried on for further 12 min. Plastic melt was then deposited between two metal plates (separated from release paper) and hot pressed using a Carver hot press (Carver, USA) at 140 °C, 40 rpm for 10 min, under a load of 8 ton obtaining 120 mm × 120 mm × 2 mm sheets.

Dumb-bell shaped specimens (ISO 527 1BA) were puchcutted from the square sheets (in Fig. 2 the PS_DR0 (transparent/white) and the PS_DR20 (black) samples are shown). The list of the prepared samples is reported in Table 2. It should be noticed that only in the case of quasi-static test all the compositions were tested. For the other tests four compositions were selected (PS_DR20 and PS_NDR20, PS_DR60 and PS_NDR60).

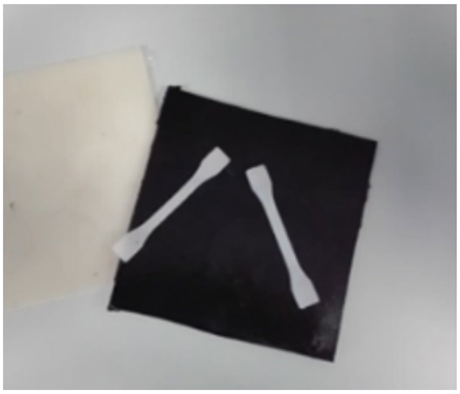


Fig. 2 Representative image of the prepared samples. Dumbell of PS sample and square sheets of PS_DR60 and PS samples

Table 2 List of the prepared samples

Polystyrene content (wt%)	DR content (wt%)	NDR content (wt%)	Samples
100	0	0	PS
90	10	–	PS_DR10
80	20	–	PS_DR20
70	30	–	PS_DR30
60	40	–	PS_DR40
50	50	–	PS_DR50
40	60	–	PS_DR60
90	–	10	PS_NDR10
80	–	20	PS_NDR20
70	–	30	PS_NDR30
60	–	40	PS_NDR40
50	–	50	PS_NDR50
40	–	60	PS_NDR60

Experimental Methodologies

The Fourier transformed infrared spectra (FTIR) were acquired only on DR and NDR using a Perkin Elmer FT-IR Spectrometer (Perkin-Elmer, USA); the working parameters were, for the transmission mode, wavenumber range 4000–400 cm^{-1}, 4 scans, resolution of 4 cm^{-1}.

De-vulcanization degree of rubber was determined by following ASTM standard D6814-02. The amount of de-vulcanization is correlated to the crosslink density, whose evaluation involves a swelling test to be performed [38, 39]. The procedure was carried out on three different samples of DR and on three reference samples of NDR. Toluene was used as solvent for the swelling test. The rubber powder was weighted ($M_{initial}$ = initial mass) and let swell in toluene for 48 h. Once reached the equilibrium swelling the excess solvent was removed using vacuum filtration: the swollen rubber was removed and put into a Buchner funnel [40]. After the filtration the swollen rubber was weighted and the solvent mass ($M_{solvent}$) determined by subtraction with respect to the rubber initial mass $M_{initial}$. Samples were then dried to a constant weight in oven at 40 °C for 72 h and the dried rubber mass (M_{final} = final mass) was measured. Crosslink density V_c was calculated through the Flory-Rehner equation according to ASTM D6814-02, as reported in Eq. (1):

$$V_c = \frac{-[ln(1-V_r)+V_r+X_l V_r^2]}{[V_s(V_r^{1/3}-V_r/2)]} \qquad (1)$$

where: $X_l = 0.3795$ is the GTR-toluene interaction parameter; $V_s = 106.2\ cm^3\ mol^{-1}$ is the molar volume of toluene $V_r = \frac{M_{final}/\rho_{rubber}}{\frac{M_{final}}{\rho_{rubber}}+\frac{M_{solvent}}{\rho_{solvent}}}$ is the volume fraction of polymer in the swollen network in equilibrium with toluene; $\rho_{solvent} = 0.866$ g cm^{-3} is the toluene density; $\rho_{rubber} = 1.18$ g cm^{-3} is the density of rubber measured through helium picnometry.

The percentage of de-vulcanization ($\%dev$) was thus evaluated according to Eq. (2):

$$\%dev = [1 - \frac{V_{c,DR}}{V_{c,NDR}}] * 100 \qquad (2)$$

The swelling ratio $R_{swelling}$ was calculated as reported in Eq. (3):

$$R_{swelling} = \frac{M_{swollen} - M_{initial}}{M_{initial}} \qquad (3)$$

where $M_{swollen}$ is the mass of the swollen rubber after filtration.

The percent mass loss ($\%massloss$) was also determined as indicated in Eq. (4):

$$\%massloss = \frac{M_{initial} - M_{final}}{M_{initial}} * 100 \qquad (4)$$

The cryofractured surfaces of PS/rubber blends containing 60 wt% of devulcanized and non-devulcanized rubber were observed through a Zeiss Supra 40 field emission scanning electron microscope (FESEM), operating at an acceleration voltage of 4 kV. The samples were metallized through the deposition of a thin coating of electrically conductive platinum palladium over the sample's surfaces inside a vacuum chamber.

Thermogravimetric analysis (TGA) was performed through a TGAQ5000 thermobalance under a nitrogen flow of 10 ml min^{-1} in a temperature interval between 30 and 650 °C, at a heating rate of 10 °C min^{-1} on specimens with a mass of around 10 mg. The temperature associated to a mass loss of 2% ($T_{2\%}$), to a mass loss of 5% ($T_{5\%}$), the temperature related to the first maximum mass loss rate (T_{peak1}), and the temperature related to the second maximum mass loss rate (T_{peak2}), were determined.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC30 calorimeter under a nitrogen flow of 10 ml min^{-1} on specimens with a mass of around 10 mg. A first heating from 25 to 200 °C was followed by a cooling stage from 200 to 25 °C and by a second heating from 25 to 200 °C, and all the thermal ramps were conducted at 10 °C min^{-1}. The temperatures associated to the glass transition during the first heating scan (T_{g1}), during the cooling scan (T_{g2}) and during the second heating scan (T_{g3}) were evaluated.

The Vicat softening temperature (VST) was determined using an ATS FAAR HDT-Vicat Tester, model MP/3 according to the ASTM D1525-09 standard. The test was conducted starting from a temperature of 40 °C, at a heating rate of 120 °C h^{-1} applying a load of 50 N. For each composition, three samples 20 mm wide and 5 mm thick were tested, and the temperature associated to a tip penetration of 1 mm was considered as the VST of the material.

The Shore D hardness test was performed using a Hilderbrand Durometer following the ASTM D2240 standard. Square samples 20 mm wide and 5 mm thick were tested, and at least five measurements were taken for each composition. The Shore D value was determined after pressing the indenter against the specimen for a time equal to 5 seconds.

The tensile properties under quasi-static conditions of ISO 527 type 1BA specimens were measured at 23 °C through an Instron 5969 tensile machine equipped with a load cell of 50 kN. Tests for the determination of the elastic modulus (E) were carried out at 0.25 mm min^{-1}, setting a maximum deformation of 1%. The strain was monitored by using an Instron model 2620–601 resistance extensometer, with a gauge length 12.5 mm. The elastic modulus was measured as secant modulus between strain levels of 0.05% and 0.25%. Tensile tests at break were performed without extensometer at a cross-head speed of 10 mm min^{-1}; the stress at break (σ_b) and the deformation at break (ϵ_b) were determined. For all the tensile tests, 5 specimens were tested for each sample.

The Charpy impact strength of PS/rubber blends was investigated through an instrumented impact pendulum by CEAST. The test was carried out following ISO 179 standard, setting the following parameter: impact angle equal to 20°, impact speed equal to 2.62 m s^{-1}, mass of the hammer equal to 2.5 kg. For each composition, five notched rectangular specimens with dimensions of 55 mm (length) × 5 mm (thickness) × 10 mm (width) and a notch depth of 2 mm were tested. The specific impact energy at the maximum load (U_i), the specific total impact energy (U_{tot}) and the maximum load (F_{max}) were determined.

Results and Discussion

From the FT-IR spectra shown in Fig. 3 it is possible to observe that in addition to the small broad band within the region 3200–3400 cm^{-1} associated with the –CH stretching vibration of hydrogens present in the styrene ring group [41], other peaks related to the typical vibrations of styrene-butadiene-rubber can be also detected. In particular, vibrations associated to the double carbon bond of the benzene ring are visible respectively at 722 cm^{-1} and at 1539 cm^{-1}, while the peak at 963 cm^{-1} is a probable indication of the presence of butadiene unit. The relative values of the bands at 1452 cm^{-1}, 1412 cm^{-1} and 1383 cm^{-1} are assigned to scissor vibrations of the –CH bond within $–CH_2–$, –R–C=CH–R– and methyl group ($–CH_3$) respectively [42]: peak associated to $–CH_2–$ group remain constant, while bands associated to –R–C=CH–R′– and methyl groups seem to slightly decrease. De-vulcanization process indeed breaks the hydrogen bonds of =CH– and those of $–CH_3$ while is not able to break so easily the hydrogen bond of the $–CH_2–$: due to the lower energy associated to the –CH bond of the first two groups (418 and 335 kJ mol^{-1} respectively) with respect to that of the $–CH_2–$ (607 kJ mol^{-1}), energy associated to the de-vulcanization process is sufficient only to break the macromolecular chain in the regions of the terminal branching and in correspondence to the double bonds [42]. The area of sulphur bonds corresponds mainly to the 600-400 cm^{-1} and is not detectable in the spectrum a part from the –C–S– stretching vibration assigned to the 803 cm^{-1} peak: it seems that the intensity of the vibration is reducing after de-vulcanization treatment as consequence of the breakdown of the –C–S– bridges [42]. The presence of unsaturation site C=C in poly-isoprene, instead, is confirmed by the peak at 1615 cm^{-1} [43] in this band region it is possible to notice a big difference between DR and NDR, probably due to the fact that the de-vulcanization process, by breaking the sulphur cross-links that formed in correspondence to the –C=C–, allows somehow the partial re-construction of some carbon double bonds waiting for a new vulcanization process.

Looking at the results regarding the investigation of the devulcanization degree, reported in Table 3, it is evident that

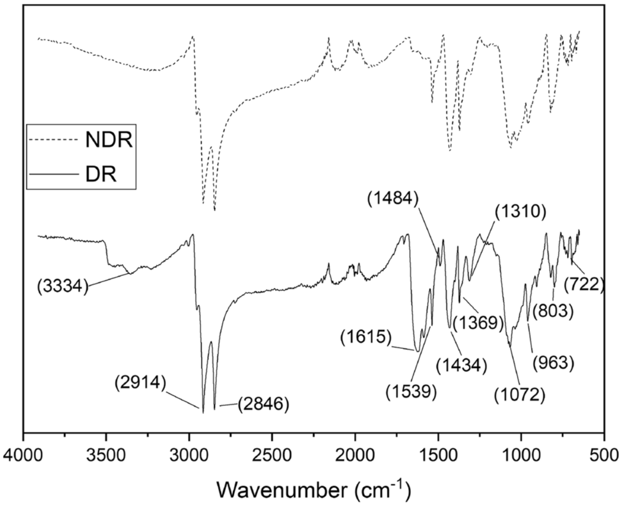


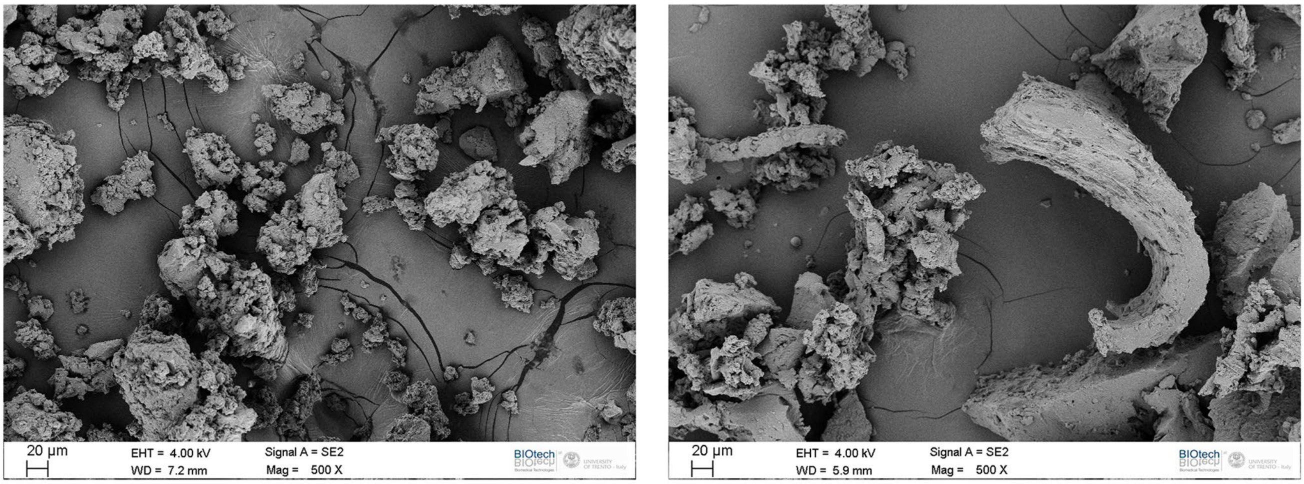
Fig. 3 IR spectra on devulcanized rubber and non-devulcanized rubber

Table 3 Results of the evaluation of the devulcanization degree

Property	DR	NDR
Cross-link density (mol cm^{-3})	0.59×10^{-3}	0.85×10^{-3}
Devulcanization degree (%)	27.7	–
Swelling ratio (–)	2.00	1.82
Mass loss (%)	8.45	5.69

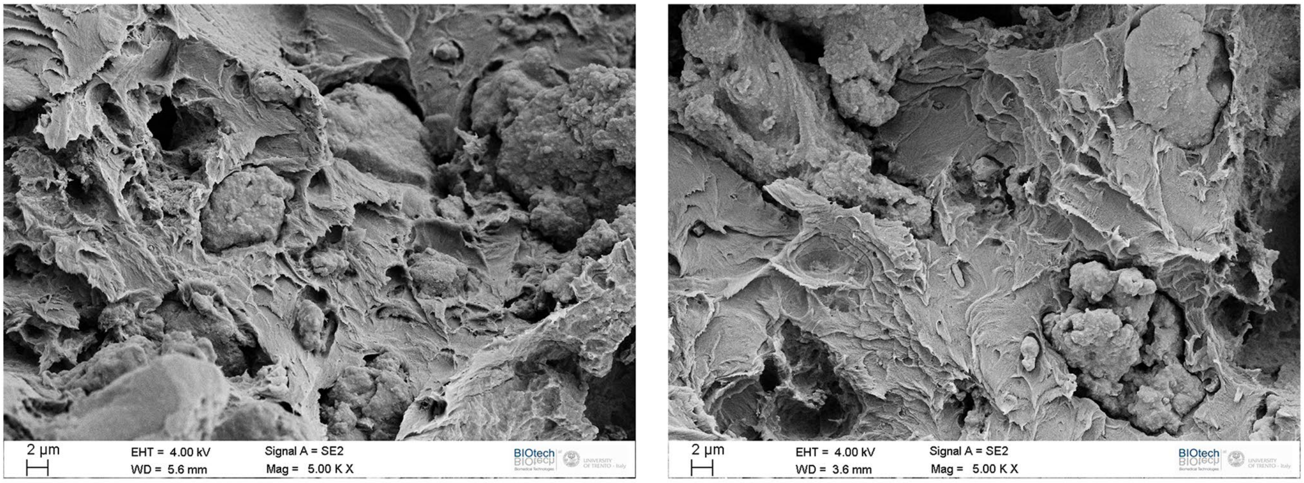
the cross-link density decreases with de-vulcanization meaning the effective breakage of C–S and S–S linkages present in the rubber as result of the shear-driven chemical activated process. From calculated values of V_c, the percentage de-vulcanization was thus evaluated according to Eq. (2): the resulting degree of de-vulcanization resulted to be equal to the 28% with respect to the reference ground tyre rubber. The above results are in good agreement with the values of swelling ratio and mass loss reported in Table 3 that were evaluated both for de-vulcanized and for not de-vulcanized rubber samples: the decreased density of cross-linking, indeed, caused higher swelling of DR within the toluene and a greater soluble fraction as consequence of the chain scission of the molecular network during de-vulcanization treatment.

FESEM observations were carried out in order to understand the morphology of the prepared blends and to analyse the rubber dispersion within the polymer matrix. FESEM micrographs of DR and NDR powders are reported in Fig. 4a, b. From these micrographs it is possible to observe that NDR particles are more aggregated in than DR, and characterized by domains with larger dimensions. Smaller granules measure just tens of micrometers, while larger particles have a mean size in the order of hundreds of micrometers. On the other hand, NDR particles seem to have sharper edges and a more flattened profile. Observing the FESEM micrographs of PS_DR60 and PS_NDR60 samples reported in Fig. 5a, b, it is possible to notice that the adhesion between the PS matrix and both types of rubber is



(a) (b)

Fig. 4 SEM micrographs on devulcanized rubber (**a**) and non-devulcanized rubber (**b**), ×500



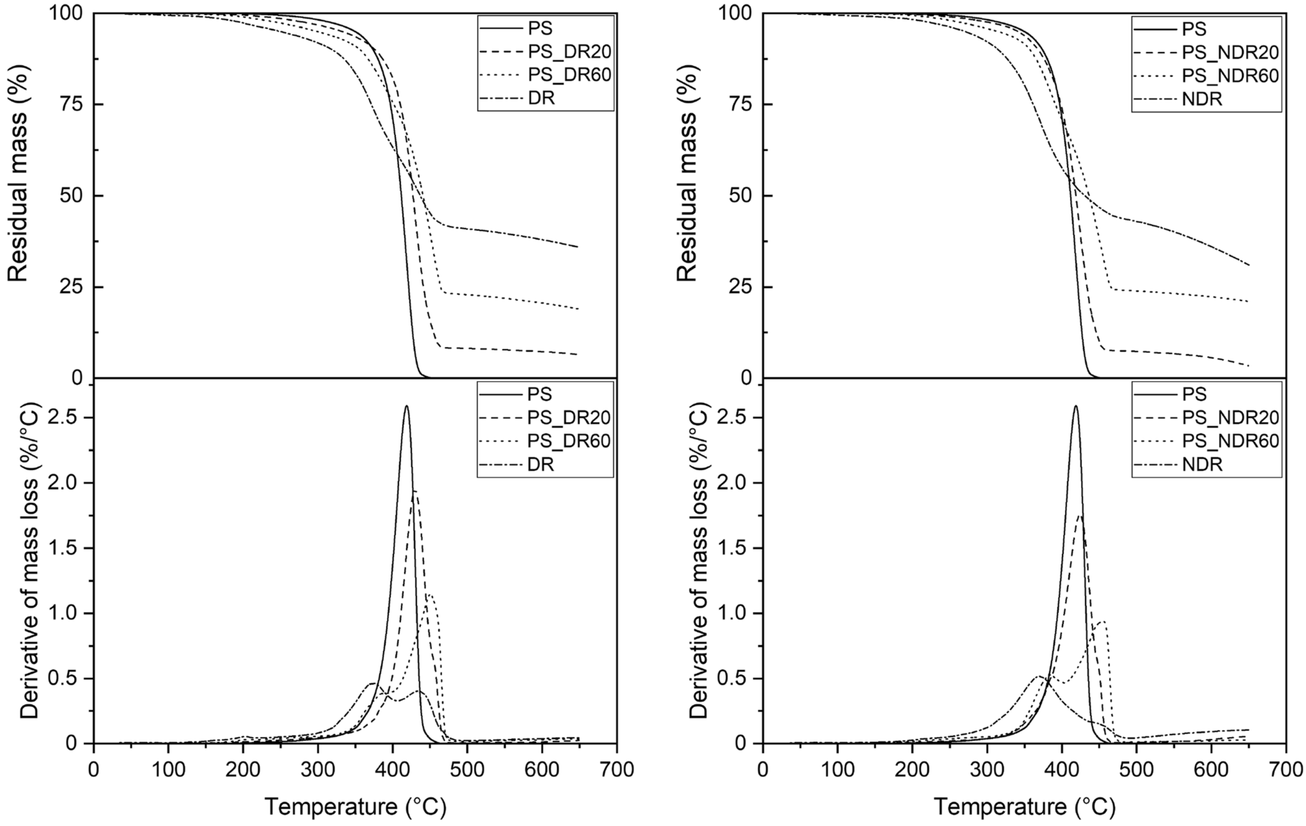
(a) (b)

Fig. 5 SEM micrographs on the cryofractured surfaces of PS/rubber blends: **a** PS_DR60, ×5000; **b** PS_NDR60, ×5000 rather poor. However, it seems that the interfacial detachment between PS and rubber is more evident in the case of NDR. Moreover, DR domains within the PS matrix seem to have a slightly lower size than the NDR particles at the same rubber amount. Both these aspects could influence the mechanical behaviour of the resulting blends.

The investigation of the thermal degradation of the prepared materials is important to assess their potential applications when elevated temperatures are involved. Therefore, thermogravimetric tests (TGA) were carried out. In Fig. 6a, b the trends of the residual mass as a function of the testing temperature, together with the corresponding derivative curves, are reported, while in Table 4 the most significant results are summarized. From the mass loss curves it is evident that both DR and NDR present lower onset degradation temperature than neat PS, with a maximum mass loss rate temperature (T_{peak1}) at around 370 °C, while the mass loss rate peak for the neat PS (T_{peak2}) is instead at about 420 °C.

It is also interesting to notice that the temperature for 2% ($T_{2\%}$) and 5% ($T_{5\%}$) mass loss of DR are 20 °C lower than those of NDR. This is most probably due to the lower crosslinking degree of DR compared to the NDR. Preliminary swelling tests performed on DR powder (not reported for the sake of brevity) showed that the devulcanization degree of DR was around 29%. As a result, all the prepared blends have $T_{2\%}$ and $T_{5\%}$ values lower than the neat matrix, especially at elevated rubber contents, and the onset degradation temperature of the blends with DR are systematically lower than those with NDR at the same rubber amount. Quite interestingly, the temperature associated to the maximum mass loss rate of the blends (T_{peak2}) is higher than that of the neat PS, and increases with the rubber amount. This is probably due to the fact that both DR and NDR present a second mass loss rate peak at about 440 °C, 20 °C higher than the T_{peak2} of neat PS.

In the case of DR and NDR, the weight loss associated to T_{peak1} and T_{peak2} occurring in the range of 300–500 °C is relative to the degradation of the polymer chain and to the evolution of the less volatile compounds. Two distinguishable peaks can be noticed: it is possible to relate the first degradation step to the degradation of the isoprene chains and to the aliphatic carbon atoms of the styrene units of SBR component, while the second step can be associated to the less volatile compounds and to the combustion of the remaining styrene benzene rings which require an higher activation energy to oxidize [44].



(a) **(b)**

Fig. 6 TGA curves and derivative TGA curves of PS/devulcanized rubber blends (**a**) and of PS/non-devulcanized rubber blends (**b**)

Table 4 Results of TGA tests

Sample	$T_{2\%}$ (°C)	$T_{5\%}$ (°C)	T_{peak1} (°C)	T_{peak2} (°C)	m_{650} (°C)
PS	306.0	349.8	–	418.8	0
PS_DR20	269.1	332.3	–	429.8	6.4
PS_DR60	231.8	298.5	387.0	450.3	19.0
PS_NDR20	289.3	341.4	–	424.0	3.4
PS_NDR60	252.2	314.9	383.7	455.1	21.0
DR	185.5	250.1	373.8	434.3	35.8
NDR	209.5	270.4	369.6	443.4	31.0

While the neat PS completely degrades in gaseous products at 650 °C, the char residue increases with the rubber amount. In fact, the char residue is of around 5–10 wt% in the case of PS_DR20 and PS_NDR20 samples, and of around 20 wt% in the case of PS_DR60 and PS_NDR60 blends. For the recycled powder samples, the residue amounts to about 30–35 wt%. This corresponds to the typical concentration of inorganic additives (carbon black and other fillers) that are present in the rubber coming from truck tyres. It can be therefore concluded that the introduction of recycled powder in PS seems to lower the thermal degradation stability of the blends at low temperature (i.e. below 300 °C), but the presence of rubber additives improves the thermal stability at elevated temperatures. A similar trend in TGA has been already observed by Hassan et al. in HDPE/DR blends [31]. In that work, the observed increase of the thermal stability at high temperature was related to the presence of CB in the devulcanized rubber. However, the experienced decrease of the onset degradation temperature does not seem to significantly limit the application fields of these blends.

In order to investigate the effect of rubber introduction on the thermal properties of the blends, also DSC tests were performed. The DSC thermograms of the prepared blends collected during the first heating scan are reported in Fig. 7, while the most relevant results are summarized in Table 5. The DSC thermograms of DR and NDR do not differ one each other: no exothermal peaks are present and this means that no further vulcanization of the rubber is occurring on heating suggesting that further vulcanization of the partially de-vulcanized rubber does not take place because no residual sulphur or curing agents are still present inside. Moreover, from the DSC thermograms of both DR and NDR it is not possible to clearly detect any thermal transition, while for the neat PS sample the T_g signal associated to the glass transition temperature at about 90 °C can be distinguished. From the T_g values in Table 5 it is possible to conclude that a slight increase of the glass transition temperature can be detected both upon addition of DR and NDR, proportionally to the recycled rubber amount. For instance, for PS_DR60 sample a T_g increase of 6 °C compared to the neat PS can be detected. This temperature increase is in contrast in comparison with the results of Mujal-Rosas et al. in which no temperature increase was detected upon addition of GTR [36].

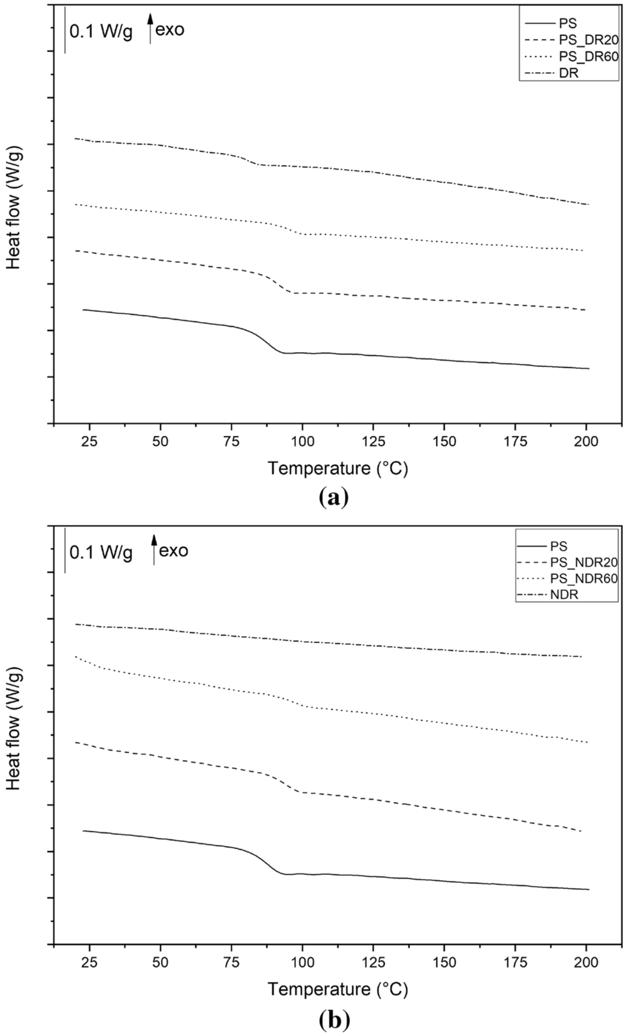


Fig. 7 DSC thermograms of PS/devulcanized rubber blends (**a**) and on PS/non-devulcanized rubber blends (**b**): first heating scan

Table 5 Glass transition temperatures obtained from DSC tests

Sample	T_{g1} (°C)	T_{g2} (°C)	T_{g3} (°C)
PS	89.6	83.4	88.5
PS_DR20	93.3	83.6	92.3
PS_DR60	96.0	–	95.0
PS_NDR20	94.4	–	94.1
PS_NDR60	95.4	–	97.1

Although FESEM micrographs reported in Fig. 5a, b did not evidence a good interfacial adhesion between the two polymeric phases, it is possible that the presence of rubber with a crosslinked nature somehow hinders the PS macromolecules mobility around the T_g, leading to a consequent increase of the glass transition temperature. It can be also hypothesized that the presence of inorganic fillers such as carbon black (CB) within recycled rubber can be partly responsible of this effect. Although further investigations will be required to have a better comprehension of this aspect, the observed T_g increase upon addition of recycled rubber could positively affect the dimensional stability of these blends at elevated temperatures.

In order to assess the effect of the addition of recycled rubber on the dimensional stability of the PS matrix at elevated temperatures, the Vicat softening temperature (VST) was measured. The obtained results are summarized in Table 6. A slight increase (of around 2 °C) of the VST can be detected upon addition of rubber, regardless to rubber type and content. This result can be explained considering the increase of T_g induced by the addition of rubber (see DSC tests). Moreover, also in this case the stabilizing effect provided by the carbon black introduced in the system via the recycled rubber should be considered. In Table 6 also the results of the Shore D hardness are summarized. As it could be expected, the addition of an elastomeric filler within a stiff thermoplastic matrix such as PS leads to a progressive decrease of Shore D values, regardless the type of rubber. In fact, at a recycled rubber content of 20 wt% Shore D of the PS is lowered of 8–9 points, while increasing the rubber concentration up to 60 wt% the measured Shore D hardness is 56, i.e. 27 points lower than that of neat PS. A similar trend has been already observed also in HDPE/DR blends [31].

In Fig. 8a, b representative stress-strain curves of PS/DR and PS/NDR blends are respectively reported, while the influence of the rubber content on the elastic modulus and on the failure properties (i.e. stress at break and strain at break) is graphically shown in Fig. 9a–c. It can be immediately noticed that the introduction of recycled rubber leads to a strong decrease of the elastic modulus. Even if the decrease of the material stiffness until a filler concentration of 20 wt% is rather limited, a harsher drop can be detected for higher rubber contents. For instance, elastic modulus of PS_DR60 sample is about 4 times lower than that of neat PS sample. This is not surprising, since the addition of an elastomeric phase within a stiffer thermoplastic polymer generally leads to a significant tensile modulus decrease [31]. This result is in accordance with the Shore D hardness trend shown in Table 4. It is important to underline that elastic modulus values of the blends with DR are systematically higher than those with NDR, at the same rubber amount (see Fig. 9a). Therefore, rubber devulcanization seems to help in the retention of the original stiffness, at least at limited filler amounts (i.e. lower than 20 wt%). A similar trend can be observed if the stress at break is considered. As it can be seen in Fig. 9b, the stress at break starts to decrease even at low rubber amounts (i.e. 10 wt%), and at a rubber concentration of 60 wt% σ_b is about five times lower than that of the neat PS. Even in this case, stress at break values of the blends with DR are slightly higher than those of the corresponding blends with NDR. According to the observations reported in literature [45], the observed deterioration of the stiffness and of the failure properties upon addition of recycled

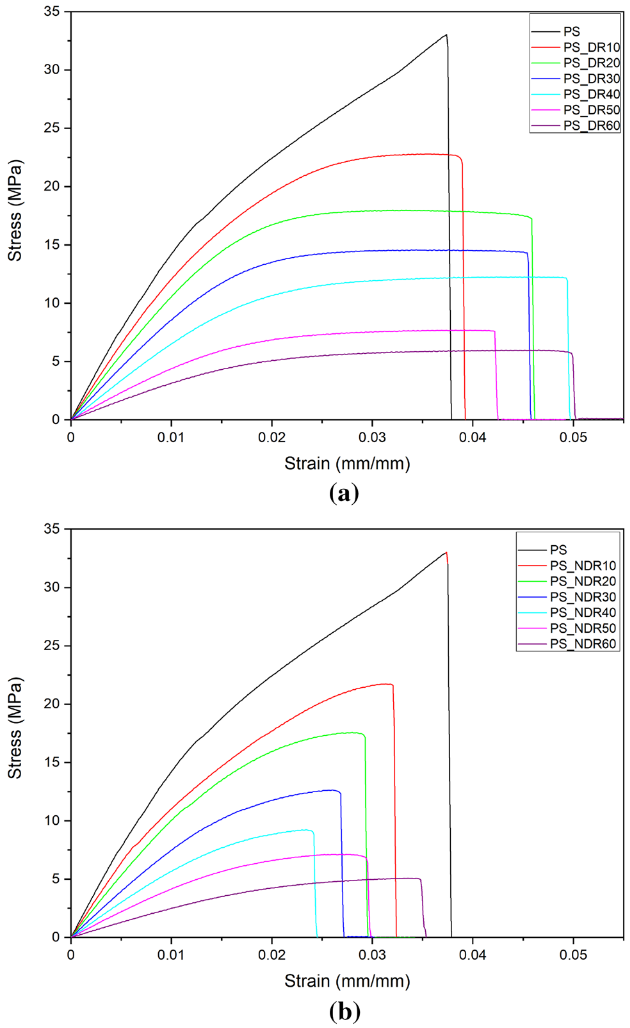


Fig. 8 Representative stress-strain curves from quasi-static tensile tests on PS blends with devulcanized rubber (**a**) and non-devulcanized rubber (**b**)

Table 6 Results of Vicat test and Shore-D hardness test

Sample	Vicat softening temperature (°C)	Shore-D
PS	114.1 ± 0.1	82.2 ± 0.2
PS_DR20	116.3 ± 0.3	73.2 ± 2.5
PS_DR60	116.2 ± 0.8	56.6 ± 1.1
PS_NDR20	116.6 ± 1.5	75.2 ± 2.5
PS_NDR60	116.0 ± 0.4	55.5 ± 2.5

rubber can be attributed to the lower interfacial adhesion between rubber and PS, and to the large size of the rubber particles that are generally used (see Fig. 5). Further efforts will be thus made in the future to apply a proper surface treatment to rubber particles and to obtain finer particles by using more advanced grinding technologies. However, it has been already noted that the properties of thermoplastic blends with rubber could be considerably improved if the rubber is partially devulcanized [10]. Considering that the dimensions of DR and NDR particles are quite similar, a possible explanation is that the devulcanization process somehow leads to a better interfacial interaction between PS and rubber domains, thus leading to a better stress transfer mechanism. However, further analysis are required to have a better comprehension of this trend. Quite interestingly, while in the case of NDR the strain at break seems to be practically unaffected by the addition of rubber, a progressive increase in the elongation at break can be detected upon addition of DR (see Fig. 9c). For instance, PS_DR60 shows an ϵ_b value 60% significantly higher than that of neat PS. The same trend has been observed also in HDPE/rubber blends [31]. As reported in that paper, it is well known that thermoplastics/elastomers blends are materials with the characteristics of both thermoplastics and elastomers. The partial disruption of the crosslinked structure in DR enhances the elastomeric character of the elastomeric phase, and hence improves the elongation at break values.

Similar conclusions can be drawn if impact properties of the prepared blends are analysed. In Fig. 10 representative force-time curves from Charpy impact tests on the prepared

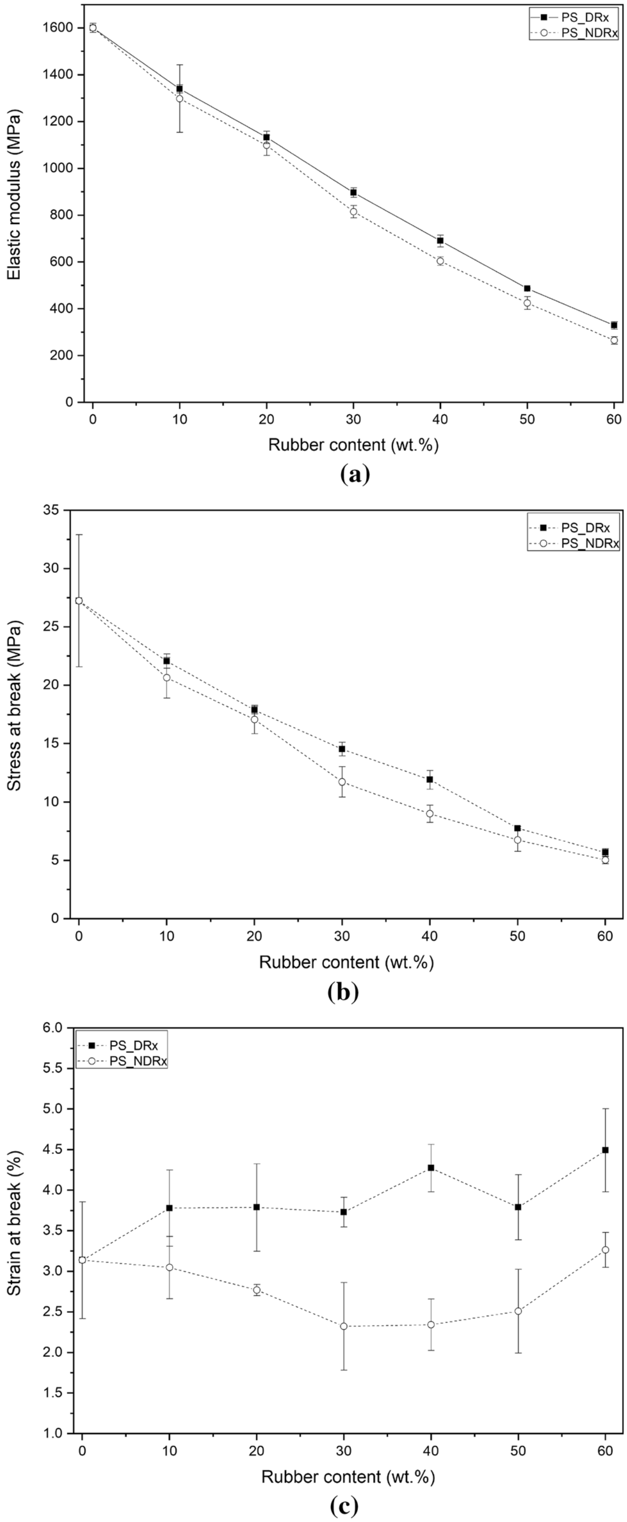


Fig. 9 Results of quasi-static tensile tests as function of the rubber content: elastic modulus (**a**), stress at break (**b**), strain at break (**c**)

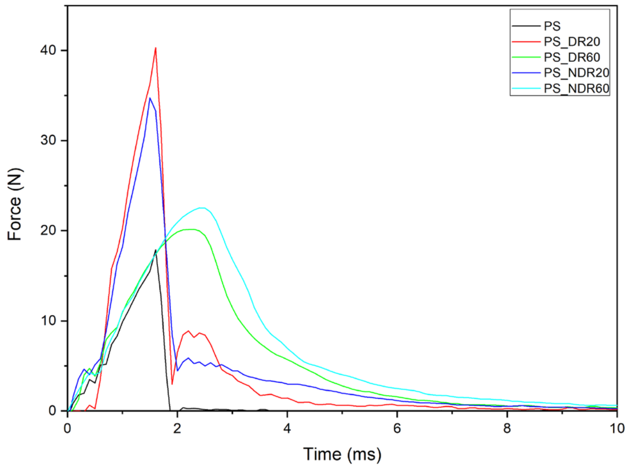


Fig. 10 Representative curves from tensile impact tests on PS/rubber blends

Table 7 Results of impact tests

Sample	F_{max} (N)	U_i (kJ m^{-2})	U_{tot} (kJ m^{-2})
PS	29.4 ± 11.7	0.3 ± 0.1	0.4 ± 0.1
PS_DR20	39.4 ± 3.3	1.1 ± 0.1	1.6 ± 0.1
PS_DR60	17.0 ± 2.5	0.8 ± 0.1	1.7 ± 0.1
PS_NDR20	28.9 ± 5.7	0.9 ± 0.2	1.3 ± 0.3
PS_NDR60	15.9 ± 5.1	0.6 ± 0.1	1.6 ± 0.3

blends are reported, while in Table 7 the most significant results are summarized. As it could be expected, the addition of recycled rubber leads to a general decrease of the maximum sustained force (F_{max}) at elevated rubber contents. Nevertheless, the specific impact energy at fracture initiation (U_i) are noticeably enhanced upon the addition of rubber. In fact, U_i values passes from 0.3 up to 1.1 kJ m^{-2} with a DR amount of 20 wt%. A more impressive effect can be observed if the total specific energy under impact conditions (U_{TOT}) is considered. in fact, U_{TOT} increases with the recycled rubber amount, and with a DR amount of 60% a fourfold enhancement of the impact energy can be detected. It should be noticed that the U_{TOT} values obtained for the PS_DR20 and the PS_DR60 are very similar; this means that an addition of 20 wt% of DR is sufficient to have a huge increase in the total absorbed energy under impact conditions. According to quasi-static tests, the impact properties of the blends with DR are systematically superior to those shown by the corresponding blends with NDR. It is therefore clear that the introduction of recycled rubber considerably improves the impact properties of a brittle thermoplastic such as PS, especially if the rubber is preliminary treated through a devulcanization process.

Conclusions

In the present work the thermo-mechanical properties of novel polystyrene/recycled rubber blends, in which different amounts of devulcanized and non-devulcanized rubber were added through melt compounding, were investigated. FESEM micrographs on the prepared blends highlighted that interfacial adhesion between PS and recycled rubber is rather poor, but the debonding seemed to be more evident in the case of NDR. Moreover, NDR domains within the PS matrix had slightly larger size compared with the corresponding DR particles. TGA tests revealed that the thermal degradation stability is significantly affected by the addition of rubber, with a decrease in the onset degradation temperature and an enhancement in the temperature associated to the maximum mass loss rate. DSC tests highlighted a slight T_g increase upon the addition of rubber, probably responsible of the observed enhancement in the Vicat grade. As expected, Shore D hardness, elastic modulus and stress at break were considerably impaired upon addition of recycled rubber at elevated concentrations. On the other hand, elongation at break and impact resistance were noticeably enhanced, especially if DR is introduced. The potentialities of the devulcanized rubber in increasing the toughness in a brittle thermoplastic resin such as PS was therefore demonstrated.

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