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# Full factorial experimental design to study the devulcanization of ground tire rubber in supercritical carbon dioxide

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ABSTRACT

In this study a $2^4$ factorial design was employed to investigate the supercritical $CO_2$ devulcanization process of ground tire rubber from end of life tires performed using diphenyl disulfide (DD) as devulcanizing reagent.

The aim of the experimental design was to investigate the influence on the process of temperature, pressure, amount of devulcanizing reagent, treatment time and their interactions.

The crosslink density, sol fraction, gel fraction and sulfur content were chosen as experimental responses. Multiple linear regression was used for modeling the relationship between each response and the process variables. Reduced regression models were obtained for each response, considering only the significant variables and interactions. The predicted results from these reduced models showed good agreement with the experimental values.

Temperature, amount of DD and DD–temperature interaction resulted the relevant parameters for the process. On the contrary, the influence of treatment time, pressure and all other interactions proved to be negligible.

These results have an important outcome since this devulcanization process can be carried out in a short time and at relatively low pressure, with subsequent energy saving.



## 1. Introduction

The supercritical fluids, in particular supercritical $CO_2$ ($scCO_2$), show ability to permeate into polymers and represent excellent solvents or plasticizers for these materials. Therefore, in the last years several researches focused on their possible applications, including polymer blending and composites, polymer modification and polymer foaming [1–3]. Moreover, other studies investigated the application of supercritical fluids to environmental friendly processes such as treatment of hazardous wastes [4], decomposition and reclaiming of pneumatic tires [5]. In particular, some authors developed a green devulcanization process employing $scCO_2$ as reaction medium for devulcanizing reagents [5–7].

The present study aims to investigate $scCO_2$ devulcanization process for ground tire rubber (GTR) from End of Life Tires (ELTs) using an experimental design approach. For process improvement, it is usually necessary to consider how a number of input variables, such as temperature, feed rate, concentration, etc. can simultaneously influence experimental responses. The use of statistical experimental design allows to get a clear picture of how these process variables behave separately and together on the experimental responses and how it is possible to control them in order to make the process more effective [8].

In the last years, the production of ELTs is rapidly increasing and they represent an important issue [9]. Waste tires are infusible due to the three-dimensional crosslinking network that is hard to decompose. The pulverization of ELTs is one of the most used recycling techniques: it consists in the separation of metallic and texture materials and in the grinding process of waste rubber down to small dimensions. However, the direct introduction of GTR in new blends with virgin rubber results in bad properties due to the presence of the sulfur crosslink network that leads to a weak adhesion and deterioration of the final properties [10]. Several devulcanization processes, such as chemical, mechanical

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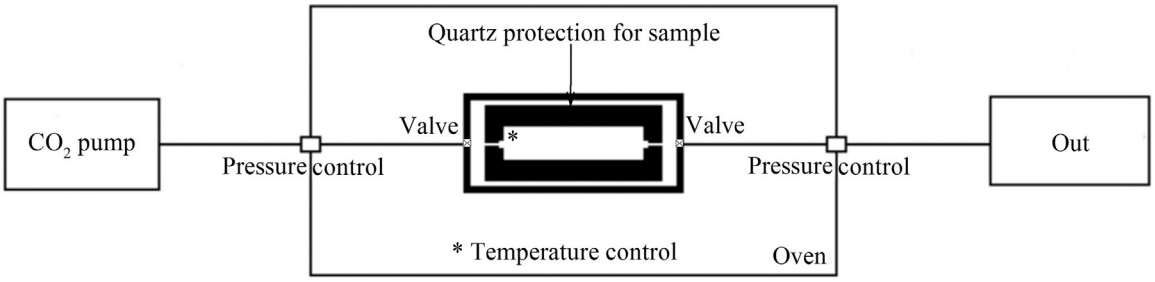


**Fig. 1.** $ScCO_2$ reactor.

**Table 1**
Factors and levels of the experimental design.

| Factor<br>Code | Min level<br>−1 | Max level<br>+1 | Central level<br>0 |
|---|---|---|---|
| Temperature (°C) | 70 | 190 | 130 |
| Pressure (MPa) | 8 | 24 | 16 |
| Treatment time (min) | 60 | 240 | 150 |
| DD/rubber (wt%) | 1 | 25 | 13 |

and thermo-mechanical [11,12], have been developed in order to produce a reclaimed rubber.

The present paper presents a statistical approach for studying the GTR devulcanization using a green devulcanization process that employs $scCO_2$ as reaction medium and diphenyl disulfide (DD) as devulcanizing reagent [5–7]. Most of the previous studies investigated this reclaiming process on several types of rubber, in particular, natural rubber (NR) and synthetic rubbers [5–7,13]. Some studies were also performed on GTR [14,15]. Although most of these researches were carried out in order to find the best devulcanizing conditions, these studies have analyzed the process variables just considering one variable at time (OVAT) [6,7]. In OVAT approach, the variables that could possibly affect the performance of the process are kept at a fixed level except for one, which is varied until the best conditions are reached. The studies showed that temperature ($T$), pressure ($P$), amount of DD and treatment time ($t$) were the variables that can mainly affect the devulcanization process, especially decreasing the crosslink density and increasing the sol fraction of the reclaimed rubber. However, this approach do not allow exploring the influence of the interaction among variables on the responses.

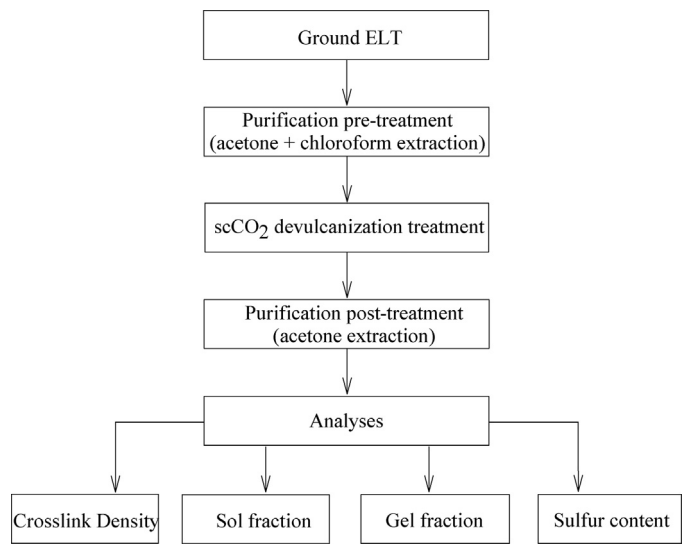


**Fig. 2.** Procedure used for the treatment and characterization.

## 2. Materials and methods

### 2.1. Design of experiment

A two level full factorial experimental design [8,16,17] was chosen to investigate the effect of each single variable and the interactions among them. The number of experiments necessary to carry out this design is $N = L^k$, where $L$ represents the number of levels for the investigation (two in our case) and $k$ represents the number of variables, or factors (four in our case).

**Table 2**
Full factorial design and experimental responses (crosslink density, CD; sol fraction, SF; gel fraction, GF; sulfur content, SC).

| Experiment | $t$ (min) | DD/rubber (wt%) | $T$ (°C) | $P$ (MPa) | CD (mmol/cm$^3$) | SF (wt%) | GF (wt%) | SC (wt%) |
|---|---|---|---|---|---|---|---|---|
| E1 | 60 | 1 | 70 | 8 | 0.073 | 2.3 | 98.2 | 2.43 |
| E2 | 240 | 1 | 70 | 8 | 0.070 | 2.6 | 97.8 | 2.40 |
| E3 | 60 | 25 | 70 | 8 | 0.073 | 1.8 | 99.1 | 2.45 |
| E4 | 240 | 25 | 70 | 8 | 0.068 | 2.6 | 98.2 | 2.37 |
| E5 | 60 | 1 | 190 | 8 | 0.046 | 9.8 | 91.6 | 2.43 |
| E6 | 240 | 1 | 190 | 8 | 0.042 | 10.9 | 91.1 | 2.53 |
| E7 | 60 | 25 | 190 | 8 | 0.035 | 14.8 | 85.9 | 2.79 |
| E8 | 240 | 25 | 190 | 8 | 0.019 | 22.6 | 79.8 | 2.84 |
| E9 | 60 | 1 | 70 | 24 | 0.070 | 3.2 | 97.8 | 2.37 |
| E10 | 240 | 1 | 70 | 24 | 0.067 | 1.7 | 98.4 | 2.36 |
| E11 | 60 | 25 | 70 | 24 | 0.073 | 5.8 | 97.1 | 2.39 |
| E12 | 240 | 25 | 70 | 24 | 0.076 | 2.3 | 97.9 | 2.43 |
| E13 | 60 | 1 | 190 | 24 | 0.046 | 11.8 | 89.6 | 2.43 |
| E14 | 240 | 1 | 190 | 24 | 0.036 | 8.5 | 91.8 | 2.35 |
| E15 | 60 | 25 | 190 | 24 | 0.021 | 15.4 | 83.0 | 2.87 |
| E16 | 240 | 25 | 190 | 24 | 0.033 | 23.5 | 79.2 | 3.17 |
| Center 1 | 150 | 13 | 130 | 16 | 0.043 | 4.6 | 95.4 | 2.24 |
| Center 2 | 150 | 13 | 130 | 16 | 0.039 | 6.8 | 93.6 | 2.43 |
| Center 3 | 150 | 13 | 130 | 16 | 0.046 | 6.3 | 94.4 | 2.51 |

**Table 3**
Analysis of variance for the interaction model of the responses.

| Variable | DF[a] | CD | | SF | | GF | | SC | |
|---|---|---|---|---|---|---|---|---|---|
| | | SS | *P*-value | SS | *P*-value | SS | *P*-value | SS | *P*-value |
| Constant | 1 | | <0.001 | | <0.001 | | <0.001 | | <0.001 |
| *t* | 1 | 0.0000422 | 0.419 | 6.002 | 0.258 | 4.101 | 0.258 | 0.00526 | 0.596 |
| DD | 1 | 0.000169 | 0.127 | 90.25 | <0.001 | 81.451 | <0.001 | 0.253 | 0.005 |
| *T* | 1 | 0.00533 | <0.001 | 564.063 | <0.001 | 534.766 | <0.001 | 0.305 | 0.003 |
| *P* | 1 | 0.000001 | 0.899 | 1.44 | 0.33 | 2.976 | 0.33 | 0.00106 | 0.811 |
| $t \times$ DD | 1 | 0.0000123 | 0.659 | 17.222 | 0.111 | 8.851 | 0.111 | 0.00681 | 0.547 |
| $t \times T$ | 1 | 0.00000625 | 0.752 | 19.36 | 0.247 | 4.306 | 0.247 | 0.0127 | 0.416 |
| $t \times P$ | 1 | 0.0000562 | 0.354 | 6.502 | 0.28 | 3.706 | 0.28 | 0.00276 | 0.7 |
| DD $\times T$ | 1 | 0.000324 | 0.046 | 66.423 | <0.001 | 82.356 | <0.001 | 0.214 | 0.008 |
| $T \times P$ | 1 | 0.000004 | 0.8 | 0.422 | 0.695 | 0.456 | 0.695 | 0.00681 | 0.547 |
| DD $\times P$ | 1 | 0.000025 | 0.531 | 1.96 | 0.5 | 1.381 | 0.5 | 0.0298 | 0.225 |
| Residuals | 8 | 0.000465 | | 50.827 | | 22.091 | | 0.138 | |
| Total | 18 | 0.00643 | | 824.472 | | 746.437 | | 0.975 | |

[a] Degrees of freedom.

**Table 4**
Estimated effects and standard error (SE) calculated through the three central experiments (Eq. (2)).

| Effect | CD | SE | $t_{(5,0.05)} \times$ SE | SF | SE | $t_{(5,0.05)} \times$ SE | GF | SE | $t_{(5,0.05)} \times$ SE | SC | SE | $t_{(5,0.05)} \times$ SE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Average | 0.053 | ±0.002 | ±0.009 | 8.7 | ±0.6 | ±2.6 | 92.3 | ±0.5 | ±2.2 | 2.54 | ±0.07 | ±0.30 |
| *t* | −0.003 | ±0.002 | ±0.009 | 1.2 | ±0.6 | ±2.6 | −1.0 | ±0.5 | ±2.2 | 0.04 | ±0.07 | ±0.30 |
| DD | −0.007 | ±0.002 | ±0.009 | 4.8 | ±0.6 | ±2.6 | −4.5 | ±0.5 | ±2.2 | 0.25 | ±0.07 | ±0.30 |
| *T* | −0.037 | ±0.002 | ±0.009 | 11.9 | ±0.6 | ±2.6 | −11.6 | ±0.5 | ±2.2 | 0.28 | ±0.07 | ±0.30 |
| *P* | −0.001 | ±0.002 | ±0.009 | 0.6 | ±0.6 | ±2.6 | −0.9 | ±0.5 | ±2.2 | 0.02 | ±0.07 | ±0.30 |
| $t \times$ DD | 0.002 | ±0.002 | ±0.009 | 2.1 | ±0.6 | ±2.6 | −1.5 | ±0.5 | ±2.2 | 0.04 | ±0.07 | ±0.30 |
| $t \times T$ | −0.001 | ±0.002 | ±0.009 | 2.2 | ±0.6 | ±2.6 | −1.0 | ±0.5 | ±2.2 | 0.06 | ±0.07 | ±0.30 |
| $t \times P$ | 0.004 | ±0.002 | ±0.009 | −1.3 | ±0.6 | ±2.6 | 1.0 | ±0.5 | ±2.2 | 0.03 | ±0.07 | ±0.30 |
| DD $\times T$ | −0.009 | ±0.002 | ±0.009 | 4.1 | ±0.6 | ±2.6 | −4.5 | ±0.5 | ±2.2 | 0.23 | ±0.07 | ±0.30 |
| $T \times P$ | −0.001 | ±0.002 | ±0.009 | −0.3 | ±0.6 | ±2.6 | −0.3 | ±0.5 | ±2.2 | 0.04 | ±0.07 | ±0.30 |
| DD $\times P$ | 0.003 | ±0.002 | ±0.009 | 0.7 | ±0.6 | ±2.6 | −0.6 | ±0.5 | ±2.2 | 0.09 | ±0.07 | ±0.30 |

Table 1 shows maximum (+1), minimum (−1) and central (0) levels for each variable used in the present study. These levels were chosen considering the type and properties of GTR, the maximum operating level for the equipment (400 °C and 70 MPa) and the $CO_2$ supercritical conditions (31.1 °C and 7.38 MPa [18]).

Sixteen experiments were carried out to investigate the experimental domain; three experiments were added to investigate the performance in the center of the experimental domain and to estimate the model validity, reproducibility and experimental error. A fully randomized execution of the nineteen experiments was carried out in order to minimize the error due to the planning of the experiments.

The crosslink density (CD), sol fraction (SF), gel fraction (GF) and sulfur content (SC) were chosen as experimental responses. The CD, SF and GF gave information on the degree of devulcanization. SC was an important quantitative indicator of the reaction between DD and GTR.

The dependence of each experimental response, y, on the factors was modeled applying the following equation [8]:

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

**Table 5**
Estimated effects and standard error (SE) calculated through higher order interactions (Eq. (3)).

| Effect | CD | SE | $t_{(5,0.05)} \times$ SE | SF | SE | $t_{(5,0.05)} \times$ SE | GF | SE | $t_{(5,0.05)} \times$ SE | SC | SE | $t_{(5,0.05)} \times$ SE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Average | 0.053 | ±0.003 | ±0.008 | 8.7 | ±1.2 | ±3.1 | 92.3 | ±0.6 | ±1.5 | 2.54 | ±0.05 | ±0.13 |
| *t* | −0.003 | ±0.003 | ±0.008 | 1.2 | ±1.2 | ±3.1 | −1.0 | ±0.6 | ±1.5 | 0.04 | ±0.05 | ±0.13 |
| DD | −0.007 | ±0.003 | ±0.008 | 4.8 | ±1.2 | ±3.1 | −4.5 | ±0.6 | ±1.5 | 0.25 | ±0.05 | ±0.13 |
| *T* | −0.037 | ±0.003 | ±0.008 | 11.9 | ±1.2 | ±3.1 | −11.6 | ±0.6 | ±1.5 | 0.28 | ±0.05 | ±0.13 |
| *P* | −0.001 | ±0.003 | ±0.008 | 0.6 | ±1.2 | ±3.1 | −0.9 | ±0.6 | ±1.5 | 0.02 | ±0.05 | ±0.13 |
| $t \times$ DD | 0.002 | ±0.003 | ±0.008 | 2.1 | ±1.2 | ±3.1 | −1.5 | ±0.6 | ±1.5 | 0.04 | ±0.05 | ±0.13 |
| $t \times T$ | −0.001 | ±0.003 | ±0.008 | 2.2 | ±1.2 | ±3.1 | −1.0 | ±0.6 | ±1.5 | 0.06 | ±0.05 | ±0.13 |
| $t \times P$ | 0.004 | ±0.003 | ±0.008 | −1.3 | ±1.2 | ±3.1 | 1.0 | ±0.6 | ±1.5 | 0.03 | ±0.05 | ±0.13 |
| DD $\times T$ | −0.009 | ±0.003 | ±0.008 | 4.1 | ±1.2 | ±3.1 | −4.5 | ±0.6 | ±1.5 | 0.23 | ±0.05 | ±0.13 |
| $T \times P$ | −0.001 | ±0.003 | ±0.008 | −0.3 | ±1.2 | ±3.1 | −0.3 | ±0.6 | ±1.5 | 0.04 | ±0.05 | ±0.13 |
| DD $\times P$ | 0.003 | ±0.003 | ±0.008 | 0.7 | ±1.2 | ±3.1 | −0.6 | ±0.6 | ±1.5 | 0.09 | ±0.05 | ±0.13 |

**Table 6**
Regression coefficients and coefficients of determination for each experimental response referred to the scaled and centered variables.

| Response | Constant | SE | DD | SE | *T* | SE | DD $\times T$ | SE | $R^2$ | $R^2$ adjusted | $Q^2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CD | 0.051 | 0.001 | −0.003 | 0.002 | −0.018 | 0.002 | −0.005 | 0.002 | 0.91 | 0.89 | 0.86 |
| SF | 8.3 | 0.6 | 2.4 | 0.7 | 5.9 | 0.7 | 2.0 | 0.7 | 0.87 | 0.85 | 0.80 |
| GF | 92.6 | 0.4 | −2.3 | 0.4 | −5.8 | 0.4 | −2.3 | 0.4 | 0.94 | 0.92 | 0.90 |
| SC | 2.52 | 0.03 | 0.13 | 0.03 | 0.14 | 0.03 | 0.12 | 0.03 | 0.79 | 0.75 | 0.69 |

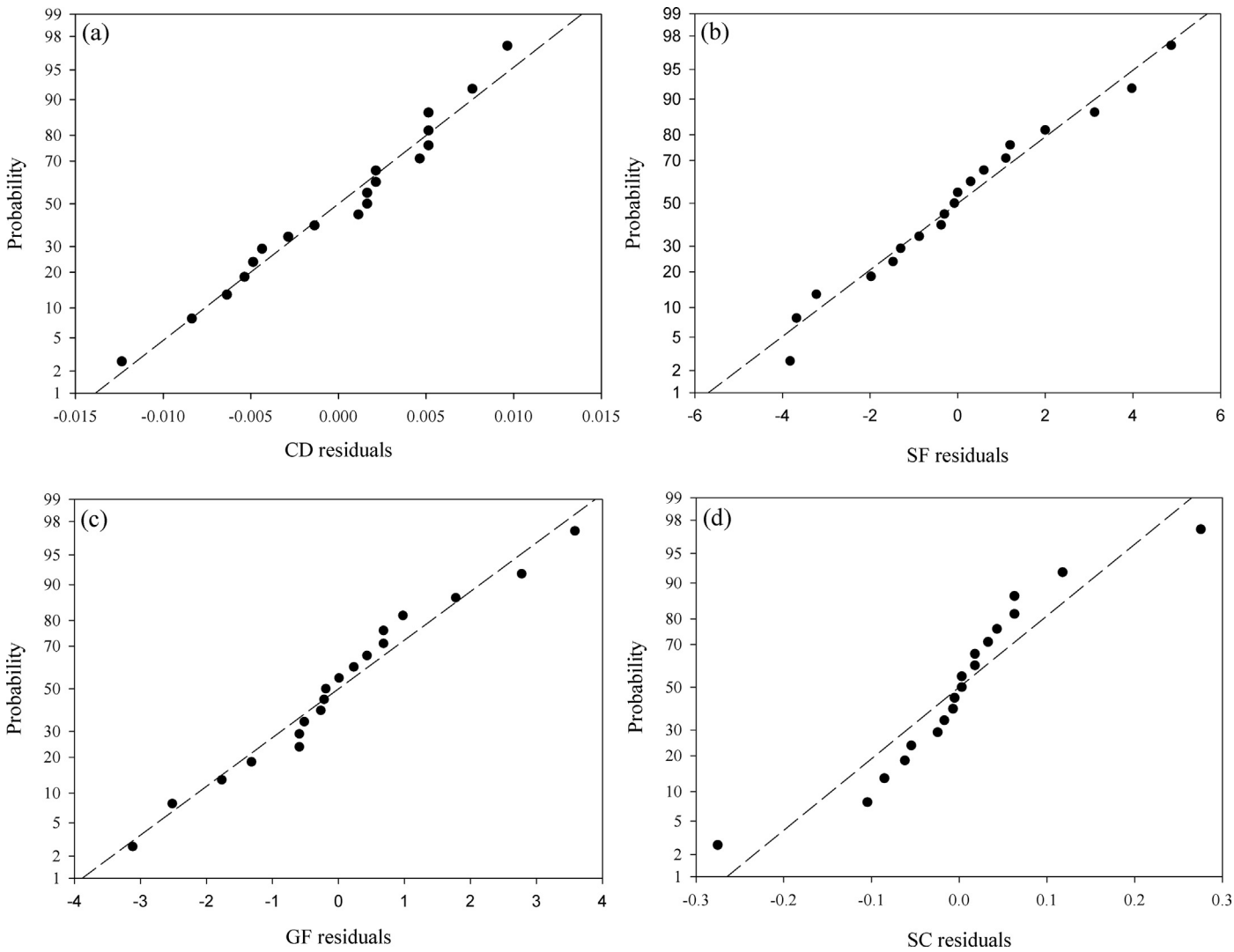


**Fig. 3.** Normal probability plot of residuals for crosslink density (a), sol fraction (b), gel fraction (c) and sulfur content (d).

where $\beta_0$ is the constant term, $\beta_i$ and $\beta_{ij}$ are the regression coefficients, $\varepsilon$ is the error, $x_i$ are the variables and n is their number. The coefficients were determined by multiple linear regression.

The analysis of variance (ANOVA) is normally used to determine which factors and which interactions have a significant influence on the process. In our $2^k$ factorial designs, the use of ANOVA is questionable to discriminate whether the factors and interactions are real [8]. Therefore, the relevance of the effects for the factors and interactions was also evaluated comparing each computed effect with the standard error (SE) through a *t*-test. The main and the interactive effects were calculated according to Box et al. [8].

The three central experiments were used to evaluate the experimental error and therefore the standard error for the effects by the following equation:

$$\text{SE (effect)} = \frac{2\sigma}{\sqrt{n}} \tag{2}$$

where $n$ is the total number of runs of the two level factorial design and $\sigma$ is the standard deviation of central experiments. Moreover, under the assumption that higher-order interactions are largely due to noise, the effect of these interactions ($b_k$) can provide a reference set for the estimation of the standard error. The standard error for main effects and two-factor interactions was also calculated applying following equation:

$$\text{SE (effect)} = \sqrt{\sum_{k=1}^{5} \frac{(b_k)^2}{5}} \tag{3}$$

In order to point out the best fitting model and to confirm the significant parameters for each experimental response, the stepwise approach was used to find the best combination of factors and interactions evaluating the coefficient of determination ($R^2$), the adjusted $R^2$ and the coefficient of determination for prediction ($Q^2$) [17,19]. In our case, $Q^2$ represents the leave-one-out cross-validated $R^2$ in which the residual sum of squares is substituted by the predicted sum of squares.

### 2.2. Materials and equipment

The GTR used in the present study was a cryo-ground rubber from truck tires, the same used and characterized in our previous paper [15]. 95 wt% of particles were smaller than 0.4 mm and the majority had dimensions between 0.15 and 0.4 mm. The rubber fraction was 53% of the total weight and it was made up of 70% NR and 30% of synthetic rubbers (BR and SBR). The DD (99% assay) was purchased from Sigma Aldrich (Germany); Carbon

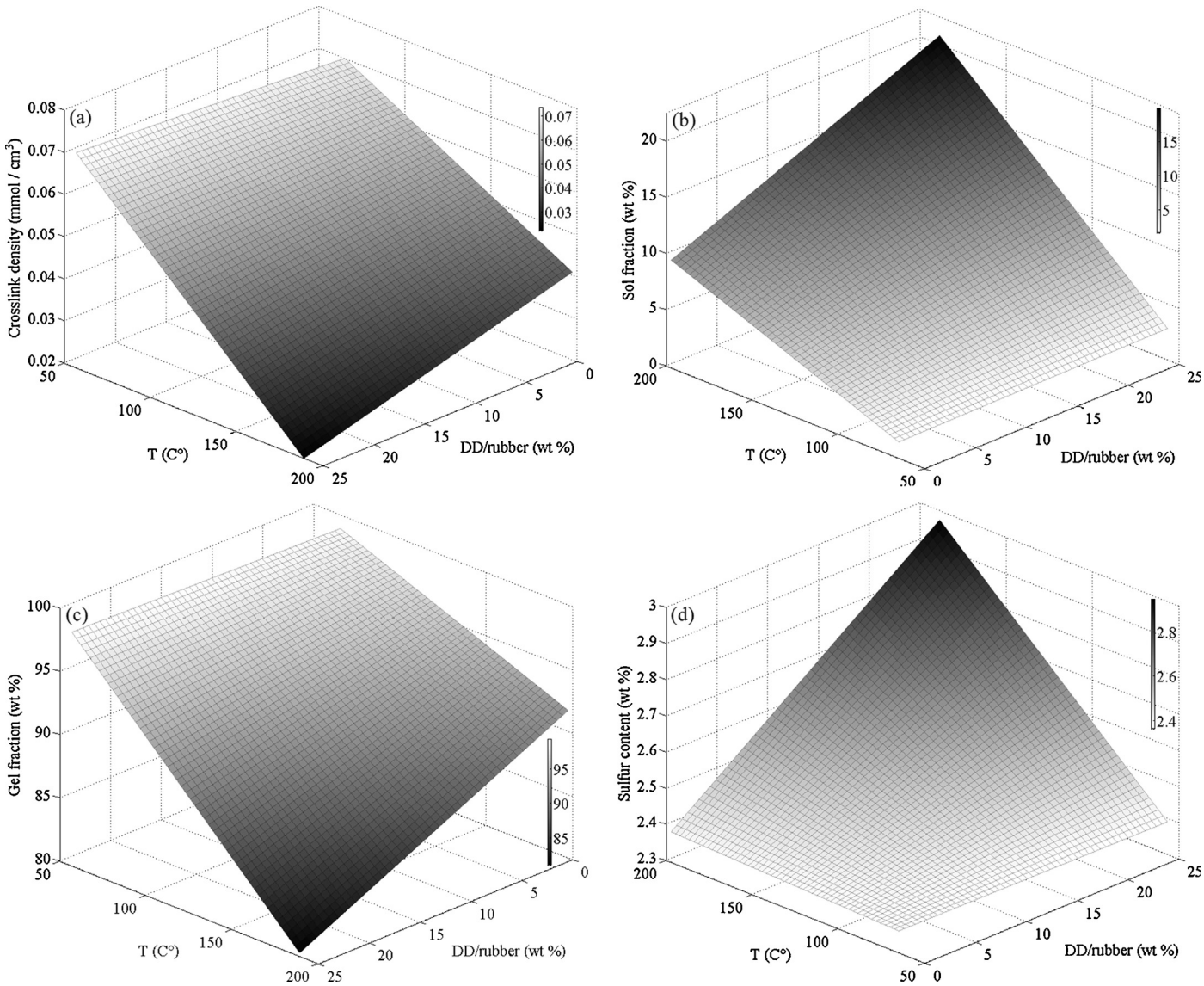


**Fig. 4.** 3-D plot for the four experimental responses as function of DD and temperature. (a) Crosslink density, (b) sol fraction, (c) gel fraction and (d) sulfur content. In order to show clearly the surfaces trends, (c) and (d) show axes with opposite directions.

dioxide (99.995% assay) from Sapio (Italy); NCS Coal Certified Reference Material FC28107 from Lab Service Analytica (Italy). Acetone, toluene and chloroform (>99% assay) were purchased from Panreac (Spain).

Each experiment was carried out in a static reactor realized by Q-Ation Ltd. (Italy) and designed for supercritical extractions. The instrument, represented in Fig. 1, has an operating range of temperature and pressure respectively between 31.1 and 400 °C and between 7.38 and 70 MPa. It is equipped with a reactor cell of a capacity up to 100 mL.

The linear regression models (Eq. (1)), ANOVA and response surfaces were calculated by MODDE 6.0 (Umetrics, Sweden) and MATLAB R2013b (The MathWorks, Inc., USA).

### 2.3. Experimental and analytical procedures

A pre-treatment of GTR was necessary to remove all chemicals that could affect experimental determinations. Thus, the GTR was firstly extracted in a Büchi Extraction System B-811 automatic Soxhlet with acetone for 16 h and then with chloroform for 4 h, according to ISO 1407 and ASTM D297 standard methods. After the extraction, the powder was vacuum dried at 50 °C for 24 h.

The obtained GTR was mixed with DD and then treated in $scCO_2$ at several conditions planned in the experimental design (Table 2).

After the devulcanization, each sample was extracted in acetone for 24 h to remove the excess of unreacted DD, dried again under vacuum and finally pressed through a two-roll mill at 40 °C keeping conditions constant in order to obtain 1-mm-thick sheets (T-GTR). These sheets were suitable to be characterized avoiding loss of material, especially during the swelling measurements.

The crosslink density, sol fraction, gel fraction and sulfur content were determined on the T-GTR. Every measurement was repeated at least three times.

The crosslink density was determined according to ASTM D6814-02 standard method through swelling measurements. 1 g T-GTR was let to swell in cold toluene for 72 h and the solvent was refreshed every 24 h. The Flory–Rehner equation was used to calculate the crosslink density. The $\chi$ interaction parameter between rubber and swelling solvent was set equal to 0.39, considering NR as main polymer and toluene as solvent. The rubber density was approximated to the NR density, considering the content of sulfur

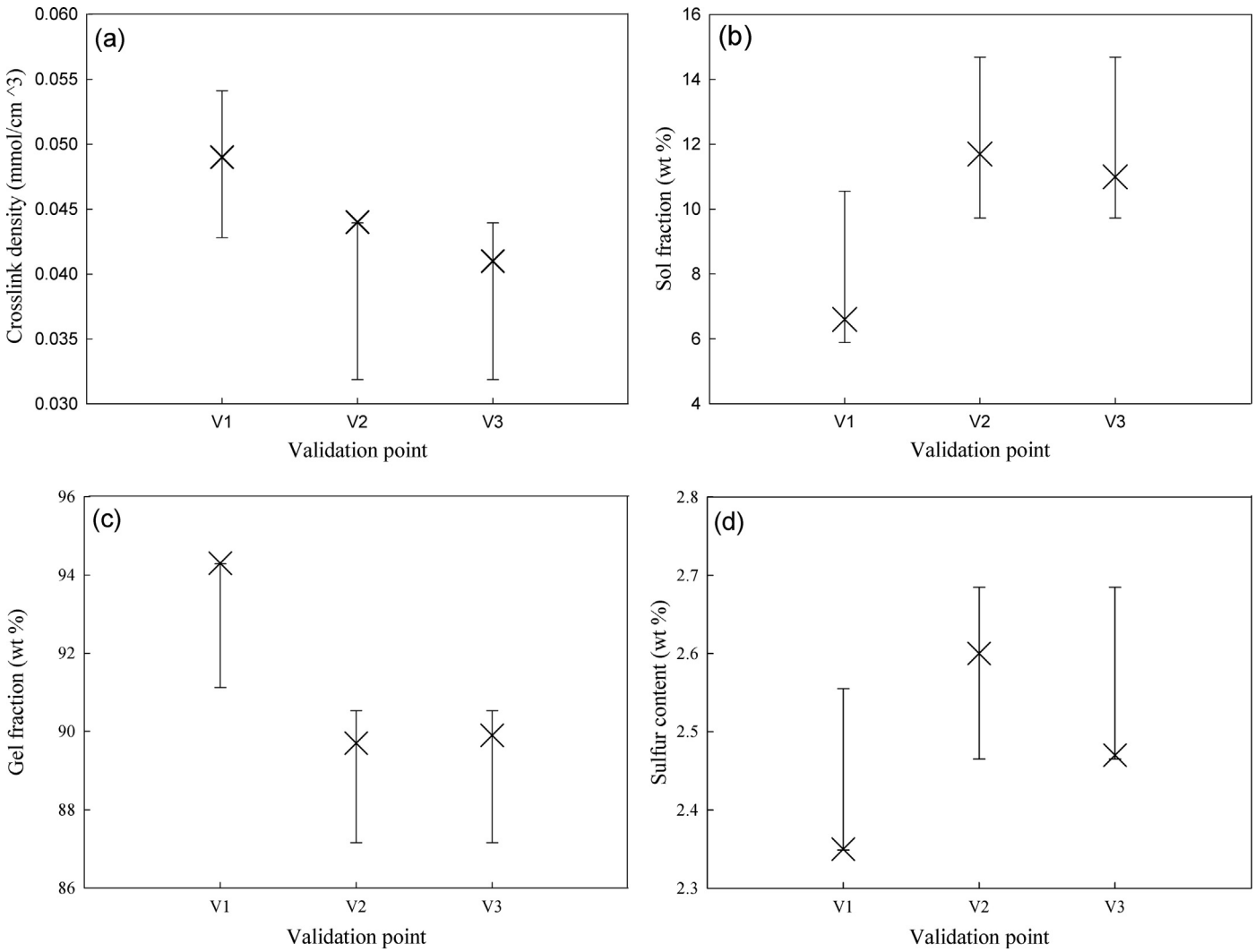


**Fig. 5.** Validation experiment results within the models error bars at 99% of confidence level.

[20] and it was 0.92 g/cm$^3$; the content of carbon black was determined by thermogravimetric analysis in order to apply the Kraus correction model. The carbon black density was chosen equal to 1.85 g/cm$^3$ and the $C$ constant was chosen to be 1.17 [21,22].

Sol and gel fractions were evaluated through a 24 h Soxhlet extraction using toluene as solvent [23] and about 1 g of T-GTR ($W_1$). The sol fraction represents the soluble polymer fraction extracted by the solvent, dried and weighed ($W_2$). The gel fraction represents the insoluble fraction after removing the sol, vacuum dried and weighed ($W_3$).

The equations used for the sol and gel fractions calculations were:

$$\text{Sol fraction } (\%) = \left(\frac{W_2}{W_1}\right) \times 100 \quad (4)$$

$$\text{Gel fraction } (\%) = \left(\frac{W_3}{W_1}\right) \times 100 \quad (5)$$

Sulfur content was determined by CHNS elemental analysis (Perkin Elmer 2400 Series II CHNS/O System) and the NCS FC 28107 as certified standard, containing 2.10 (wt%) of sulfur.

Fig. 2 shows the complete procedure scheme used for the treatment and characterization.

## 3. Results and discussion

### 3.1. Regression models

The experimental conditions and the obtained responses are resumed in Table 2.

A preliminary regression model, evaluated for each response, was an interaction model including the four factors and all two-factor interactions [17]. Higher-order interactions were omitted since in real phenomena, the effect relevance decreases with increase of the interaction order [8]. This assumption allowed excluding three- and four-factor interactions to privilege the quality of the model and to avoid over-fitting. The ANOVA was carried out on this first model, thus it was possible to point out which factors and interactions were statistically significant [16]. Table 3 shows the ANOVA for the four responses containing all the factors and two-factor interactions. The $P$-values of $T$, DD and their interaction ($T \times$ DD) are lower than 0.05 and therefore these parameters proved to be significant [16].

The standard error, estimated both by the central points (Eq. (2)) and by higher-order interactions (Eq. (3)), was also used to evaluate whether the effect of either factors or two-factor interactions were significant. Tables 4 and 5 show the estimated effects, their standard error (SE) and the 95% interval evaluated using the three central points and the higher-order interactions, respectively.

**Table 7**
Validation experiment conditions within the studied domain.

| Experiment | Treatment time (min) | DD (wt%) | Temperature (°C) | Pressure (MPa) |
|---|---|---|---|---|
| V1 | 60 | 5 | 150 | 24 |
| V2 | 60 | 10 | 180 | 24 |
| V3 | 120 | 10 | 180 | 15 |

Both this approach and the ANOVA, applied to each experimental response, identified the same significant factors and interactions. Temperature, content of DD and their interaction resulted the only significant parameters, while the other factors and interactions resulted negligible. The DD resulted unimportant only for the crosslink density, whereas $T$ and their interaction resulted significant. However, even for this experimental response, the DD was considered in the final reduced model in order to preserve the hierarchy among factors.

The effect of pressure was negligible; as a result, the treatment can be conducted at relatively low pressure. Nevertheless, pressure must be, at least, equal to that of supercritical $CO_2$, since $scCO_2$ acts as the solvent media for the devulcanization reaction.

Treatment time resulted the least important factor, indeed the devulcanization reaction employing DD involves radical reactions, resulting very fast in comparison to the treatment times tested.

Therefore, a final reduced model was calculated by multiple linear regression for each experimental response, considering only significant factors and interactions. In order to confirm that the models obtained were the optimal ones, a stepwise approach was used to find the best combination of factors and interactions evaluating the coefficient of determination for prediction ($Q^2$).

Table 6 shows the regression coefficients and the coefficients of determination for each experimental response referred to the scaled and centered variables. The model obtained for the gel fraction exhibits the highest $R^2$, $Q^2$ and the smallest difference between these two coefficients, resulting in the best model (Table 6). All final reduced regression models were statistically significant at 95% and without any lack of fit considering the same probability [8].

Moreover, for a sound evaluation of models, the residuals distribution was studied. Fig. 3(a)–(d) shows the normal probability plots of the residuals for each response. No evident anomalies are present for crosslink density (a), sol (b) and gel fractions (c). For sulfur content (d), two runs appear to be highly discrepant. Nevertheless, the normal distribution for residuals was confirmed by the Shapiro–Wilk normality test for 95% confidence interval [24] for each response.

In order to visualize the influence of $T$ and DD on the devulcanization process, a 3-D graph (Fig. 4) was plotted for each experimental response using the reduced models. The plotted surfaces do not show any maximum. Temperature proved to be the most important factor for this devulcanization process, since high $T$ causes the degradation of the rubber network. Increasing the temperature a significant variation of responses was observed, especially at high amounts of DD. Indeed, at high $T$ values the decomposition of DD generate more benzene sulfide radicals [7,12,25] that lead to the chain scission and crosslink rupture, reducing the crosslink density, the gel fraction and increasing the sol fraction as shown in Fig. 4(a)–(c) [12,15]. These radicals react with the rubber chain and with the crosslink network increasing the sulfur content of the T-GTR (Fig. 4(d)).

### 3.2. Validation

Internal and external validations were carried out in order to test the reduced models predictive power within the studied domain. Indeed, for the optimization procedure and for future predictions, both a good descriptive and good prediction capacities of models are required.

The leave-one-out cross validation was used for internal validation. In this procedure, each observation is predicted by the model without including that observation. The prediction power of the reduced regression models is given by $Q^2$ (Table 6) which is based on this procedure [17,19] and it was already used to select the best models.

In addition to the internal validation, also an external model validation was performed. The response of new experimental runs in three points within the experimental domain (V1, V2 and V3 in Table 7) was predicted and compared to the experimental results. These experiments were chosen varying either the significant parameters for the final reduced models ($T$ and DD) or the negligible ones ($t$ and $P$).

Fig. 5(a)–(d) shows the experimental crosslink density, sol and gel fraction and sulfur content obtained for these validation points compared to the predicted values. It can be seen that each experimental value is contained within the models error bars, resulting in accordance with the predicted ones.

## 4. Conclusions

The aim of the present study was to investigate the $scCO_2$ devulcanization process of a GTR by varying treatment time, temperature, percentage of devulcanizing reagent DD and $CO_2$ pressure. A full factorial experimental design was used to define the experimental conditions within the variables domain. A set of four responses was used to characterize the devulcanized GTR.

The experimental dataset was modeled by multiple linear regression. The most significant variables were temperature, DD percentage and their interaction. The regression models developed in the study resulted in a reliable prediction of devulcanization indicators within the experimental domain. Treatment time resulted the least important factor and the influence of pressure resulted negligible.

The same evidence was not observed in previous studies performed on natural rubber and butyl rubber where pressure, treatment time, temperature and amount of devulcanizing reagent had strong influence on the devulcanization reaction.

Indications regarding the reaction mechanism were also obtained. High T and decomposition of DD generate radicals that react with the rubber chain and with the crosslink network increasing the sulfur content of the T-GTR.

These results have an important outcome since this devulcanization process can be carried out in a short time and at relatively low pressure, with subsequent energy saving.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.supflu.2014.06.001.

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