

## Investigation of new composite materials based on activated EPDM rubber waste particles by liquid polymers

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**ABSTRACT:** Despite of the variety of existing techniques, there is still a continuous demand in the development of more efficient recycling technologies, for economic and environmental reasons. A new approach for recycling EPDM rubber waste has been recently introduced utilizing a solvent free activation process by addition of liquid polymers (LP). The present study investigates the influence of the content and varying types of activated rubber waste particles (RWP-LP) in new composites. By varying the proportion of RWP-LP in the range from 25 up to 75 v/v % information about optimized compositions of new compounds were obtained. It was found that the ratio and type of RWP-LP induce significant differences in terms of cure characteristics, mechanical properties, cross-link density and morphology. Promising results with high potential application for the production of seal and sealing systems on the industrial scale were obtained by using up to 50 v/v % of RWP-LP with low ethylene amount. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42097.

**KEYWORDS:** applications; composites; mechanical properties; recycling; rubber

Received 23 September 2014; accepted 10 February 2015

DOI: 10.1002/app.42097

### INTRODUCTION

In comparison with thermoplastic material, which can be reshaped when heat is applied, a thermoset material is more difficult to be recycled due to the three-dimensional networks formed during vulcanization. Since its introduction on the market in the early 1960s ethylene propylene diene monomer (EPDM) is one of the most important synthetic rubbers. EPDM exhibits excellent heat, ozone, aging, weathering and chemical resistance being employed in a wide variety of applications of technical goods such as automotive profiles, building and construction, sealing and fitting systems and even as modifier for thermoplastic materials. For sustainability reasons and due to the legislative restriction<sup>1,2</sup> concerning the disposal of the waste rubber, the development of suitable recycling methods is on demand. Considering the above mentioned reasons, the rubber waste recycling became a very important research topic nowadays, aiming effective methods that are able to permit the waste rubber usage in new compositions obtaining final products of high quality. Different studies have been conducted in the past years, with regard to the recycling and reclaiming processes in terms of waste EPDM rubber. Most of the recycling processes are based on the devulcanization of the material, which can

mainly be achieved through physical and chemical processes.<sup>3</sup> Among the most used types of physical processes are: mechanical,<sup>4,5</sup> thermo-mechanical,<sup>6–11</sup> ultrasonic,<sup>12–16</sup> and microwave.<sup>17–21</sup> In the chemical process different organic amines,<sup>22–24</sup> disulfides,<sup>25,26</sup> mercaptans,<sup>27</sup> and inorganic systems<sup>28–30</sup> have been intensively studied. All the above mentioned processes are aimed to break the crosslinks formed during vulcanization. However, one of the disadvantages results from the fact that not only crosslinks formed during vulcanisation process are cleaved, but also partially the main chain scission of the polymer occurs,<sup>31</sup> having as a consequence the diminishing of physical-mechanical properties. Other important shortcomings of the devulcanization process consist in the fact that process safety is reduced and high quantities of odorous chemicals are required.<sup>3</sup> The surface treatment of rubber waste powder represents another method used for rubber recycling. This process is based on the addition of a crosslinkable polymer and a curing system. The purpose of surface activation is to increase the interaction between rubber waste particles and the new matrix when they are mixed together. Different paths of surface treatment have been studied including chemical,<sup>32–35</sup> physical,<sup>36</sup> mechanical,<sup>37</sup> and biological<sup>38–40</sup> activation. First studies were performed by

**Table I.** The Main Properties of the Liquid Polymers

Properties	Trilene <sup>®</sup> 67	Trilene <sup>®</sup> 66	Trilene <sup>®</sup> 77	Trilene <sup>®</sup> 76
Colour	Pale yellow	Pale yellow	Pale yellow	Pale yellow
Specific gravity	0.86	0.84	0.86	0.86
Molecular weight (Da)	7.700	8.000	7.500	7.500
Degree of unsaturation (% diene)	9.5	4.5	10.5	4.0
Diene type	ENB	ENB	ENB	ENB
Ethylene/propylene	45/55	45/55	75/25	75/25

ENB—5-ethylidene-2-norbornene.

Stark<sup>35,41</sup> who proposed a technology whereby the surface of the cured rubber scrap was modified by using a liquid unsaturated polymer soluble in a certain solvent and a curing agent. The yielded dry powder was further used at high concentrations (25–75%) as an additive to virgin rubber to give products with acceptable loss of physical properties. The elastomer types of rubber scrap are essentially hydrocarbons, i.e., NR, CR, NBR, SBR, IIR, and EPDM. In his work, Stark presented the method in an elemental way, with little information on the processability and mechanical properties of the recycled compounds.

Later on, the Vredestein rubber recycling company developed a product named Surcrum<sup>®</sup> based on crumb rubber, activated with high molecular weight polymer dispersion and a curing system. The process was applied for different industrial and postconsumer waste such as NR and SBR. The NBR- and EPDM-based Surcrum<sup>®</sup> are still under development.<sup>32</sup>

However, the chemical activation has been mostly applied for rubbers coming from tire industry and less intensive studies have been described for the EPDM rubber. Therefore, in order to get a better insight of this process a comprehensive and systematic work is necessary to be done.

Our group reported recently an easy, solvent free activation method of EPDM rubber waste particles (RWP) by means of low molecular weight polymers also referred to as liquid polymers (LP).<sup>42</sup> The rubber waste particles were activated using two different types of LP with low ethylene amount and different content of 5-ethylidene-2-norbornene diene monomer (ENB). LP are used to activate particles surface and act as compatibilizer with the raw polymer matrix. In order to find the best blend composition the ratio between RWP and LP and the influence of the curative system content were investigated. Very good results were obtained by using a volume fraction of 0.8 RWP activated with the LP together with a suitable curative system. The blend compositions show a very good morphology and the obtained mechanical properties represented more than half from the values of the start material. The activation of the rubber waste particles with liquid polymers enhances the ability of the activated particles (RWP-LP) to form chemical bonds with a new raw polymer matrix during vulcanization. The obtained results exhibit a high potential of the RWP-LP to be further used as substitute of the raw material in new composites.

Therefore, the objective of the present study is to investigate raw material substitute compounds that contain between 25 and

75 v/v % of RWP-LP and to compare their properties with a reference compound. The application area of the new composites is directed towards the production of seals and sealing systems. Moreover, two new types of activated particles were applied in this study. The particles were activated with two LP containing high amount of ethylene and different amount of ENB. The advantage of using higher amount of ethylene gives the possibility to obtain composites with better flow at high extrusion temperature, higher tensile strength values and higher loading potential. The RWP-LP were used in the rubber compounds as a substitute of the raw material and not as filler. The influence of the amount and type of RWP-LP was investigated in terms of cure characteristics, mechanical properties, crosslink density and morphology of final compounds. Very promising results were obtained on the compounds containing up to 50 v/v % content of RWP-LP with low ethylene amount. This work implies not only the recycling of EPDM, but also reveals a potential application of the resulting raw material substitute compounds, namely minimizing the environmental pollution and creates economic benefits.

## EXPERIMENTAL

### Materials

The EPDM waste rubber (RWP) was grounded at room temperature from a typical sulfur-cured EPDM vulcanizate, supplied by M.D.S. Meyer GmbH, Germany. The EPDM raw rubber used in this study (Keltan 9650Q from Lanxess, Germany) is composed of 53 wt % ethylene and 6.5 wt % 5-ethylidene-2-norbornene (ENB). The Mooney viscosity ML (1 + 8) measured at 150°C was 60 MU. Carbon black of type N550 was supplied by Avokal GmbH, Germany. As plasticizer the paraffinic oil type Mabanol Base Oil 500 MSN from Mebanol GmbH & Co. KG, Germany was used. The liquid polymers with the trade name Trilene<sup>®</sup>, used for activation of the RWP, were supplied by Lion Copolymer (USA) and the main properties are given in Table I. Toluene with a purity of 99.7% from Sigma-Aldrich Chemie GmbH, Germany was used for the swelling measurements. The zinc oxide (ZnO) and sulfur (S) were obtained from Melos GmbH, Germany. The stearic acid was obtained from Carl Roth GmbH + Co. KG, Germany, and *N*-cyclohexyl-2-benzothiazole-sulfenamide (CBS) was obtained from Sun & Bright Industrial Ltd., China. All chemicals were used as received.

### Methods

**Physical Characterization of RWP.** The void volume of the RWP was measured at room temperature using a commercial

**Table II.** EPDM Compounds Formulations

Ingredient	Reference sample	
	Amount (phr)	
Keltan 9650Q	100	
LP		100
RWP		560
Carbon black N550	120	
Paraffinic oil	100	
ZnO	4	2
Stearic acid	2	1
CBS	3	3
Sulfur	1.5	1.2

RWP-LP—activated EPDM rubber waste particles; phr—parts per hundred rubber (including liquid polymer); LP—liquid polymer; RWP—rubber waste particles; ZnO—zinc oxide; CBS—N-Cyclohexyl-2-benzothiazolesulfenamide.

method of Brabender, Germany. The sample of a known weight and density was introduced in a graduated cylinder and compressed by applying a pressure of 250 MPa for 60 s. At the end, the pressure was again reduced and the void volume was calculated from the difference between sample after compression and decompression. The particle size distribution was measured by laser diffraction technique using HELOS—laser diffraction system, compliant with ISO 13320:2009 (Sympatec GmbH, Germany). This technique allows analysing particle size from 0.1  $\mu\text{m}$  to 3.5 mm.<sup>43</sup> The density of the sample was determined by means of an ELATEST instrument of Brabender GmbH, Germany.

**Thermal Characterization of RWP and Raw Material Substitute Compounds.** The thermal characterization was performed by means of thermal gravimetric analyses (TGA) using a Mettler TGA / sDTA 851e thermogravimetric analyzer (Mettler-Toledo GmbH, Germany). The TGA analysis was used to determine the thermal and oxidative stability and the composition of the RWP, reference compounds and the raw material substitute compounds. The sample (ca. 5–10 mg) was heated from ambient temperature to 600°C in N<sub>2</sub> atmosphere, then switched to O<sub>2</sub> atmosphere up to 900°C, with a heating rate of 10°C min<sup>-1</sup> under 50 mL min<sup>-1</sup> N<sub>2</sub> respectively O<sub>2</sub> atmosphere.

**Compounding and Curing. Mixing.** The preparation of ternary mixtures consisting of EPDM, RWP, and -LP was performed in two mixing steps using a laboratory internal mixer type Haake PolyLab QC from Thermo Scientific, Germany. In the first stage, the LP and the RWP were mixed for 15 min at 100°C and a rotor speed of 40 rpm, in the following also denoted as activated particles. In the second stage, the EPDM raw polymer was mixed for 10 min at 90°C and 40 rpm together with the activated particles followed by addition of carbon black, oil, activators (ZnO and stearic acid), and crosslinking agents (CBS and sulfur).

The formulations of the reference sample (R) and of the activated particles (RWP-LP) are compiled in Table II. The composition of the RWP-LP contains 560 phr RWP and 100 phr LP,

which corresponds to 0.8 and 0.2 volume fractions, respectively. Furthermore, rubber compounds with varying content of activated rubber particles were produced and investigated. Those compounds are based on the reference compound, which was substituted with 25, 50, and respectively 75 v/v % by the RWP-LP. The R abbreviation is standing for the reference sample, the letters A (Trilene<sup>®</sup>67), B (Trilene<sup>®</sup>66), C (Trilene<sup>®</sup>77), and D (Trilene<sup>®</sup>76) are standing for the type of the liquid polymer used for activation and the numbers 25, 50, and 75 are standing for the percentage (vol %) of the RWP-LP used to substitute the raw material from the reference sample. In this case the raw material refers not only to the raw polymer but to the whole compound, including also oil, carbon black and curatives, as described in the recipe of the reference sample.

To simplify the name of the new compounds we used the abbreviations. For example the RA25, RA50, RA75 is standing for the samples where the reference compound was substituted with 25, 50, and respectively 75 v/v % by the RWP-LP using to activate the particles the LP Trilene 67.

**Vulcanisation and rheological properties.** The curing characteristics and the complex viscosity of the rubber compounds were determined according to ISO 6502:2009 using a Dynamic Moving Die Rheometer type D-MDR-3000 from MonTech Werkstoffpruefmaschinen GmbH, Germany. The cure curves of the samples were measured at 180°C and the complex viscosity was determined at 100°C in the frequency range from 0.2 to 20 Hz. The cure rate index (CRI) was determined using the following relation:

$$\text{CRI} = \frac{100}{\text{curetime-scorchtime}} \quad (1)$$

Sheets of 2 mm thickness were prepared from the compounds by compression moulding at 180°C and 10 MPa pressure in an electrical heated hydraulic press, type Polystat 200T (Schwabenthan, Germany), according to the optimum cure times obtained from the rheometer tests.

**Mechanical properties.** The hardness of the vulcanizates was measured using a Shore A Durometer (Karl Frank GmbH, Germany) according to ISO 7619-1:2010. Tensile tests were performed in accordance with ISO 37:2011 on dumbbell shaped specimens using a universal testing machine Zwick 1120 from Zwick GmbH & Co. KG, Germany. The nominal force of the load cell was 2000 N. For the tensile tests a preload of 1 N was applied. The tests were performed at constant crosshead speed of 200 mm/min. Hardness and tensile tests were carried out at room temperature (23 ± 2°C).

The compression set tests were performed using standard test specimens with a diameter of 13 mm and a thickness of 6 mm, at various temperature and time conditions, in accordance with ISO 815-1/-2:2014: at 23°C for 72 h, 70°C for 24 h, and -10°C for 70 h. In all tests, the compression strain used was 25%.

**Determination of the Crosslink Density.** The crosslink density of the samples was determined with two methods: swelling studies and temperature scanning stress relaxation (TSSR) tests.

**Swelling measurements.** The crosslink density of the samples was determined according to a procedure, described in the

literature,<sup>44</sup> based on the equilibrium swelling in toluene. Samples of known weight,  $m_o$  ( $20 \times 20 \times 2 \text{ mm}^3$ ) were immersed in toluene at  $24^\circ\text{C}$  for 48 h until the samples reached the maximum swelling. The solvent was replaced after 24 h with fresh toluene to remove the extracted components.

After 48 h the samples were removed from toluene and the surfaces were quickly wiped with tissue paper and weighted to find the swollen weight of the samples. The samples were further dried at  $50^\circ\text{C}$  for 48 h, cooled in a desiccator and then weighted again. The relative gel content with respect to the initial mass  $m_o$  was calculated from the difference between  $m_o$  and  $m_d$ , where  $m_d$  is the mass of the sample after drying. Considering the density of the sample  $\rho_p$  and the density of the solvent  $\rho_s$  ( $0.87 \text{ g/cm}^3$ ), the mass  $m$  of the swollen sample was used to calculate the polymer volume fraction,  $V_p$ , given by the eq. (2).

$$V_r = \frac{V_p}{V} = \frac{1}{\left(1 + \frac{m - m_d}{m_d}\right) \cdot \frac{\rho_p}{\rho_s}} \quad (2)$$

where  $V_p$  is the volume of the dry sample,  $V$  is the total volume of the swollen sample.

The crosslink density, which represents the effective number of chains per unit volume, was calculated according to the Flory-Rehner Equation:<sup>45</sup>

$$v_e = - \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_s \left( V_r^{1/3} - \frac{V_r}{2} \right)} \quad (3)$$

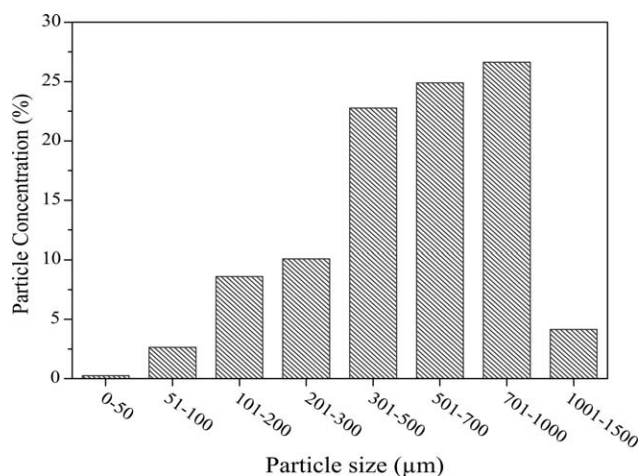
where  $v_e$  is the crosslink density ( $\text{mol/m}^3$ ),  $V_r$  is the polymer volume fraction,  $V_s$  is the solvent molar volume ( $106.5 \text{ cm}^3/\text{mol}$  for toluene) while  $\chi$  is the EPDM-toluene interaction parameter, obtained from literature as 0.49.<sup>46</sup>

**Temperature scanning stress relaxation.** The crosslink density of the samples was also determined from temperature scanning stress relaxation measurements using a TSSR instrument from Brabender GmbH, Germany. The TSSR test method and details of the instrument are described elsewhere.<sup>47,48</sup> The sample was placed into the electrically heated test chamber at the initial temperature of  $23^\circ\text{C}$  and a nominal strain of 50%. While the temperature remains constant, the isothermal test period starts subsequently. During this time most of the short time relaxation process occurs and the sample reaches a nearly stable state. After the isothermal relaxation test is finished, the sample is heated linearly at a constant rate of  $2 \text{ K/min}$ , until the stress relaxation has been fully completed or rupture of the sample has occurred. The apparent crosslink density was determined from the maximum slope of the stress temperature curve in the initial part of the curve according to the eqs. (4) and (5) as described in the literature<sup>44,49</sup> in more detail:

$$v_e = \frac{k}{R \cdot (\lambda - \lambda^{-2})} \quad (4)$$

$$v_e = \frac{\rho}{M_c} \quad (5)$$

where  $v_e$  is the apparent crosslink density ( $\text{mol/m}^3$ ),  $R$  is the universal gas constant,  $\lambda$  is nominal strain ratio,  $\kappa$  is the temperature coefficient of stress, e.g. the derivative of mechanical stress with respect to temperature,  $\rho$  is the mass density, and  $M_c$  is defined



**Figure 1.** Particle size distribution of RWP obtained by laser diffraction method.

as the average molar mass of the elastically active network chains. It is noted that eq. (4) is based on the well-known theory of rubber elasticity but it applies only for ideal rubber networks. Therefore, application of eq. (4) leads to an apparent crosslink density values in this case, because of the complex composition and structure of the investigated compounds.

**Determination of the morphology of the samples.** The morphology of the samples was investigated by using scanning electron microscopy (SEM). The SEM images of the tensile fractured surfaces of the specimens were obtained using a JEOL JSM 6510 scanning electron microscope (JEOL GmbH Germany). The cryogenically fractured surfaces were coated with a thin layer of gold prior to examination, using a Fine Coater JEOL JFC 1200.

## RESULTS AND DISCUSSION

### Physical Characterization of RWP

The characterization of RWP was carried out by particle size distribution, void volume, density, and DSC. The particle size distribution of the RWP, presented in Figure 1, shows that most of the particles, in a percent of 74%, had an average size between 300 and 1000  $\mu\text{m}$  (50 and 18 mesh). It is well known that ambient grinding technique produces a powder with an irregular shape, rough surface, and relatively large surface area.<sup>42</sup> In a study regarding the rubber powder characterization by using solid shear extrusion process, Bilgili *et al.*<sup>5</sup> mentioned that the particles with rough surface and irregular shape enhance particle—matrix adhesion, which represents a positive aspect in the case of surface activation process where the interfacial adhesion between the activated rubber waste particles and the raw polymer matrix is very important. The void volume (free space) of the RWP was 30% and the density was found to be  $1.19 \text{ g/cm}^3$ .

### Thermal Characterization of RWP and Raw Material Substitute Compounds

The composition of RWP was determined through thermal gravimetric analysis under  $\text{N}_2$  and  $\text{O}_2$  flow. The TG-DTG curves of the RWP are shown in Figure 2. The first mass loss, at  $362^\circ\text{C}$  is due to the volatilisation of the oil present in particles. The



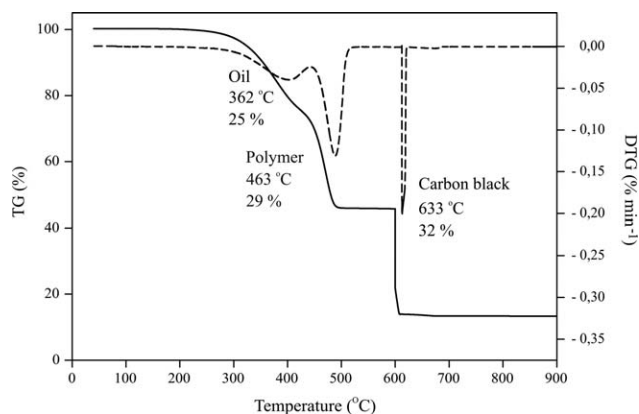


Figure 2. Thermogravimetric analysis of RWP.

second mass loss at 463°C appears due to polymer degradation and the third mass loss at 633°C is attributed to the carbon black content presented in the sample. From the TGA results we can conclude that the RWP contain a paraffinic oil<sup>50</sup> type which represents 25% of the sample composition. The polymer content in the sample is 29.4% and carbon black content is about 32%. A residual mass of 13.6% is representing the inorganic oxide ash.

Thermogravimetric analyses were as well performed for the reference sample and raw material substitute compounds in order to verify the thermal and oxidative stability. The TG-DTG curves of the compounds are shown in Figure 3 and the compounds composition is given in Table III. By analyzing the TG-DTG curves (Figure 3) the same behavior of the different compounds versus heating was observed. The volatilization of the oil take place in the range 364 to 366°C, the degradation of the polymer between 472 and 478°C and the weight loss of carbon black is in the range 595 to 608°C. From the data presented in Table III, it is obvious that by increasing the amount of RWP-LP in rubber compounds the oil and the carbon black amount decreases while the polymer and residual mass increases.

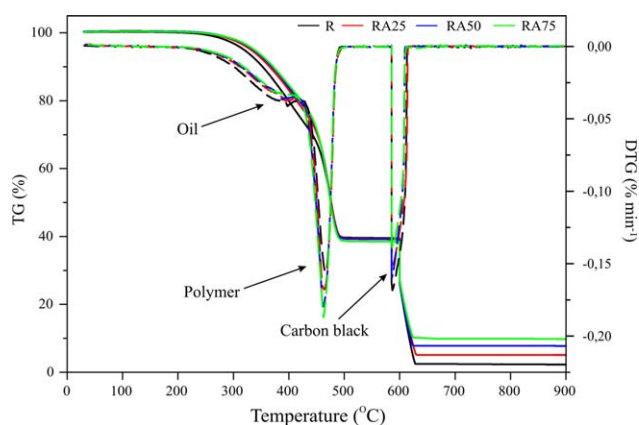


Figure 3. Thermogravimetric analysis of the reference and raw material substitute compounds (solid lines—TG curves; dashed lines—DTG curves). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Table III. Samples Composition Calculated from TG-DTG Curves

Description	Oil	Polymer	Carbon black	Residue
$T_p$	364–366°C	472–478°C	595–608°C	>608°C
Mass loss	wt %			
R	27.3	33.0	37.0	2.5
RA25	22.3	38.7	34.1	5.1
RA50	21.5	39.6	31.1	7.8
RA75	20.1	41.6	28.3	10.0

$T_p$  is the peak of the first derivative; wt—weight percent.

### Influence of Content and Type of the Activated Particles on Curing Characteristics

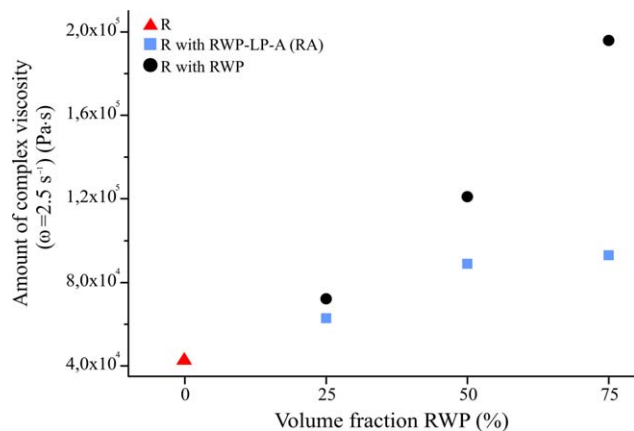
The rheometer tests for all samples were recorded at 180°C. In Table IV the values of minimum torque ( $M_L$ ), maximum torque ( $M_H$ ),  $\Delta M$  ( $M_H - M_L$ ), cure time ( $t_{90}$ ), scorch time ( $t_{s2}$ ), and cure rate index (CRI) are presented.

The obtained values show that the increase of the RWP-LP content in the rubber compounds leads to an increase of the minimum torque  $M_L$  and a decrease of the maximum torque  $M_H$  and torque difference  $\Delta M$  ( $= M_H - M_L$ ) in comparison to the reference sample (R). The increase of  $M_L$  is related to the viscosity of the samples. Since the void volume of the RWP is 30%, it could be possible that the raw EPDM is trapped in these voids, increasing the effective volume fraction of RWP and consequently increasing the samples viscosity. By measuring the complex viscosity of the samples and making a comparison between reference sample (R) and the compounds where 25, 50, and 75 v/v % of the raw material was substituted, it appears obvious that the values of the viscosity are increasing with the addition of RWP-LP content. By use of inactivated particles (RWP) instead of activated particles (RWP-LP) it can be observed that the complex viscosity of the sample increases dramatically (Figure 4).

Table IV. Cure Characteristics of EPDM Compounds

Samples	$M_L$ (dNm)	$M_H$ (dNm)	$\Delta M$ (dNm)	$t_{90}$ (min)	$t_{s2}$ (min)	CRI ( $\text{min}^{-1}$ )
R	1.78	17.86	16.08	9.50	1.69	12.7
RA 25	2.89	16.82	13.93	14.55	0.98	7.4
RA 50	4.12	14.54	10.42	8.77	0.79	12.5
RA 75	4.77	12.65	7.88	6.87	0.74	16.3
RB 25	2.65	14.83	12.18	13.33	0.99	8.1
RB 50	3.92	12.83	8.91	5.78	0.83	20.2
RB 75	4.94	10.70	5.76	3.85	0.87	33.6
RC 25	2.59	16.15	13.56	13.47	1.09	8.1
RC 50	4.07	14.90	10.83	9.08	0.82	12.1
RC 75	5.28	13.14	7.86	6.88	0.76	16.3
RD 25	2.68	15.16	12.48	12.21	1.08	9.0
RD 50	4.02	13.18	9.16	4.30	0.89	29.3
RD 75	5.14	11.36	6.22	3.84	0.85	33.4

$M_L$ —minimum torque;  $M_H$ —maximum torque;  $\Delta M$  ( $= M_H - M_L$ )—the difference between the maximum and the minimum torque during curing;  $t_{90}$ —cure time;  $t_{s2}$ —scorch time; CRI—cure rate index.

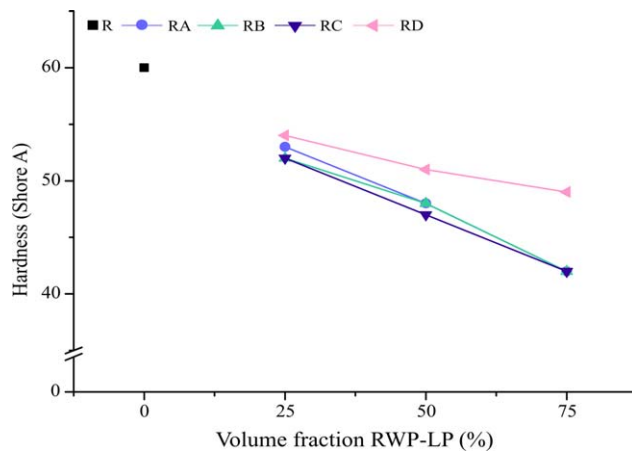


**Figure 4.** Amount of complex viscosity (angular frequency of 2.5 s<sup>-1</sup>, at 100°C) of the samples versus the volume fraction of activated and inactivated particles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Consequently, it can be stated that the processibility of the material is significantly improved by use of RWP-LP. It is obvious that the liquid polymers are able to occupy the free space between the rubber waste particles and to reduce the space where the raw material can be trapped, therefore reducing the viscosity. Comparable behavior was observed in a study made by Gibala *et al.*<sup>51</sup> where compositions containing ambiently ground rubber showed a higher viscosity in comparison with those using cryogenically ground rubber. The reduction of the maximum torque can be attributed to the migration of sulfur from the raw EPDM into the RWP phase.<sup>52,53</sup> Both the scorch time  $t_{s2}$  and the cure time  $t_{90}$  decrease, while the cure rate index increases with the RWP-LP loading. The values of the cure rate index, which is a measure of the rate of the cure reaction<sup>54</sup> presents lower values by addition of the RWP-LP for the compounds where the LP with higher content of ENB were used (RA and RC) in comparison with the compounds where the LP with lower content of ENB were used (RB and RD). The decrease in scorch time is attributed to the migration of the accelerators from RWP to the matrix.<sup>42</sup> Similar observations were made in other studies where different compounds, such as SBR,<sup>53</sup> EPDM,<sup>55</sup> or NR,<sup>56</sup> containing ground vulcanized rubber were used. The cure time  $t_{90}$  is decreasing by increasing the volume fraction of RWP-LP, showing lower values in comparison with reference sample (R) when 50 and 75 v/v % of the RWP-LP are added. The decrease in cure time is extremely favourable because it increases the production rate.<sup>54</sup>

#### Influence of Content and Type of the Activated Particle on Mechanical Properties

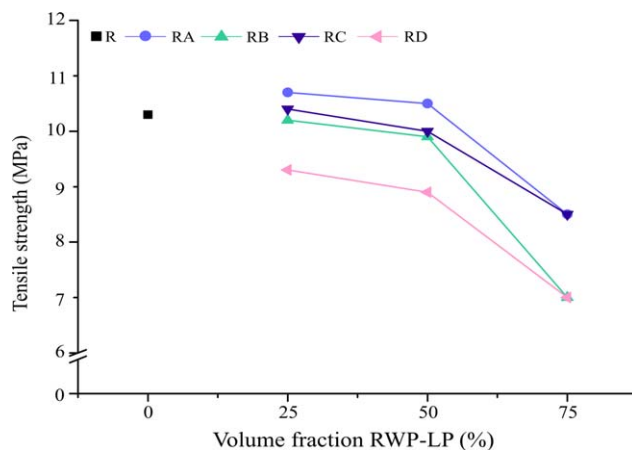
The values of mechanical properties for the evaluated compounds are illustrated in Figure 5 to 7. The hardness (Figure 5) decreases by increasing the content of the activated particles in the compound. By substituting up to 50 v/v % of the raw materials the hardness of the samples decrease slightly for all four polymers but still remains in the required range for elastomeric seals, according to the requirements of the standard ISO 7619-1:2010, respectively 50 ± 5 Shore A.



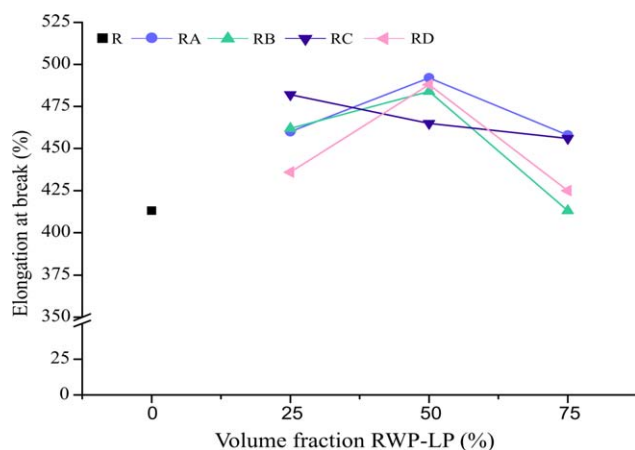
**Figure 5.** Influence of content and amount of RWP-LP on hardness of vulcanizates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The tensile strength decreases with increasing RWP-LP content, showing higher values for the samples RA and RC where the content of ENB is higher (see Figure 6). By substituting up to 50 v/v % of the raw material with the activated particles, the obtained tensile strength values are above the requirements of 9 MPa according to the standards for elastomeric seals (ISO 37:2011), being even higher for the RA samples in comparison with reference sample (Figure 6).

Our results showed that by increasing the RWP-LP content the elongation of break of all samples exhibit higher values in comparison with the reference compound (R) (Figure 7). In comparison with other studies, this represent a significant result, taking in consideration that it is possible to substitute up to 75 v/v % of the raw EPDM and to obtain an elongation at break higher than 400%. The results obtained for the elongation at break are in contrast with the results obtained in other studies,<sup>56,57</sup> but are in agreement with the results reported by Jacob *et al.*<sup>55</sup> While studying the effect of crumb rubber on the properties of rubber compounds based on SBR, Kruželák *et al.*<sup>57</sup> reported that the addition of the modified crumb rubber causes



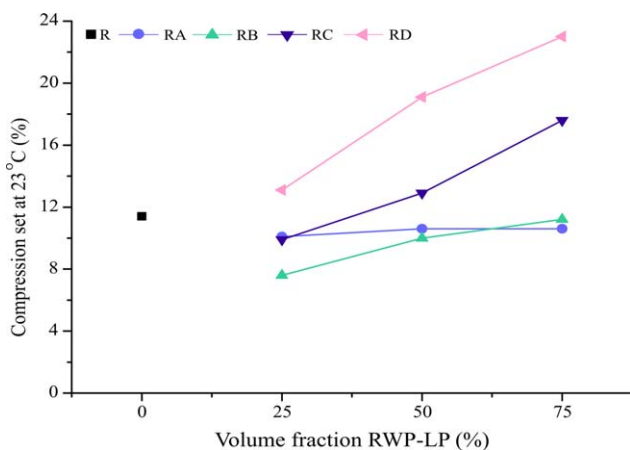
**Figure 6.** Influence of content and amount of RWP-LP on tensile strength of vulcanizates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** Influence of content and amount of RWP-LP on elongation at break of vulcanizates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

a significant decrease of elongation at break. Padke *et al.*<sup>56</sup> reported as well a decrease of elongation at break while studying the effect of cryoground rubber (CGR) in the powder form on properties of NR. It has been noted that stress concentration around the ground particles and the poor adhesion between the two phases caused the reduction of tensile strength and elongation at break. Contrariwise in a study performed by Jacob *et al.*<sup>55</sup> on EPDM compounds was reported that the addition of the ground vulcanizate leads to an increase of the elongation at break. In this case, the increase of the elongation at break was attributed to the filler effect, contained by the ground vulcanizate. Based on the results obtained in our study, it can be stated that the improvement of the elongation at break values is due to the liquid polymers used for the activation of RWP. Using the activated particles leads to a better adhesion and compatibility between the raw rubber matrix and the RWP-LP.

Besides hardness, elongation at break and tensile strength, an essential property of the sealing systems is the remaining deformation, characterized by determination of compression set. Thereby, for performing under high stress over a long period of time, a low compression set value is necessary. To prove the



**Figure 8.** Influence of content and amount of RWP-LP on compression set of vulcanizates at 23°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

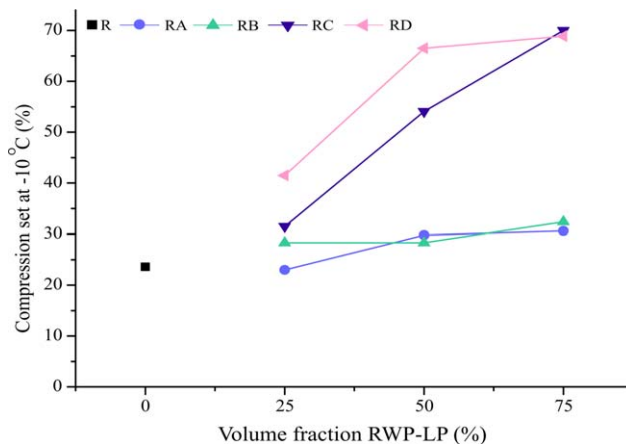
flexibility of the material at high and low temperature, compression set tests at three different temperatures were performed.

The results show that the ethylene content influences the behavior of the samples in terms of compression set values (Figures 8–10). The samples with a low ethylene content (RA and RB) exhibit very good compression set values at 23°C (Figure 8) being even lower in comparison with reference compound (R). Interestingly, for these samples, the amount of RWP-LP has no (RA) or only small (RB) influence on compression set values. Contrariwise, the compounds with higher content of ethylene (RC and RD) show a strong increase of the compression set values by increasing the content of RWP-LP.

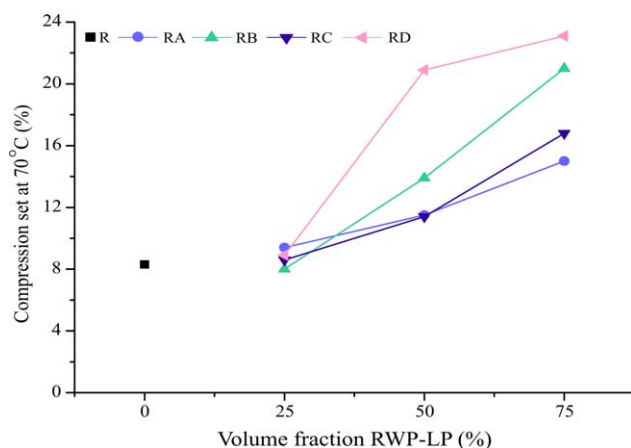
Similar behavior was observed for the compression set tests performed at  $-10^{\circ}\text{C}$  (Figure 9). The high ethylene content seems to induce an unwanted increase of the remaining deformation, while a low ethylene content shows in all cases only minimal changes, keeping the compression set values close to the value of reference compound.

By increasing the test temperature to  $70^{\circ}\text{C}$  all samples exhibit an increase of the compression set values when increasing the activated particles content (Figure 10). Although at this temperature the influence of the ethylene content on the remaining deformation is minor, the ENB percentage seems to be of major importance. Samples with low ENB content (RB and RD) show a significantly increase of compression set values by increasing the RWP-LP content. Interestingly, in the samples with high ENB percentage (RA and RC) the RWP-LP can substitute up to 75 v/v % of the raw material and the remaining deformation is still below the required limit (up to 20%) for this type of products, i.e. sealing systems.

It was previously shown that the ethylene content in EPDM rubber has a considerable impact on low temperature behavior.<sup>58</sup> When the ethylene content is higher than 65% the possibility to form semi-crystalline segments increases and therefore the polymer behaves more thermoplastic. Accordingly, the compression set values are highly dependent on the test temperature. At high temperatures, such as  $70^{\circ}\text{C}$ , the ethylene crystalline segments melt and the polymer becomes fully



**Figure 9.** Influence of content and amount of RWP-LP on compression set of vulcanizates at  $-10^{\circ}\text{C}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

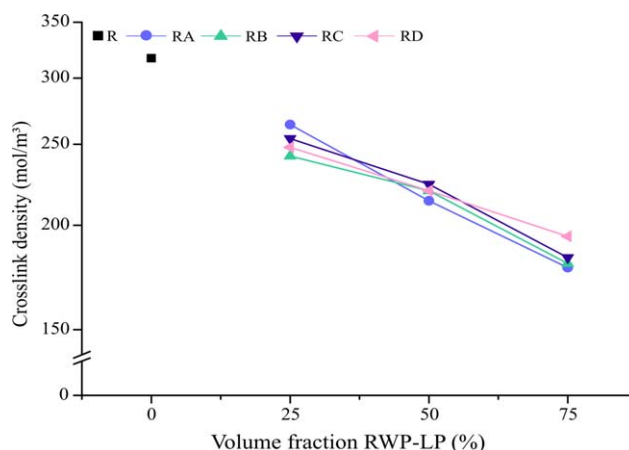


**Figure 10.** Influence of content and amount of RWP-LP on compression set of vulcanizates at 70°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

amorphous, therefore giving relatively low compression set values.<sup>58</sup> By lowering the temperature, the ethylene content already leads to higher compression set values at 23°C, while at -10°C this effect is extreme, inducing very poor compression deformation behavior. However, this drawback can be overcome by increasing the ENB content in the compound. As the results show, at higher ENB content compression set at 70°C is improved. The samples with the same ethylene content but higher ENB percentage gave better compression set values at all three set temperatures than the samples with lower ENB percentage. This behavior is attributed to the ability of ENB to disrupt the crystalline segments developed by the ethylene content<sup>58,59</sup> thus decreasing crystallisation and consequently improving the compression set values at low temperatures. The ethylene content and ENB percentage of the LP used for activation of the RWP have a strong influence on the compression set values even at low concentration, respectively 0.2 volume fractions.

#### Influence of the Activated Particle Type and Content on Crosslink Density of the Samples

One of the methods used to determine the apparent crosslink density of the cured samples was based on equilibrium swelling in toluene by applying the Flory-Rehner equation.<sup>45</sup> The apparent crosslink density values determined by swelling measurements are presented in Figure 11. The results show that the apparent crosslink density of the samples show a gradually decrease by increasing the RWP-LP loading in the compounds in comparison with the reference sample. The other method used for the determination of the crosslink density was TSSR and the obtained results are presented in Figure 12. Due to the complexity of the system and the heterogeneous structure of the samples, the absolute values of the crosslink density obtained via these two methods are not identical, but it is obvious that the results obtained from TSSR measurements are qualitatively consistent with the results obtained from swelling. The apparent crosslink density decreases by increasing the content of activated particles in the compounds. The results obtained via the above mentioned methods are thus in good agreement with the results obtained from the cure curves.

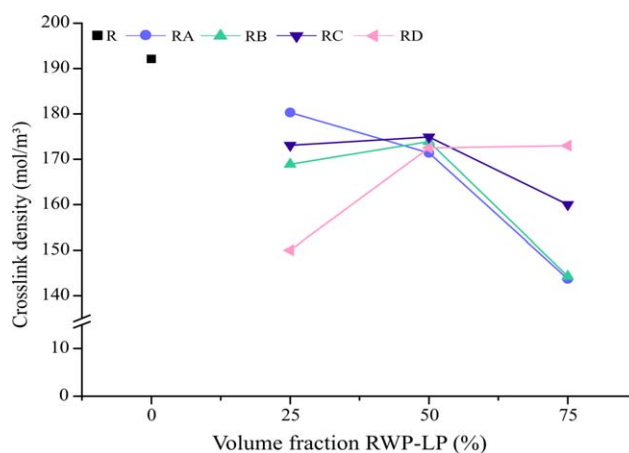


**Figure 11.** Apparent crosslink density determined by swelling measurements. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The substitution of the raw material with different amount and type of RWP-LP has a significant influence on the cure characteristics, mechanical properties, crosslink density, and the morphology of the new raw material substitute compounds. With the increase of RWP-LP amount an increase of  $M_L$  and CRI and a slight decrease of cure time,  $M_{Hb}$ ,  $\Delta M$ , and scorch time occurs (Table IV). As mention CRI is a measure of vulcanization rate, therefore the shortest  $t_{90}$  of compounds results in the highest value of CRI. In this case the samples with high ENB content (RA and RC) present smaller CRI values, indicating a slower cure. This behavior is attributed to the high ENB content, which requires a higher cure time due to the more active crosslink sites in the rubber compound.

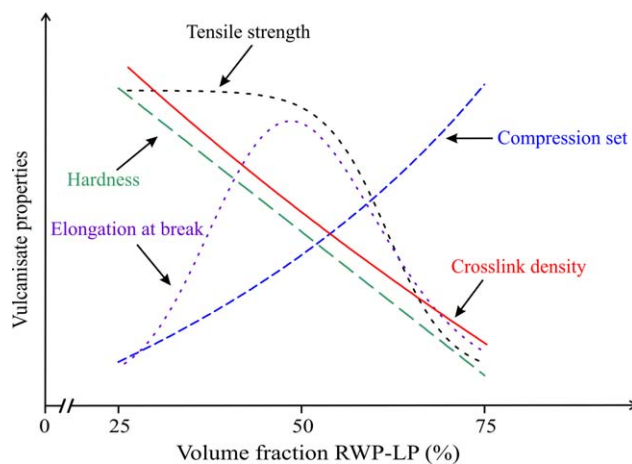
In Figure 13, a schematic sketch of the variation of several vulcanizates properties as a function of RWP-LP volume fraction is presented. As the volume fraction of RWP-LP increases, hardness, crosslink density and tensile strength decrease while compression set and elongation at break increases.

The decrease of hardness by increasing the loading of RWP-LP in the raw material substitute compounds can be ascribed to higher amount of LP and lower content of carbon black. As can be seen



**Figure 12.** Apparent crosslink density determined by TSSR measurements. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 13.** Vulcanizate properties versus volume fraction RWP-LP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

from the TG results (Table III) a higher amount of RWP-LP leads to a decrease of carbon black content, and thus to a decrease of hardness. Due to their low molecular weight a high amount of LP in the compounds can be another reason of the decrease in hardness. The excellent values obtained for elongation at break can be assigned to the LP used for activation of the RWP which can act as a coupling agent between the particles and the raw polymer matrix, making the material more flexible.

From the obtained results it seems likely that the values of the tensile strength are more influenced by the ENB content than the ethylene amount, as expected. This behavior can be ascribed to the ENB content which has a strong impact on crosslink density. The higher the ENB content, the higher the number of reactive centres for sulfur cured networks. The compression set values are influenced by both ethylene and ENB content. At  $-10^{\circ}\text{C}$  and  $23^{\circ}\text{C}$  the samples with lower amount of ethylene give lower or slight increased values while the samples with high ethylene content show a continuous increasing trend in comparison with reference compound (R). This behavior is due to the crystalline regions formed by ethylene sequences at high ethylene content. Due to crystallinity, the mobility of the polymer chains is reduced and thus, the ability of the material to return back into the undeformed state is hindered. At a test temperature of  $70^{\circ}\text{C}$  all samples show an increase of compression set values with increasing amount of RWP-LP. The explanation might be related to the fact that at high temperatures the polymer networks tend to rearrange and at the same time the possible polysulfidic crosslinks may convert into shorter bonds which consequently can inhibit the full recovery of the material. However, the samples with higher ENB content present better values and this is attributed to the possibility of forming more crosslinks and therefore improving the compression set. These results correspond to the trends which are expected for these properties, as already described in the literature.<sup>60</sup>

High potential application on the industrial scale was obtained by using up to 50% of the activated particles with low ethylene amount. For the activated particles which contain high content of ethylene the substitution of the raw material was possible only up to 25%.

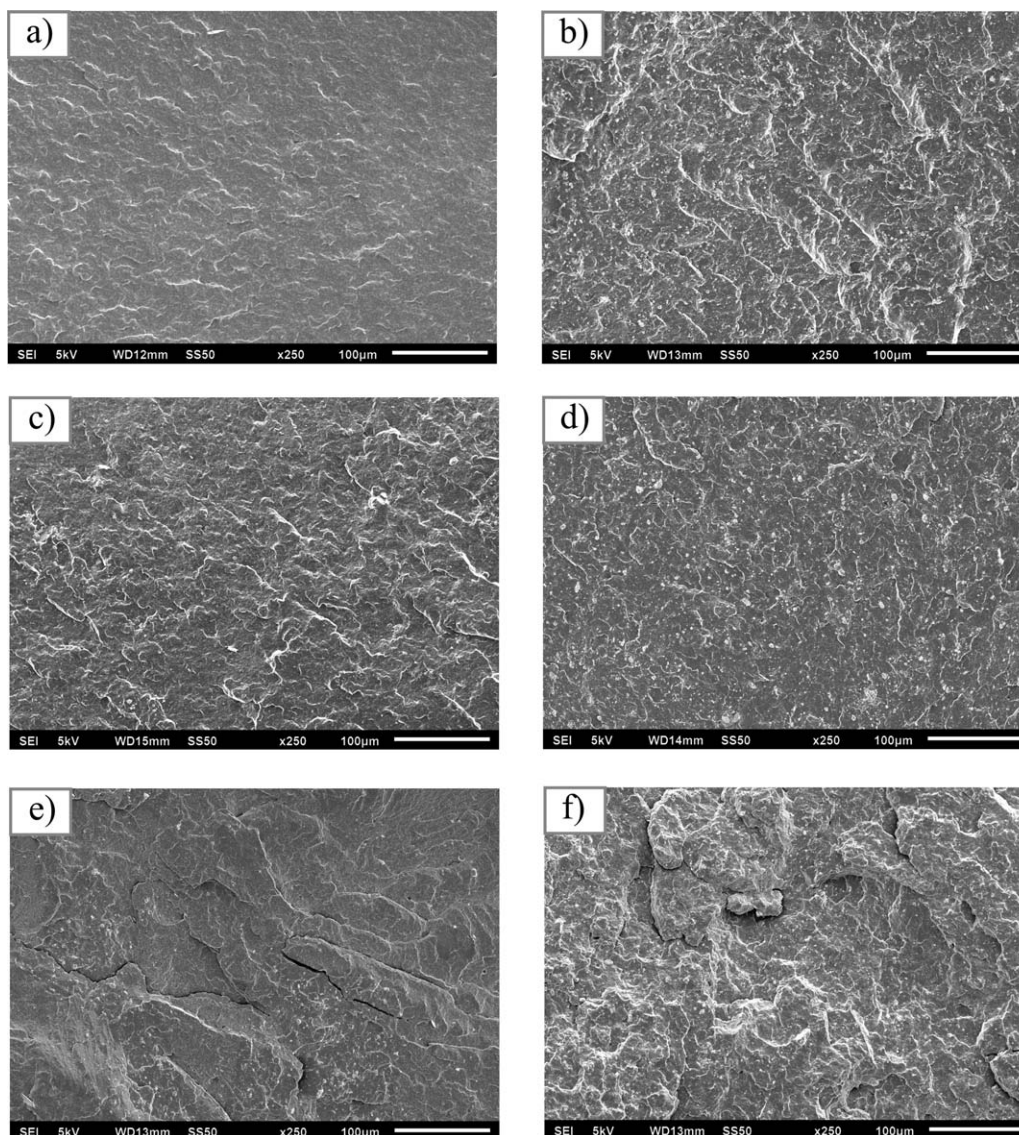
### Morphology Using SEM

Scanning electron microscopic images have been recorded in order to have an insight into the dispersion behavior of the samples and to analyse the microstructure of the compounds. The liquid polymer used in all cases was Trilene 67. The morphologies at the fracture surface of the tensile specimens for the reference sample, activated particles and the compounds containing 25 and 75 v/v % of activated, respectively inactivated particles are shown in Figure 14(a–f). The reference sample (R) presents a smooth surface with a good uniformity and homogeneity [Figure 14(a)]. The RWP-LP-A [Figure 14(b)] and the RA samples with 25 [Figure 14(c)], respectively 75 v/v % [Figure 14(d)] of activated particles show a very good dispersion and uniformity. Despite the high content of particles [Figure 14(b,d)] which are visible in the SEM images, the samples reveal a good homogeneity and uniformity in comparison with reference sample (R). For a lower RWP-LP content [Figure 14(c)] the particles are not so visible anymore, showing a structure close to the R. On the contrary, the compounds which contain 25 [Figure 14(e)] and 75 v/v % [Figure 14(f)] of the inactivated particles reveals an inhomogeneous structure with rough surface and fissures. It can be clearly seen that even the content of the inactivated particles is low [Figure 14(e)] the particles shows a poor dispersion in the rubber matrix, forming agglomerates.

### CONCLUSIONS

The goal of this work was to develop an easy, optimized, solvent-free activation method of RWP by use of LP with low molecular weight, different grades of unsaturated 2-ethylidene-5-norbornene termonomer, and varied ethylene content. The activation of RWP was performed by constant amount of LP/RWP and curative system. The reference compound was substituted with 25, 50, and respectively 75 v/v % by the RWP-LP for a recipe employed in the production of sealing systems. It was shown that an advantage of using RWP-LP instead of RWP is represented by the reduced viscosity of the samples, thus improving compound processability. The diene and ethylene content of the LP used for activation, proved to play an important role with respect to the compression set values of the samples. The compression set was strongly influenced by the ethylene content values at  $23^{\circ}\text{C}$  and  $-10^{\circ}\text{C}$  and by the ENB percentage at all three temperatures.

The crosslink density determined by equilibrium swelling and TSSR show the same tendency, respectively a slowly decrease by increasing the RWP-LP content. The SEM images reveal a good compatibility and homogeneity of all samples in comparison with the reference compound (R), even if high amount of RWP-LP was used. The obtained new compounds are suitable for the production of high quality products, such as elastomeric seals according to ISO 9631:2003 and ISO 4633:2002 standards. In order to fulfil the above mentioned standards, the particles activated with the liquid polymers containing lower ethylene content (LP-A and LP-B) are the most adequate to be used for the production of sealing systems. By using these types of polymers it was possible to substitute the raw material with RWP-LP up to 50 v/v % with very promising results. On the contrary, for the samples where the LP have a higher content of ethylene the substitution of the raw material was possible only up to 25



**Figure 14.** SEM images of: a) R; b) RWP-LP-A (0.8 v/v % RWP); c) RA25; d) RA75; e) R with 25% RWP; f) R with 75% RWP.

v/v %. This was due to the poor compression set values obtained. This study provides an important framework for the rational recycling methods designed to produce raw material substitute from recycling elastomers, aiming to contribute to economic and environmental sustainability by minimizing the disposal costs and conserving the resources.

The authors express their thanks to the German Federal Environmental Foundation, special to Dr. Jörg Lefevre and M.D.S. Meyer GmbH for the financial support of this work. The authors are also grateful to the Lion Copolymer Geismar (USA), LLC for the liquids polymers samples.

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