Improvement of elastomer swelling measurement for sulfur cross-link density determination

Karolis Petrauskas[1],

Vaida Žaržojūtė[2],

Artūras Jukna[3],

Svajus Asadauskas[1]*

[1] Tribology Laboratory,
Center for Physical Sciences
and Technology (FTMC),
Saulėtekio St. 3,
10257 Vilnius, Lithuania

[2] Department of Polymer Chemistry,
Vilnius University,
Naugarduko St. 24,
03225 Vilnius, Lithuania

[3] Joint Stock Company
"Gumos Technologijos",
Biržiškų St. 19,
11111 Vilnius, Lithuania

Due to growing demand from both environmental and industrial sectors the extent of rubber recycling is constantly increasing. Recycled rubber ranges from slabs of thermochemical reclaim, resembling virgin rubber, to fine rubber powders of diverse surface morphologies. Cross-Link Density (CLD) changes may characterize the effectiveness of rubber processing, but their measurements are often problematic. Most difficulties arise during determination of the volume fraction of polymer in the swollen rubber gel, also known as the V_r parameter (comparable to swell ratio), which closely relates to CLD. Vacuum, blotting and centrifugation were used to remove a swelling solvent (benzene) from the surface of the swollen rubber matrix. Centrifugation was more accurate for evaluating V_r of morphologically different types of rubber. Mechanical shear was used to produce a porous rubber sheet, while addition of acetamide and NaCl generated powder of devulcanized rubber. These samples were tested along with tire buffings and SBR sheets to show that extraction duration and time, needed to establish the swelling equilibrium between rubber and benzene, could be reduced from 72 h to less than 24 h in the case of porous or powdered rubbers. While compressed rubber might need longer durations, the overall time consumption for the CLD analysis could be shortened significantly, which helps in evaluating recycled rubber more thoroughly.

Keywords: rubber, recycling, powder, mechano-chemistry

INTRODUCTION

For more than a century, rubber waste has posed a threat to the environment due to its low rates of degradation and overall bulkiness [1]. Recently, because of strict environmental regulations and a general transition towards sustainability the amount of rubber products that end up in the landfills has slowed down, but environmental, logistical, economical and other issues still persist, especially in the case of End of Life Tires (ELT) [2]. A large ELT portion is burned as fuel, but some waste rubber is recycled as well. During recycling, its three-dimensional matrix is inevitably altered, various bonds get broken, with particular attention directed towards the selective cleavage of comparatively weak sulfur–sulfur cross-links in the rubber matrix [3, 4].

Disruption of these bonds leads to reduction of Cross-Link Density (CLD) in the vulcanized matrix, i.e. rubber devulcanization. Devulcanized products can vary significantly: from rubber crumb produced by mechanical grinding of rubber articles [5] to fine rubber powder produced mechano-chemically [6], to bulky lumps of thermo-chemically reclaimed material [7].

When the quality of recycled rubber needs to be assessed, the determination of rubber CLD values is often employed, which directly relates to the effectiveness of disruption of the three-dimensional matrix [3, 8–12]. The traditional way of determination of this parameter relies on swelling the rubber article in an appropriate solvent, calculating the volume of polymer in the swollen rubber matrix that has reached the swelling equilibrium (V_r parameter, informally called "swell ratio") and calculating the CLD value by using the Flory–Rehner equation [13]. The need of standardization

* Corresponding author. Email: asadauskas@chi.lt

of this procedure resulted in ASTM D6814 methodology. Unfortunately, the standard does not specify if certain precautions should be taken in those cases when rubber, that is being analysed, is in a highly porous, finely powdered of otherwise different from a compressed sheet lump or other bulk item, associated with conventional rubber. Due to difficulties arising from the CLD determination of fine powders certain research groups completely omit this characterization step [10, 14].

One of the main obstacles in successful CLD determination is the qualitative removal of an excess amount of a swelling solvent from the surfaces of the analysed rubber. While the adherent solvent can by removed from small regularly shaped rubber sheets by blotting, that is suggested by ASTM D6814 methodology, the same technique might be unfit for rubber powder, which is comprised of small and often irregularly shaped particles. Furthermore, the D6814 method involves prolonged extraction and swelling stages, which can easily exceed one week of testing. Industrially, such durations are often non-feasible, especially in quality control or manufacturing. In addition, blotting is sensitive to the compression force during wiping, various ambient conditions (temperature, humidity, durations, etc.) and other operator-related factors. As a consequence, wider applicability of the D6814 method is limited, resulting in poor understanding of CLD variations in rubber articles. This is particularly problematic for rubber recycling, because CLD is difficult to quantify and the benefits of devulcanization are often disregarded. Obviously, poor understanding of recycled rubber properties is very detrimental for its utilization as a secondary raw material in new items.

Successful attempts to characterize processed rubber powders in terms of CLD were performed by Weber et al. [11] and Bilgili et al. [12]. Both groups used centrifugation of swollen rubber powders for the removal of excess amounts of an adherent solvent. Weber et al. successfully characterized styrene-butadiene rubber (SBR) and ethylene-propylene diene monomer (EPDM) rubber powders in this fashion. Bilgili et al. have proved that such determination of rubber's V_r parameter is well suited for mechanically produced powders that are both small in size and irregularly shaped. Unfortunately, different techniques for a qualitative adherent solvent removal were not compared side-by-side and it is still unknown if one method has any advantages over the other. It does not become evident whether testing durations can be reduced either.

In our experiments we evaluated the differences of three solvent removal techniques for a qualitative removal of an adherent solvent from the surface of the swollen rubber matrix. Blotting, vacuum filtration and centrifugation were adapted for V_r parameter determination and measurement fluctuations were quantified. Furthermore, we assessed the differences that might arise from the shape and structure of the analysed rubber sample in terms of

adhered solvent removal and establishment of the swelling equilibrium. The main goal of this research is to improve the accuracy of devulcanization measurements and reduce their duration in order to make CLD determination more suitable for industrial settings.

EXPERIMENTAL

Materials
Two granulometric fractions (2000 μm > d > 850 μm and 850 > d > 425 μm) of truck tire tread buffings were supplied by "Gumos Technologijos" (Lithuania). Each shipment of buffings was carefully mixed by intensive shaking and agitation to assure a homogeneous distribution of rubber particles within the whole volume. SBR sheet was supplied by "Alsaflex", acetone (p.a. grade) and benzene (p.a. grade), used for extractions and swelling experiments, were purchased from "Eksparas" (both from Lithuania) and used without further purification. Methanol of 99% purity ("Avsista", Lithuania) was used for density measurements. Acetamide (p.a. grade) and NaCl (p.a. grade) used for production of reclaimed rubber powder and methanol (puriss.), used for determination of densities of rubber, were obtained from "Labochema" (Lithuania) and used without further purification.

Production of various rubber samples for analysis
A two-roll mill X(S)K-360 (Wuxi Double Elephant Rubber and Plastic Machinery Co. Ltd. China) was used to process the rubber feedstock (truck tire tread buffings) into reclaimed rubber powder and sponge-like reclaimed rubber material ("sponge"). The rolls of 36 cm diameter were made of stainless steel, without additional polishing or texturing. Rolls were manually compressed to a minimal working nip size, approx. 100 μm. The velocity ratio of rollers was fixed at 1:1.25.

For reclaimed rubber powder production presieved truck tire tread buffings ("+20 Mesh" fraction of d > 850 μm) were premixed with 3% (wt./wt.) of water, 1% (wt./wt.) of acetamide and 0.4% (wt./wt.) of NaCl and processed on the two-roll mill for 16 passes, assuring the roll temperature from 10 to 20°C. The resulting reclaimed rubber powder was sieved into granulometric fractions and the "−20+40 Mesh" fraction (850 μm > d > 425 μm) was used for later experiments.

For reclaimed rubber sponge production truck tire tread buffings ("+20 Mesh" fraction d > 850 μm) were processed on the two-roll mill for 24 passes without addition of any chemicals, until a rubber agglomerate ("sponge") was produced as porous sheet-like crumbs of 1 to 2 mm thickness and up to 3 cm in size. Reclaimed rubber sponge was used in later experiments without any further processing.

A vulcanized SBR sheet was supplied as a smooth, continuous sheet. Before analysis, it was wiped with a dry

lint-free cloth to remove any debris and cut into roughly $3 \cdot 10 \cdot 2$ mm (W · L · H) rectangles by heavy duty scissors. The resulting rectangles were used in later experiments without any further treatment.

Extraction of polar compounds from rubber samples
Before swelling experiments, plasticizers and polar substances, such as processing and vulcanization aids, antidegradants etc., were removed from the rubber matrix by extraction in hot acetone. The amount of the rubber sample, that was deemed sufficient for further analysis (about 10 g), was placed into an extraction thimble, made of cellulose, and put into a Soxhlet extractor. The full volume of the extractor was utilized by accommodating 3 thimbles with the specimens of the same rubber type into one extractor. Approx. 350 mL of acetone was used for extraction that was carried out over the course of 20 h or longer. After the extraction, the thimbles with rubber samples were removed from the Soxhlet apparatus and the excess solvent was evaporated using air stream in the fume hood. Afterwards, the samples were dried to a constant mass in a forced draft air oven SNOL ("Umega", Lithuania) at 80°C for 18 h, cooled and kept in a desiccator until further analysis.

Visual and SEM inspection of rubber samples
The samples, prior to swelling experiments, were inspected visually. No distinct morphological differences could be observed, only SBR sheets seemed to have a smooth, glossy surface texture, therefore were not analysed further. The samples of reclaimed rubber powder, reclaimed rubber sponge and truck tire tread buffings were extracted in acetone and dried, then evaluated microscopically. Scanning Electron Microscope (SEM) images were taken with a Helios NanoLab 650 Scanning Electron Microscope (FEI, Netherlands). Each sample was sputtered with a conductive layer of chromium at 2–5 nm thickness using a Quorum Q150T ES device (Judges Scientific Plc, UK) with manufacturer-calibrated deposition parameters (voltage, current, duration, etc.) before their SEM analysis.

Determination of the volume fraction of rubber in the swollen rubber gel – parameter V_r
About 1 g of the extracted and dried rubber was put into a clear 40 mL glass vial, the vial was then filled to the top with benzene ($\rho = 0.876$ g/cm³ at 20°C) and securely enclosed with a PTFE cap. The rubber sample was allowed to swell to an equilibrium point for 72 h in the dark at (21 ± 1)°C. Afterwards, swollen rubber was removed from the solvent, surface dried to remove the adherent solvent and weighed (m_1). After weighing, the rubber sample was dried in a forced draft air oven at 80°C for 18 h, cooled in a desiccator and weighed (m_{rubber}). The amount of the solvent in the swollen rubber matrix was calculated using the formula (1) given below:

$$m_{solvent} = m_1 - m_{rubber}. \tag{1}$$

The density of rubber was determined using a 9.895 ml ($V_{pycnometer}$) glass pycnometer (BRAND™) and methanol ($\rho_{methanol} = 0.792$ g/cm³ at 20°C), as a solvent, that does not swell rubber. A dry and empty pycnometer was weighed ($m_{pycnometer}$), then filled to 2/3 of the volume with the extracted, swollen and dried rubber sample and weighed again (m_2), then the rubber sample was flooded with methanol. When rubber in the pycnometer was fully covered with methanol, air bubbles, trapped on the rubber surface, were removed by stirring the sample with a micro-spatula. When no more air bubbles were present, the pycnometer was topped with methanol and weighed (m_3). The density of the rubber sample was determined using the formula (2) given below:

$$\rho_{rubber} = \frac{m_{rubber}}{V_{rubber}} = \frac{m_2 - m_{pycnometer}}{V_{pycnometer} - \dfrac{m_3 - m_2}{\rho_{methanol}}}. \tag{2}$$

For every sample V_r determination was performed on at least three specimens and the average value was used for later calculations. The V_r value of the rubber sample was calculated using the (3) formula given below:

$$V_r = \frac{\dfrac{m_{rubber}}{\rho_{rubber}}}{\dfrac{m_{rubber}}{\rho_{rubber}} + \dfrac{m_{solvent}}{\rho_{solvent}}}. \tag{3}$$

It is clear that the incomplete removal of the solvent from the surface of rubber will give a higher number for the $m_{solvent}$ parameter, consequently lowering the V_r value.

Removal of excess solvent using blotting technique
After the swelling equilibrium is achieved, the swollen rubber sample is removed from the solvent by the means of a spatula and put between two layers of blotting paper. The top layer of the blotting paper is gently dabbed to allow a good contact of the blotting paper and the rubber sample. After 10 seconds, the top layer of the blotting paper is removed, the rubber sample is collected to a pre-weighed weighing jar and immediately weighed.

Removal of excess solvent using vacuum filtration
After the swelling equilibrium is achieved, the swollen rubber sample is removed from the solvent by means of a spatula ant put into a Buchner funnel with a paper filter that is already attached to an Erlenmeyer flask with a vacuum system. The vacuum is turned on for 10 seconds and the rubber sample is gently shuffled with the spatula to ensure the removal of the solvent. After the filtration procedure, the rubber sample is collected to a pre-weighed weighing jar and immediately weighed.

Removal of excess solvent using centrifugation of the sample

After the swelling equilibrium is achieved, about 3 g of the swollen rubber sample is removed from the solvent by means of a spatula ant put into a 14 cm^3 centrifugation vial that is divided by the solvent permeable cotton membrane into two compartments: upper one for the swollen rubber and the bottom one for the separated solvent. The vial is plugged with a stopper, the stopper-vial contact is covered with a layer of Parafilm™ and then the vial is put into a centrifuge (Z206A Hermle, Germany) and centrifuged for 1 minute at 1000 rpm (relative centrifugal force of 120 g). After the centrifugation procedure is over, the swollen rubber sample is collected from the upper part of the centrifugation vial into a pre-weighed weighing jar and immediately weighed.

RESULTS AND DISCUSSION

Mechano-chemical conversion of ground rubber into devulcanized powder

A fraction of large particles (2000 μm > d > 850 μm) of truck tread buffings was used as a feedstock for production of reclaimed rubber powder and reclaimed rubber sponge. For production of reclaimed rubber powder acetamide was chosen as a devulcanizing compound because of its heavily polar nature, ability to donate/accept a proton and react with Lewis acids. Addition of sodium chloride acted as an increase of the ionic strength of the system thus shielding charged particles from one another and not letting them recombine. The usage of polar compounds bearing amide groups can be used for rubber reclamation purposes [15], especially in conjunction with ashless salts [16]. Even though some work is done in this field, the reasonable mechanism for this type of rubber processing is still shrouded in unknown factors. In our work we propose that during mechanical processing disulfide and polysulfide bonds stretch, their polarity increases and then their reaction with acetamide molecules can occur. The addition of NaCl helps in shielding of charged chemical groups, which increases the yield of powdered rubber. Water acts both as a solvent of a devulcanizing agent and a proton donor/acceptor for reactive chemical species situated on relatively immobile polymeric chains (Fig. 1).

When devulcanizing agents are used during the processing of rubber, the thermal energy generated by rubber particle stretching and relaxation is used for promotion of chemical reactions, thus only mildly increasing the temperature of rubber. Reactive chemical groups are shielded and/or deactivated, therefore the amount of fine powder increases over the course of further processing (Fig. 2A). When rubber is processed under the same conditions without any devulcanizing agent, the rubber particles heat up due to lack of thermal energy dissipation. Reactive chemi-
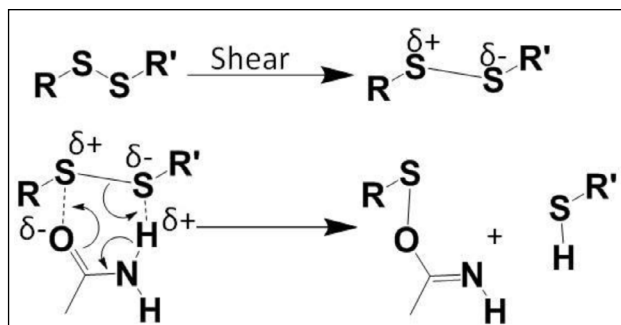

Fig. 1. The proposed mechanism of the acetamide reaction with polarized cross-links in the rubber matrix during mechanical processing. R and R' are polymeric chain residues

cal species, generated by bond cleavage, are not shielded or deactivated and have an ability to recombine or react with adjacent polymeric chains. As a result, a new interconnected three-dimensional matrix is produced (Fig. 2B).

It is important to note that the mechanism and optimization of mechano-chemical processing of rubber is out of the scope of this study. The reclaimed rubber powder (fraction 850 μm > d > 425 μm was isolated by sieving) and the reclaimed rubber sponge were analysed without any further processing.

Morphological characterization of tested rubbers

Four different samples, bearing various surfaces and morphologies, were chosen for the experiments:

• Particles of truck tire tread buffings, the particle size between 850 and 425 μm (Fig. 3A);

• Reclaimed rubber powder, the particle size between 850 and 425 μm (Fig. 3B);

• Reclaimed rubber sponge, agglomerates of an approximate size around 1 cm (Fig. 3C); and

• SBR rectangles of an approximate size of 3 · 10 · 2 mm (W · L · H) (Fig. 3D).

From the pictures, presented in Fig. 3, it is clear that the SBR rectangles are of the most uniform size and have smooth surfaces. This type of rubber is usually used in the industry for various applications, such as gaskets, friction reducers, etc., and could be referred to as a typical industrial example. Reclaimed rubber powder and truck tire tread buffings of the same size look rather similar, but there is a clear difference in the shapes of the particles. Truck tread buffings are comprised of elongated, sometimes even thread shaped particles while the particles of reclaimed rubber powder are mostly round. Reclaimed rubber sponge aggregates are of an irregular shape with sizes around 1 cm. To gather more information about the surface structure of truck tread buffings, reclaimed rubber powder and reclaimed rubber sponge, SEM images were taken (Fig. 4).

It is clear from the SEM images given in Fig. 4 that the truck tire tread buffings have a rather smooth surface.
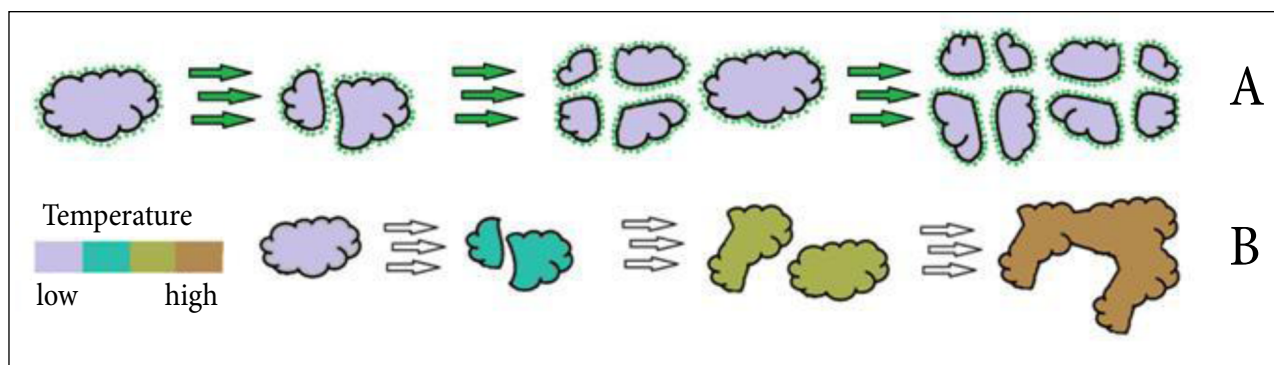
Fig. 2. Mechano-chemical processing of crumb rubber with the addition of a devulcanizing agent (A); mechanical processing of crumb rubber without added chemicals (B)
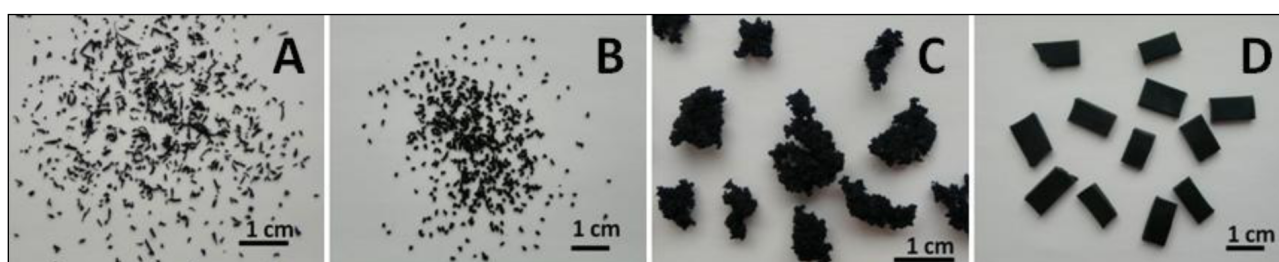

Fig. 3. Different rubber samples used for experiments: sieved buffings (A), reclaimed rubber powder (B), reclaimed rubber sponge (C) and SBR sheets (D)
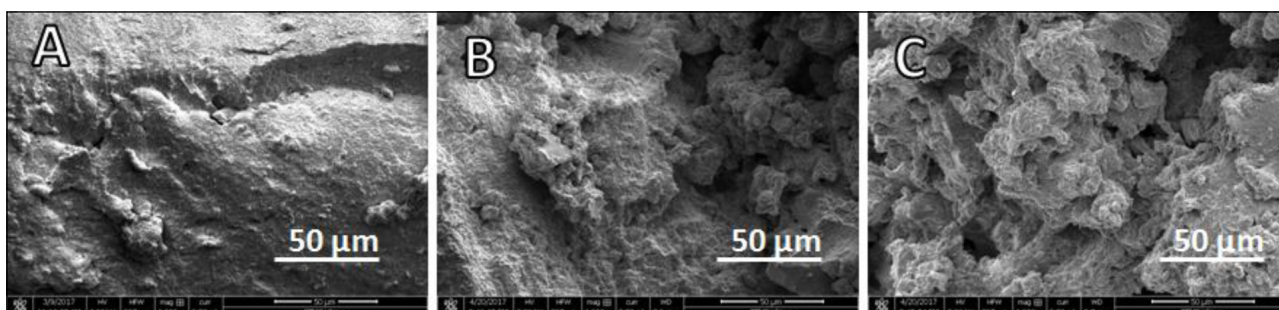

Fig. 4. SEM images of truck tire tread buffings (A), reclaimed rubber powder (B) and reclaimed rubber sponge (C)

They have some signs of plastic deformation but severe destruction is not evident. The reclaimed rubber powder and the reclaimed rubber sponge were both produced by ambient grinding; therefore both samples have irregular surfaces, filled with pores and crevices. Surface irregularities are more expressed in the reclaimed rubber sponge which might imply that it is comprised of smaller particles sticking together. This fact supports the idea that during processing of rubber many particles aggregate together, although with major discontinuities in the three-dimensional matrix of rubber. The extent of aggregation is diminished by usage of a devulcanizing agent. It could be concluded that all samples have surfaces, correlating with their production techniques, and are typical examples of samples, encountered in the industry [1, 17].

Comparison of different drying techniques

To assess the differences between different types of solvent removal techniques all four rubber samples were swollen to equilibrium points in benzene, the excess amounts of the solvent were removed using the previously described methodologies, the rubber samples were weighed and dried. From the obtained data the values of volume fractions of rubber in the swollen rubber gels (V_r) for different samples and different solvent removal techniques were calculated. The results of the experiment are presented in Table 1.

Different experimental procedures produced quite large deviations between the same samples, as listed in Table 1. However, it must be noted that the employed samples represent very different types of rubber surfaces (see Fig. 3 and Fig. 4). Buffings and powder are composed of fine particles, but

Table 1. **Assessment of different methods for removal of an adherent solvent**

Rubber sample	Method	V_r values	St. dev.	St. dev., %
Truck tire tread buffings	Blotting	0.286	0.007	2.45
	Vacuum filtration	0.222	0.058	26.13
	Centrifugation	0.282	0.01	3.55
Reclaimed rubber powder	Blotting	0.303	0.008	2.64
	Vacuum filtration	0.327	0.004	1.22
	Centrifugation	0.314	0.001	0.32
Reclaimed rubber sponge	Blotting	0.304	0.007	2.30
	Vacuum filtration	0.254	0.004	1.57
	Centrifugation	0.318	0.005	1.57
SBR sheet	Blotting	0.367	0.002	0.54
	Vacuum filtration	0.329	0.077	23.40
	Centrifugation	0.365	0.002	0.55

the surface of buffings is much smoother than that of powder. The other two rubber types, sponge and sheet, contain much larger particles, but again the surface of the latter is much smoother. The particle size, its topography and the surface area are the key factors in determining the strength of solvent adherence. Its release from the surface can be affected significantly by the procedures of solvent removal. Therefore, it is not surprising that the deviations in V_r values are clearly evident, especially when a graphical assessment of different methods of adherent solvent removal is presented in Fig. 5.

It is clear from the results, presented in Table 1 and Fig. 5, that the removal of a solvent by vacuum filtration had poor repeatability. The data scatter was substantial in comparison with other techniques of solvent removal. Furthermore, the fluctuation of data was sporadic: V_r values for the truck tire tread buffings, reclaimed rubber sponge and SBR sheet were a lot smaller than the V_r value obtained after blotting and centrifugation methods, while the V_r value for the reclaimed rubber powder showed the opposite trend. The fluctuation and scatter of data obtained by vacuum filtration rises from the morphological differences of rubber samples and the vacuum filtration itself: it is hard to ensure a uniform removal of a solvent from an irregularly shaped sample by filtration. Furthermore, rubber samples encounter an increased air flow around them during filtration,
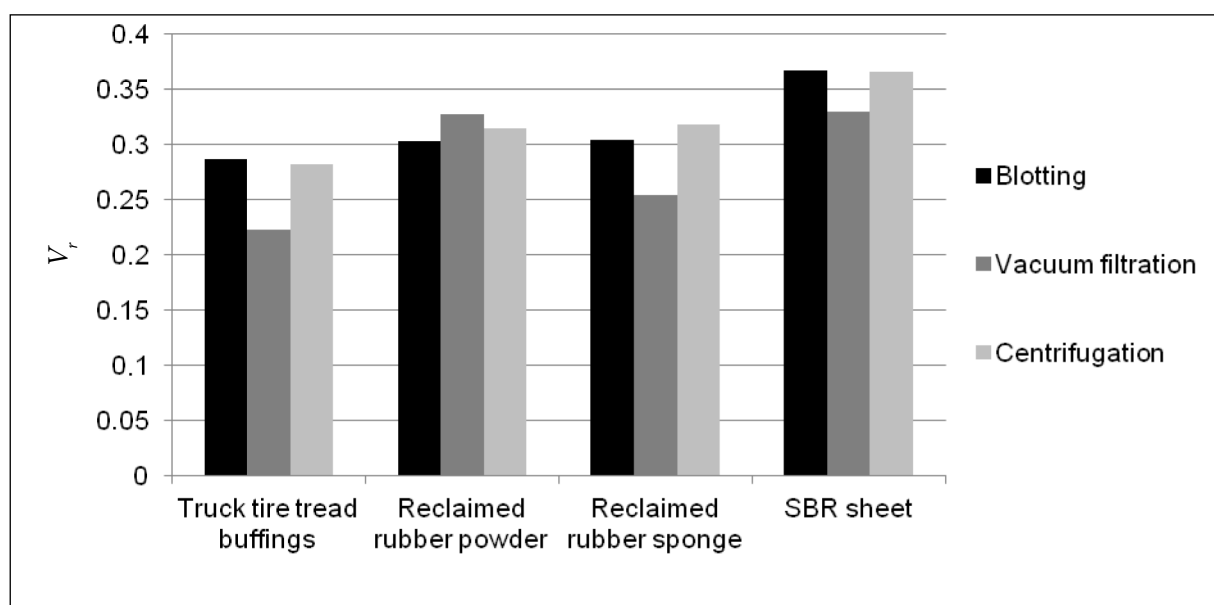

Fig. 5. Values of the volume fractions of rubber in the swollen gel, V_r, in four different types of rubber, as measured by different solvent removal techniques: 1) blotting; 2) vacuum filtration; 3) centrifugation

which could cause the removal of a solvent from the swollen rubber matrix instead of its surface (drying) as it could be seen in the reclaimed rubber powder scenario.

Blotting and centrifugation methods performed much more similarly. It is interesting to note that there is a little difference whether the solvent is removed by either blotting or centrifuge if the rubber surface is smooth. When drying with blotting paper it is easy to remove all the excess solvent from the surface due to its flat shape. The same idea could be applied during centrifugation, because virtually no solvent is trapped in pores and micro-crevices on smooth surfaces.

When reclaimed rubber powder, porous and irregularly shaped rubber is analysed, the centrifugation method outperformed blotting in two different aspects. First of all, the centrifugation method yielded a lower scatter of data. Secondly, marginally higher V_r values show that more solvent was removed from the surface of rubber during centrifugation than during blotting. This is easily understandable: the solvent that is adhered to the surface of rubber is affected by centrifugal force and thus removed, while drying with blotting paper requires a direct solvent–paper interaction to be removed, which is hard to achieve when the surface is uneven or small particles are analysed.

The truck tire tread buffings were analysed by an additional operator (B) and the resulting V_r values were compared to those in Table 1. The results of this experiment are presented in Table 2. Evidently, all techniques are quite operator-sensitive, which shows how important it is to establish the best procedure for solvent removal. The results presented in Table 2 confirm that the worst method of solvent removal is vacuum filtration.

To see how the method of solvent removal affects the scatter of data over a longer analysis period additional series of experiments were performed. Truck tire tread buffings (size of particles between 850 and 425 μm) were analysed repeatedly to determine their volume fractions of the rubber in the swollen gel at equilibrium points (V_r). All conditions, except the method of adherent solvent removal, were kept constant. The blotting and centrifugation solvent removal techniques were repeated 19 times over the course of 1 month by two operators. The average V_r values were calculated as 0.285 ± 0.007 (±2.5%) for blotting and 0.283 ± 0.002 (±0.7%) for centrifugation. It is clear that

when the blotting technique is used for solvent removal, it is harder to reproduce the analysis conditions. Parameters, such as sample residence time between the sheets of blotting paper, or the distribution of rubber powder, could vary, therefore the method, where many of these variables are removed, should be beneficial to the analysis results. Analysis of 38 consecutive samples illustrated very well that V_r values obtained by two different methods are very similar, yet the standard deviation of data is about three times smaller when the centrifugation method is used. This strongly supports the feasibility of the centrifugation method for eventual CLD determination.

One more conclusion can be drawn from the excellent repeatability of ±0.7% when using the centrifugation method. The studied specimens were sampled from a mixture of rubber waste, i.e. tread buffings of many different truck tires. Obviously, the specimens themselves could contain different components depending on the sampling manner and even timing, because commercial manufacturers use various formulations for tread rubber. Nevertheless, when using one shipment of well mixed buffings, this variation becomes negligible.

Effects of swelling duration on V_r measurements

For the correct measurement of V_r parameter the swelling equilibrium between the rubber sample and the swelling solvent has to be assured. Usually it is recommended to swell rubber samples for 72 h [8, 9, 3, 10, 11] in a swelling solvent of choice, which assures that the solvent molecules penetrate the 3D matrix of rubber polymers and the diffusion flux becomes negligible. The actual duration, which might be needed for the diffusion flux to subside, varies for different types of rubber. Solvent migration rates are also affected by the particle shape and morphology, for example, penetration might be different when comparing smooth rubber sheets to fine rubber powder that, in the case of reclaimed rubber powder, could sometimes possess a significant amount of porosity. In the following experiment the reclaimed rubber powder, truck tire tread buffings and SBR sheets were swollen in benzene and the specimens were analysed after a predetermined amount of swelling duration had passed. The excess solvent from specimen surfaces was removed using the centrifugation method, three specimens were analysed for every data point. All specimens of

Table 2. **Inter-operator repeatability during V_r value determination in the buffing samples using different solvent removal techniques**

Method	Operator	V_r values	St. dev.	St. dev., %
Blotting	A	0.286	0.007	2.45
	B	0.282	0.003	1.06
Vacuum filtration	A	0.222	0.058	26.13
	B	0.308	0.014	4.55
Centrifugation	A	0.282	0.01	3.55
	B	0.283	0.001	0.35

the same rubber sample were swollen in the same vial to reduce data fluctuations. The results of the experiment are given in Fig. 6.

The experiment revealed that the macro-structure of the analysed rubber particle played an important role on solvent diffusion. SBR specimens in the form of $10 \times 3 \times 2$ mm sheets with smooth surfaces and a relatively low surface area reach the swelling equilibrium much later than the powdered samples of buffings and reclaimed rubber. Moreover, surface morphology differences play only a minute role in swelling of fine rubber powders: powder, that has a distorted surface (reclaimed rubber powder), demonstrates swelling rates similar to that of powder, whose surface is relatively smooth (truck tire tread buffings). The minute deviation of data could be attributed to the origins of the samples: both rubber powders were obtained from industrial facilities, therefore non-homogeneities should be expected. In conclusion it is evident that the amount of time required to reach the equilibrium between the solvent and the swollen matrix of rubber is dependent on the compound composition and the size of the rubber article that is being analysed.

Durations needed for rubber extraction with acetone

Prior to swelling experiments rubber samples have to be extracted of any small molecular compounds, such as vulcanization and processing residues etc., using a polar solvent, such as acetone. The swelling equilibrium experiment has shown that the powdered rubber samples swell to the equilibrium point much faster than unprocessed rubber sheets and this fact could be attributed to a larger overall surface area of powdered rubber. Having this idea in mind, another conclusion about the rubber–solvent interaction could be

drawn: it is possible that the time required for the qualitative extraction of rubber with acetone could be shorter for powdered rubber than it is required for unprocessed rubber sheets. Unfortunately, due to a great variety of Soxhlet extractor sizes, heating sources, etc. this supposition was not tested systematically.

CONCLUSIONS

When rubbers cross-link densities are evaluated, the key step is the determination of the V_r value of swollen rubber. Consequently, the efficient removal of the swelling solvent that is adhered to the surface of rubber is essential. Three different methodologies were examined: removal of a solvent by blotting with a paper towel, removal of a solvent by vacuum filtration, and removal of a solvent by centrifugation. After evaluation, the method of solvent removal by vacuum filtration was deemed unsatisfactory: standard deviations of experimental results were too great. Removal of a solvent by blotting with a paper towel and removal of a solvent by centrifugation yielded much more consistent results: V_r values of rubbers were similar, standard deviations of test results did not vary significantly for smooth particles. It is important to note that for rough and porous surfaces centrifugation methodology showed lower scattering of experimental results than drying with blotting paper. There is no need of a direct contact between the excess solvent and blotting paper, which proves difficult to achieve when the solvent is in various pores and crevices of rubber. It is also important to state that when the centrifugation method is used, the atmosphere in the test tube is saturated with solvent vapours, thus diminishing the evaporation of a solvent from the swollen rubber matrix (see Fig. 7).
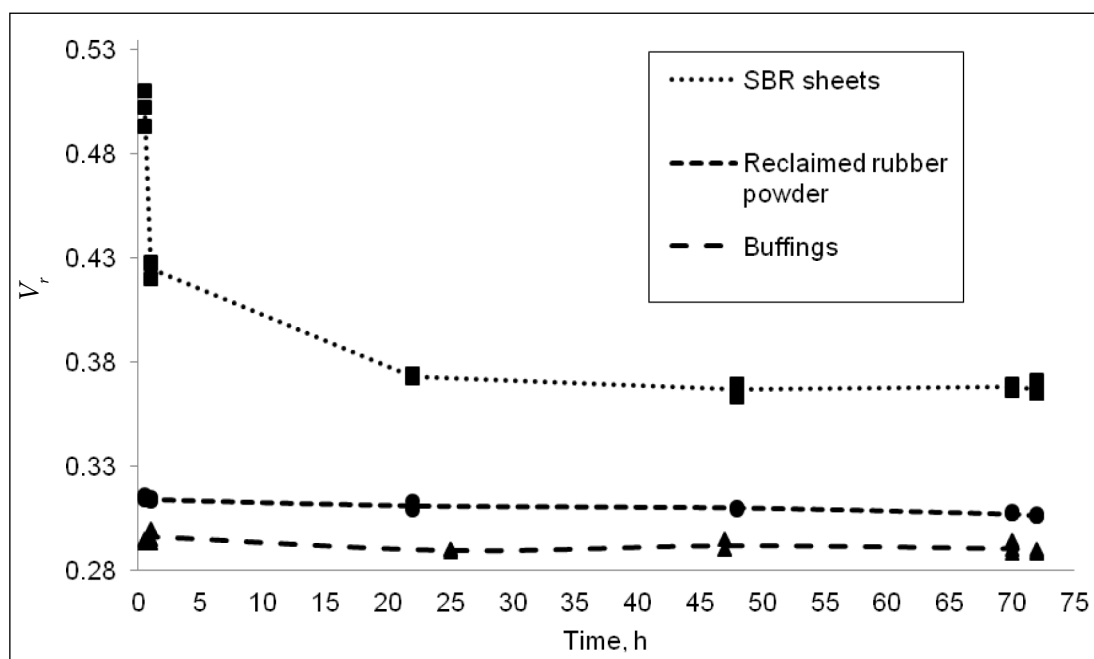

Fig. 6. Influence of swelling durations on V_r determination by centrifugation in specimens with major differences in surface morphology
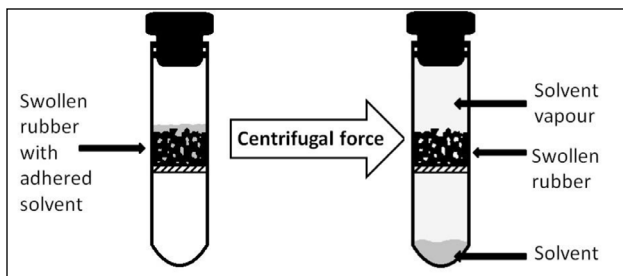
Fig. 7. Scheme of the centrifugation method used in determination of the V_r value of rubber samples

Another important conclusion that could be drawn from our experiment is that the time needed to reach the swelling equilibrium is dependent on the size of the analysed rubber article: fine rubber particles swell to the equilibrium much faster than smooth rubber sheets. This phenomenon could be attributed to an increased surface to the volume ratio of rubber powders in comparison to sheets.

The measurement of V_r values is crucial in determining the extent of devulcanization in recycled rubber. Standard test methods are slow and not adapted to a wide range of different rubber samples available in the industry. The solvent–rubber interaction and swelling trends, established in this study, as well as improvements in the solvent removal make it possible to reduce the testing durations and improve the overall quality of the obtainable results.

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References

1. M. Myhre, S. Saiwari, W. Dierkes, J. Noordermeer, *Rubber Chem. Technol.*, **85**, 408 (2012).
2. *ETRMA End-of-life-tyre Report 2015* [http://www.etrma.org/tyres/ELTs].
3. J. Shi, K. Jiang, D. Ren, et al., *J. Appl. Polym. Sci.*, **129**, 999 (2012).
4. L. Imbernon, S. Norvez, *Eur. Polym. J.*, **82**, 347 (2016).
5. S. Ramarad, M. Khalid, C. T. Ratnam, A. Luqman Chuah, W. Rashmi, *Prog. Mater. Sci.*, **72**, 100 (2015).
6. J. Karger-Kocsis, L. Meszaros, T. Barany, *J. Mater. Sci.*, **48**, 1 (2013).
7. B. Adhikari, D. De, S. Maiti, *Prog. Polym. Sci.*, **25**, 909 (2000).
8. S. Rooj, G. C. Basak, B. K. Maji, A. K. Bhowmick, *J. Polym. Environ.*, **19**, 382 (2011).
9. F. Cavalieri, F. Padella, F. Cataldo, *J. Appl. Polym. Sci.*, **90**, 1631 (2003).
10. Y. Li, S. Zhao, Y. Wang, *Polym. Degrad. Stab.*, **96**, 1662 (2011).
11. T. Weber, A. Zanchet, R. N. Brandalise, J. S. Crespo, *J. Elastomers Plast.*, **40**, 147 (2008).
12. E. Bilgili, H. Arastoopour, B. Bernstein, *Powder Technol.*, **115**, 277 (2001).
13. P. J. Flory, J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).
14. I. Mangili, M. Lasagni, M. Anzano, et al., *Polym. Degrad. Stab.*, **121**, 369 (2015).
15. Lev-Gum Ltd., United States Patent 6831109 B1, December 14, 2004.
16. JSC Devulco, World Patent Application WO2014062043A1, June 24, 2014.
17. M. Sienkiewitz, J. Kucinska-Lipka, H. Janik, A. Balas, *Waste Manage.*, **32**, 1742 (2012).

Karolis Petrauskas, Vaida Žaržojūtė, Artūras Jukna, Svajus Asadauskas

METODO, SKIRTO SKERSINIŲ SIEROS RYŠIŲ TANKIUI NUSTATYTI, TOBULINIMAS KEIČIANT ELASTOMERŲ BRINKIMO ĮVERTINIMĄ

Santrauka

Antrinis gumos panaudojimas nuolatos didėja kylant aplinkosauginiams ir pramoniniams reikalavimams. Perdirbant gumos atliekas gaunamos įvairios struktūros: nuo termocheminio regenerato luitų, primenančių žaliavinį kaučiuką, iki smulkių gumos miltelių, pasižyminčių skirtingomis paviršių morfologijomis. Gumos perdirbimo efektyvumą galima apibūdinti skersinių sieros ryšių tankio pokyčiais, tačiau juos išmatuoti sudėtinga. Tam būtina nustatyti polimero tūrį išbrinkusiame gumos gelyje (V_r parametrą), tačiau atsiranda problemų dėl skirtingos paviršių morfologijos. Ant išbrinkusios gumos matricos paviršiaus likusio brinkinimo tirpiklio (benzeno) likučiams pašalinti buvo naudojama vakuminė filtracija, nusausinimas ir centrifugavimas. Centrifugavimas pagerino įvairių perdirbtos gumos tipų V_r parametro nustatymo tikslumą. Naudojant mechaninę šlytį pagaminti poreti perdirbtos gumos lakštai, o papildomai įvedus acetamidą ir NaCl – perdirbtos gumos milteliai. Tiriant šiuos mėginius kartu su SBR gumos lakštais ir padangų nuorėžomis nustatyta, kad brinkimo pusiausvyra smulkiuose gumos milteliuose nusistovi greičiau nei didesniuose glotnios gumos gabaluose. Spartesnė skersinių sieros ryšių tankio nustatymo procedūra labai naudinga siekiant nuodugnesnio perdirbtos gumos įvertinimo.