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Environmentally-friendly physico-chemical rapid ultrasonic recycling of fumed silica-filled poly(dimethyl siloxane) vulcanizate

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Fumed silica-filled PDMS, where quite a strong interaction exists between the filler and matrix via hydrogen bonding, was recycled by means of an extruder with high power ultrasound attachment. It was found that the reinforcing filler plays an important role in the devulcanization process. Compared to the precipitated silica-filled PDMS, higher power is consumed during the devulcanization process of fumed silica-filled PDMS due to a strong interaction between the fumed silica particles and PDMS chains. The decrease in crosslink density after the devulcanization process shows that the process is quite dependent on the concentration of fumed silica. Throughout a simulation of scission of chemical bonds during the process, the influence of the concentration of filler on the devulcanization was investigated. The scission of main chains (Si–O) and crosslinks (Si–C and C–C) concurrently occurs during the process. Crosslinks are predominantly severed in the absence of fumed silica while the main chain rupture tends to increase with the filler concentration. The main chain scission leads to the deactivation of filler which reduces gel fraction and crosslink density of the revulcanizates. The mechanical properties of the revulcanizate show that the fumed silica significantly affects the final properties of the recycled PDMS.

1 Introduction

Development of economic and viable processes to recycle used tires and waste rubbers still remains a tremendous problem that scientists/engineers should solve, not only to protect against environmental pollution but also to prevent the depletion of natural resources. Among various mechanical and chemical recycling methods, ultrasonic treatment has been suggested as a promising technique since it possesses various advantages. Ultrasonic recycling is a fast continuous extrusion process with a residence time of a few seconds. The process does not require use of any chemical agent for devulcanization and does not generate by-products. It is an energy efficient environmentally friendly physical process. Another attractive feature of this process is the direct usability of the treated rubber by means of revulcanization which is similar to the vulcanization of virgin material. Various types of elastomers have been studied including ground tire rubber, natural rubber, styrene-butadiene rubber, EPDM, butadiene rubber, and polyurethane. These studies reveal that ultrasonic waves, at a certain level of pressure and moderate temperature, can rapidly break down the three-dimensional rubber network. This is caused by cavitation which is created by high intensity ultrasonic waves in the presence of pressure and heat. Driven by ultrasound, microscopic cavities, typically present in any rubber due to the existence of voids and imperfections, pulsate with amplitude depending upon the ratio between ambient and ultrasonic pressure (acoustic cavitation). This leads to mechanochemical degradation of overstressed bonds around pulsating cavities.

Consumption of poly(dimethyl siloxane) (PDMS), composed of alternating silicone and oxygen atoms in the main chain, is growing very rapidly due to its unique chemical composition and excellent properties. The applications range from consumer products to industrial applications, such as household and personal care products, textile treatments, and antifoams for food processing. The bond energies of the crosslinked PDMS network, consisting of Si–O bonds in the main chains and Si–C and C–C bonds in the crosslinks, are substantially higher than those of other sulfur-cured synthetic rubbers, consisting of C–C in the main chains and C–S and S–S in the crosslinks. Therefore, the breakage of the crosslinks in PDMS is more difficult to achieve than in other rubbers. The traditional recycling of PDMS is classified into three categories: (1) thermal depolymerization in a thermal cracking bed reactor or in a closed vessel, (2) chemical treatment using various chemical agents, (3) mechanical grinding waste scraps and compounding with virgin material. In addition, high power ultrasound has been successfully used to recycle unfilled and precipitated silica-filled, PDMS vulcanizates, where incorporated filler plays a significant role in recyclability of the vulcanizate. For the unfilled system, almost identical physical properties of revulcanized PDMS as those of virgin vulcanizate were achieved, while approximately 80–90% recovery of mechanical properties was obtained for the precipitated silica-filled system. Since PDMS itself is too weak, fumed silica is most frequently used for reinforcing purposes. Therefore, the investigation of the effect of fumed silica on recycling of PDMS was the initiative of this study.

2 Experimental

A polymeric network was prepared by crosslinking PDMS, SE 64 made by General Electric Company with weight-average molecular weight \( M_w = 4.14 \times 10^5 \) and number-average molecular weight \( M_n = 2.34 \times 10^5 \) (measured by gel permeation chromatography, GPC). It contained 0.6 mol% vinyl groups. Fumed silica, Aerosil 200® (Degussa Co.), having a surface area of 200 m\(^2\) g\(^{-1}\) was used as a reinforcing filler. Dicumyl peroxide (DCP), LUPEROX® 500R (Pennwalt Corp.), was used as the curative. Various concentrations of silica were incorporated in PDMS by a Moriyama mixer having a chamber capacity of 3 L. Half the amount of filler was added in PDMS and after 3 min the rest was added and mixed for 7 min at room temperature. The silica-filled PDMS compounds were then homogenized by a two-roll mill (Dependable Rubber Machinery Co.). 0.5 phr DCP was added to compounds on the two-roll mill at 25 °C. After mixing, the compounds were pre-cured at 170 °C by a compression molding press (Wabash) into 260 \( \times \) 260 \( \times \) 12 mm\(^3\) slabs and then post-cured in a ventilated oven at 200 °C for 2 hours.

The bound rubber content in uncured PDMS compounds was determined by the Soxhlet extraction method using benzene as a good solvent. Extraction in a cellulose thimble was carried out for...
5 days. The remaining non-extracted part (gel) was dried at 50 °C for 48 hours in a vacuum oven. The amount of bound rubber was determined as the ratio of the amount of rubber in the unextracted gel to the amount of rubber in the compound.

The vulcanized sheets were ground into particles using a Nelmor grinding machine with 5 mm screen. These PDMS particles were then fed into a rubber extruder with an ultrasonic die attachment to achieve devulcanization. The temperature of the extruder barrel was set at 180 °C. The screw speed was 20 rpm and both the die and horn cooling water flow rate were set to be 0.09 m³ h⁻¹. The gap, δ, between the flat face of the horn and the die exit surface was either 0.35 mm or 0.63 mm. The material flow rate, Q, was 0.32 g s⁻¹. A 3000 W ultrasonic power supply, a converter and a booster were used to provide longitudinal vibrations to the horn at a frequency of 20 kHz. The amplitudes, A, of the ultrasonic wave were 5, 7.5 and 10 μm. The devulcanized silicone rubber exiting from the die was collected for further investigation. The devulcanized rubber was revulcanized with 0.5 phr DCP in slabs of dimensions of 180 × 130 × 3 mm³ at 170 °C for 10 min. The revulcanized samples were also post-cured under the same conditions as virgin compounds.

Gel fractions of the vulcanized and devulcanized samples were measured by Soxhlet extraction, using benzene as the solvent. The extraction time was set at 24 hours. Crosslink densities were determined by the swelling method. The weights of the swollen samples were measured after removing the surface solvent. Then the samples were dried in a vacuum oven at 50 °C for 24 hours and were weighed again. The crosslink density, χ, was calculated using the Flory–Rehner equation.

The mechanical properties of the virgin vulcanizates and revulcanized samples were measured at an elongation speed of 50 mm min⁻¹ by aInstron 5567 tensile test machine with a 500 N load cell following ASTM D 412–92.

3 Results and discussion

3.1 Energy consumption

The power consumption instantaneously monitored by a watt meter was recorded during the devulcanization process and is represented as a function of ultrasonic amplitude at various filler concentrations in Fig. 1. It is seen that the power consumption increases with the filler concentration and ultrasonic amplitude for all concentrations of the filler. Compared to the precipitated silica-filled system, higher energy is consumed in the fumed silica-filled system. This observation is more pronounced at higher ultrasonic amplitudes. For example, 2000 watts were needed for 40 phr fumed silica-filled PDMS at 10 μm, while 1490 watts were consumed for 40 phr precipitated silica-filled PDMS at the same amplitude. The measured ultrasonic power consumption includes the useful power and the losses. One cannot estimate experimentally what portion of the power is used by devulcanization. Also the power expended on heat dissipation in the material and power transmitted by the travelling wave through the rubber cannot be separated. Apparently, ultrasound may break both chemical crosslinks between PDMS chains and physical crosslinks between rubber chains and filler particles. It is thought that more energy is used to break the physical crosslinks in the highly filled system due to the increased amount of bound rubber in fumed silica-filled PDMS compounds, as indicated in Fig. 2. The amount of bound rubber is strongly related to the interaction between the filler and matrix polymer, the surface area of the filler, the solubility of the extraction agent, molecular weight of the matrix polymer, the concentration of filler in the compound and the extraction time and temperature. The bound rubber content is 79.2% at a concentration of fumed silica of 10 phr and it continuously increases up to 94.6% at 40 phr causing an increase of the concentration of physical crosslinks with an increase of the concentration of fumed silica in PDMS vulcanizates. This explains why a higher power consumption for devulcanization of PDMS vulcanizates is required at a higher concentration of filler. The degree of breakage of the chemical and physical crosslinks is estimated in the following simulation.

3.2 Breakage of 3-dimensional network

The degree of devulcanization is quantified by the reduction of the crosslink density and gel fraction. In measuring the crosslink density of the filled system, the Kraus correction was employed in order to avoid misleading values due to the presence of filler. Details of the Kraus correction procedure can be found elsewhere. It is noted that the Kraus correction constant of 1.93 was experimentally obtained and used for the calculation. Fig. 3 depicts the normalized crosslink density as a function of ultrasonic amplitude at various filler concentrations. It is clearly seen that the
decrease in crosslink density is strongly dependent on the filler concentration and the amplitude. For the unfilled system, 89% of crosslinks are broken at 10 μm of ultrasonic amplitude, while only 28% of crosslinks are ruptured in the 40 phr filled system at the same amplitude. However, it is not easy to estimate how many of the main chains and crosslinks are ruptured during the process. In order to investigate the effect of filler on the breakage of the main chains and crosslinks during the devulcanization process, a simulation, based on the classical theory of branched polymers by Dobson and Gordon22,23 and adopting Flory molecular weight distribution, was conducted for the different filler concentrations.

The breakage of main chain and crosslinks is expressed as a function of the ratio of scission rates, $k_p/k_a$, which is an adjustable parameter. $k_p$ and $k_a$ denote the rate of main chain and crosslink rupture, respectively.26 Two are limiting cases. One of them corresponds to $k_p/k_a \to 0$ when only rubber main chains are subjected to breakage (line 2 in Fig. 4). In the opposite limiting case $k_p/k_a \to \infty$ when only rubber main chains are subjected to breakage (line 2 in Fig. 4). It is demonstrated in Fig. 4 that the experimental points lie in between the two limiting cases indicating that both rupture of main chain bonds and breakage of crosslinks occur during devulcanization. It is seen that the $k_p/k_a = 7.40 \times 10^{-4}$ in the case of unfilled PDMS provides a fairly good agreement between the experimental and theoretical data. It should be noted that the model predicts a higher rate of crosslink scission in comparison with that of main chain bond rupture for devulcanization of PDMS. This is quite reasonable because in this case main chain bonds are stronger than crosslink bonds. Moreover, the difference between main chain and crosslink bond energies in peroxide-cured PDMS is higher than in sulfur-cured synthetic rubber. Fig. 4 shows the experimental and calculated results of the normalized gel fraction vs. the normalized crosslink density for filled and unfilled silica-filled PDMS. The physical-chemical characteristics of vulcanized PDMS used in the calculations are shown in Table 1. The resulting $k_p/k_a$ values for different filler concentrations from the simulation are given in Table 2. For filled silica-filled PDMS systems, higher values of $k_p/k_a$ are obtained at

![Fig. 4 Normalized gel fraction vs. normalized crosslink density of devulcanized unfilled and fumed silica-filled PDMS.](image)

![Fig. 5 Crosslink density (g) and gel fraction (g) of virgin, devulcanized, and revulcanized fumed silica-filled silicone rubber vs. filler loading. Rubber was devulcanized at a flow rate of 0.32 g s⁻¹, a gap of 0.63 mm, an amplitude of 10 μm, and 180 °C.](image)

<table>
<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Unit</th>
<th>PDMS</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Density</td>
<td>$\rho$</td>
<td>kg m⁻³</td>
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<td>24</td>
</tr>
<tr>
<td>Molecular weight: number-averaged</td>
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<tr>
<td>Molecular weight: weight-averaged</td>
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<td>Monomeric: molecular weight</td>
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<td>25</td>
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<tr>
<td>Crosslink density in gel</td>
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<td>%</td>
<td>0.08</td>
<td>18</td>
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</table>

Table 2 The $k_p/k_a$ values for unfilled and fumed silica-filled PDMS

<table>
<thead>
<tr>
<th>Filled silica-filled</th>
<th>Unfilled</th>
<th>10 phr</th>
<th>20 phr</th>
<th>30 phr</th>
<th>40 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_p/k_a$</td>
<td>$7.40 \times 10^{-4}$</td>
<td>$1.97 \times 10^{-2}$</td>
<td>$4.26 \times 10^{-2}$</td>
<td>$6.16 \times 10^{-2}$</td>
<td>$6.91 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

40 phr than at 10 phr, indicating that a greater amount of the main chains are subjected to rupture in highly filled PDMS. In addition, approximately a 100-fold increase in the $k_p/k_a$ ratio is seen for the 40 phr filled compound ($k_p/k_a = 6.91 \times 10^{-2}$) compared to the unfilled system ($k_p/k_a = 7.40 \times 10^{-4}$) indicating the severity of main chain breakage in the filled system. 3.3 Mechanical properties of recycled PDMS

Fig. 5 represents crosslink densities and gel fractions of virgin vulcanizates, devulcanized and revulcanized rubbers. It is seen that a significant decrease in both crosslink density and gel fraction upon ultrasonic devulcanization is achieved during devulcanization. However, they are not recovered after revulcanization compared to those in virgin vulcanizates although the same amount of curative as in virgin rubber was used. Since a crosslink reaction is achieved through the participation of vinyl groups in methyl vinyl silicone rubber, further crosslinking reaction through the vinyl groups upon revulcanization is limited since vinyl groups are consumed in the first stage of curing. Another reason is a possibility of a partial deactivation of the filler. It is known that rubber molecules are bonded onto the filler surface and penetrated into pores existing in silica filler leading to bound rubber. The mobility of such chains is considerably restricted. This means that the chains of bound rubber can be more easily broken than those of the non-bound rubber during ultrasonic treatment. Accordingly, after ultrasonic treatment a considerable amount of bound rubber chains are broken. This process may lead to a partial deactivation of filler causing the loss of reinforcement. The depletion of vinyl groups and the deactivation of filler may be the reasons for the low crosslink density and gel fraction of revulcanized PDMS. These results may be also related to the mechanical properties of the revulcanized samples.

30 phr fumed silica-filled devulcanized rubber was blended with virgin 30 phr fumed filled silicone rubber at various concentrations. Fig. 6 represents the stress-strain behavior of the blend vulcanizates. The ultrasonically treated PDMS was able to be revulcanized (line 5 in Fig. 6), but the mechanical properties were significantly reduced due to the low crosslink density and gel fraction as
mentioned earlier. Varying concentrations of the ultrasonically treated PDMS were blended with virgin material. In the case of 25/75 devulcanized/virgin blend revulcanize, almost identical 100% modulus was achieved as that of virgin vulcanize (line 1 in Fig. 6). However, the elongation at break shows a 66% recovery. Compared to our previous work on precipitated silica-filled PDMS, the recovery of the mechanical properties was lower. Considering the stronger interaction of fumed silica than precipitated silica in PDMS, this could be explained by the fact that more bound rubber chains are subject to breakage upon ultrasonic devulcanization in the fumed silica/silicone rubber system.

4 Conclusion

The fumed silica-filled PDMS, where quite a strong interaction exists, such as hydrogen bonding, was devulcanized by an extruder with a high power ultrasound attachment. Compared to traditional recycling methods, this process provides facile reclamation of used rubber products since it is continuous, fast and does not involve any chemical agents. In addition, the recycled rubber obtained by this process can be directly revulcanized similar to vulcanization of virgin material. In this study, it is found that the reinforcing filler plays an important role in the devulcanization process. Compared to precipitated silica-filled PDMS, higher power is consumed during the devulcanization process of fumed silica-filled PDMS due to a strong interaction between the fumed silica particles and PDMS chains. The decrease in crosslink density after the devulcanization process shows that the process is quite dependent on the concentration of fumed silica. By means of simulation, the influence of the concentration of filler on the devulcanization process was thoroughly investigated. The scission of main chains and crosslinks concurrently occurs during the process since the experimental data lie between the two extreme cases of main chain breakage and crosslink rupture. Crosslinks are predominantly severed in the absence of fumed silica while the main chain rupture tends to increase with the filler concentration. For example, approximately a 100-fold increase in the $k_p/k_c$ ratio is found for a 40 phr filled compound compared to an unfilled system. The main chain scission leads to the deactivation of filler which reduces the gel fraction and crosslink density of the revulcanizates. The mechanical properties of the revulcanize show that the fumed silica significantly affects the final properties of the recycled PDMS.

Acknowledgments

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