

Preparation and Properties of Swellable Thermoplastic Elastomer Alloys Based on Elastomeric Powder, Polypropylene, and Superabsorbent Polymer

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ABSTRACT: This paper focuses on the development of swellable thermoplastic elastomer alloys based on elastomeric powder, polypropylene, and superabsorbent polymer. The mechanical and swelling properties of the resulting materials were investigated at varying concentrations of the components and by compatibilization between the rubber particles of the elastomeric powder and the polypropylene phase using the peroxide 2,5-dimethyl-2,5-di(*t*-buthylperoxy)hexane as compatibilizer. The materials obtained could be processed by injection molding in the same way as thermoplastics. The mechanical and swelling properties of the materials could be controlled by shifting the concentrations of the components. The swelling properties in different swelling media were investigated. A maximum of 120% of the relative increase of mass was obtained

using KOH solution. The positions of the SAP particles within the material were detected by a combined method of SEM and EDX scan. Elastomeric powder and thermoplastic build the matrix material, in which the SAP particles are embedded mechanically. A schematic illustration of the material structure was developed, and the liquid was suspected to be transported by diffusion into the material matrix as well as along the interface between SAP and the matrix material. The results obtained can be used for the design of improved sealing concepts, as they evidence a good method of using recycled elastomers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1290–1296, 2011

Key words: blends; compounding; elastomers; hydrogels; swelling

INTRODUCTION

Recycled waste elastomers in the form of elastomeric powders have major potential for technical applications. Used in the past at best as cost-effective materials for secondary products, they are increasingly recognized as high-quality raw materials. Such elastomeric powders can be used as functional additives serving for the modification of duromers, thermoplastics, lacquers, paints, and powder coatings.

At the end of the 1980s, extensive studies on the manufacturing of elastomeric alloys and blends with the use of elastomeric powders as dispersed elastomer phase were taken up.^{1,2} According to research on compounds, preference was given to natural rub-

ber (NR) and/or styrol-butadien rubber (SBR) with polyethylene (PE) or polypropylene (PP).

Comprehensive knowledge is available on the influence of process parameters in melt-mixing on the properties of these compounds. The melt-mixing process was investigated on discontinuous laboratory kneaders and continuous twin-screw extruders.^{3,4} Compounds with elastomeric powders based on ethylene-dien-polypropylene rubber (EPDM) and NR/SBR in the concentration range from 15 to 80 wt % for PP homo and PP random copolymers were investigated.

Studies regarding the coupling of the thermoplastic phase and the disperse elastomeric powder phase were carried out. One possibility is the modification of the elastomeric powder surface by physical, biological, or chemical methods.^{5–7} Otherwise it is possible to modify the thermoplastic.⁸ Using these methods, an improvement of the properties of the compounds was realized.

An improvement of interactions between the disperse elastomeric phase and the thermoplastic phase can also be achieved by *in situ* compatibilization (droplet copolymerization at the phase interfaces) in reactive melt-mixing of elastomeric powders and

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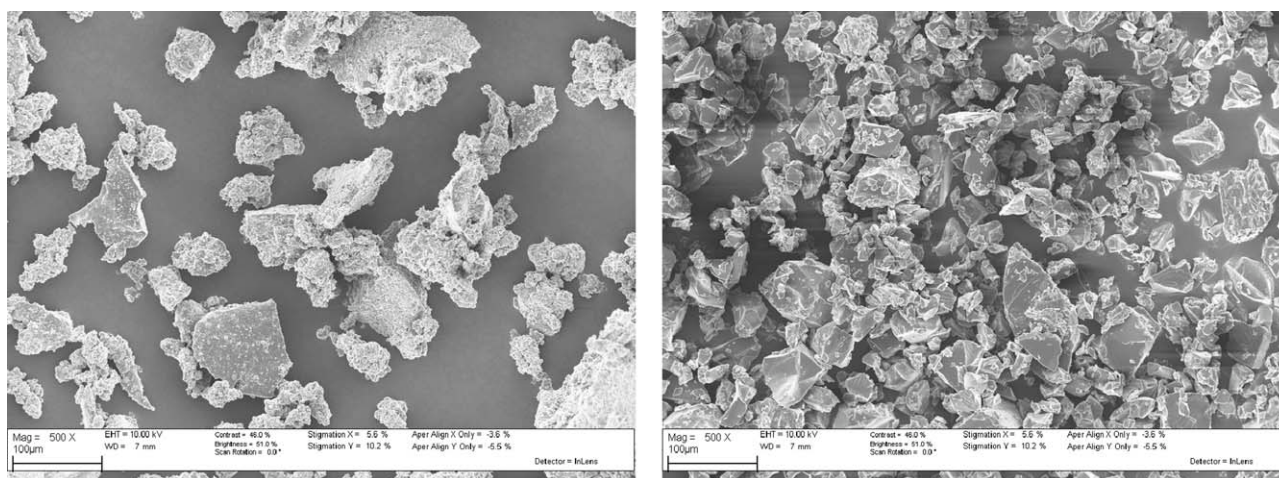


Figure 1 Left: NR/SBR elastomeric powder, truck tyre treads, ambient grinding, hardness 75 Shore A, particle size $<350\ \mu\text{m}$; right: polyacrylate, particle size $<100\ \mu\text{m}$.

thermoplastics. In compounds based on NR/SBR, elastomeric powders, and polyolefines, organic peroxides cause a reduction of the interfacial surface tension. Because of their chemical structure and low molecular weight, they have a compatibilizing effect between the more polar NR/SBR elastomeric powder and the non-polar polyolefine matrix.^{9,10} For EPDM elastomeric powders in compounds based on polypropylene reactive compounding was performed in a laboratory kneader and a twin-screw extruder (throughput $10\ \text{kg h}^{-1}$). Using an organic peroxide, the mechanical properties of the reactive-mixed alloy could be improved compared to physical blending.¹¹ For NR/SBR elastomeric powders in combination with polypropylene, a discontinuous method has been described that results in the formulation of elastomeric alloys (EA) by using a radical donator–radical acceptor system.¹² Based on the discontinuous method, recently completed research work exhibits the development at a continuous method and examined it on a precommercial scale.¹³

In this work, we will focus on the development of water swellable materials that can be used as self-repairing systems in the field of sealing technology by combining the properties of elastomeric powders (EP), thermoplastics (TP), and superabsorbent polymers (SAP). With the materials obtained, new self-repairing sealing systems can be developed, as already established for polymeric hydrogels.¹⁴ The products that can be realized from the material obtained are applicable particularly in the field of civil engineering and pipe technology,¹⁵ e.g., in the form of a sealing ring for sealing sewer pipes or sealing gas/water house service lines as well as cable wall ducts. In case of a leakage and contact with the spilling water, the swellable sealing ring increases its volume and seals the leakage without accompanying measures. The material can be processed in the same way

as thermoplastics, and thus cost-effective products can be realized, e.g., by injection molding. The results show that elastomeric powders can be used in innovative materials that are suitable for new, high-quality applications and thus offer a good option for the use of recycled waste elastomers in the form of elastomeric powders.

EXPERIMENTAL

Materials

As main recipe components (matrix material) and elastomeric powder (EP) based on NR/SBR rubber (Rubber Resources B.V., Maastricht, The Netherlands) with particle sizes of $<350\ \mu\text{m}$ (see Fig. 1) and a thermoplastic PP-copolymer (TP) of the type random polypropylene (Moplen RP 220M, Basell, Germany) were used. The weight ratio between elastomeric powder and thermoplastic was investigated at two levels (EP : TP = 50 : 50 and EP : TP = 60 : 40).

The dynamic stabilization of the matrix was investigated by adding a compatibilizer (C) of the Type 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane (Akzo Nobel Polymer Chemicals B.V., Amersfoort, The Netherlands). The compatibilizer was added in a concentration of 0 and 2% relative to the total quantity of EP and TP. A superabsorbent polymer (SAP) was used as swellable component. This involved a 75% part-neutralized sodium polyacrylate (BASF, Ludwigshafen, Germany), using a grain size $<100\ \mu\text{m}$ (see Fig. 1). The concentration of the SAP varied between 0 and 30 wt %. This leads to the compound formulations shown in Table I.

Preparation

The method of melt-mixing proved to be unproblematic and was carried out based upon established

TABLE I
Formulation of the Compounds (for all Components Calculated in wt %)

| Compound No. | SAP (wt %) | EP : TP = 50 : 50 | | EP : TP = 60 : 40 | | C (wt %) |
|--------------|------------|-------------------|-----------|-------------------|-----------|----------|
| | | EP (wt %) | TP (wt %) | EP (wt %) | TP (wt %) | |
| 1 | – | 50.00 | 50.00 | 60.00 | 40.00 | – |
| 2 | 10.00 | 45.00 | 45.00 | 54.00 | 36.00 | – |
| 3 | 15.00 | 42.50 | 42.50 | 51.00 | 34.00 | – |
| 4 | 20.00 | 40.00 | 40.00 | 48.00 | 32.00 | – |
| 5 | 25.00 | 37.50 | 37.50 | 45.00 | 30.00 | – |
| 6 | 30.00 | 35.00 | 35.00 | 42.00 | 28.00 | – |
| 7 | – | 49.02 | 49.02 | 58.82 | 39.22 | 1.96 |
| 8 | 9.82 | 44.20 | 44.20 | 53.05 | 35.36 | 1.77 |
| 9 | 14.75 | 41.79 | 41.79 | 50.15 | 33.43 | 1.67 |
| 10 | 19.69 | 39.37 | 39.37 | 47.24 | 31.50 | 1.57 |
| 11 | 24.63 | 36.95 | 36.95 | 44.33 | 29.56 | 1.48 |
| 12 | 27.11 | 35.70 | 35.70 | 42.90 | 28.60 | 1.43 |
| 13 | 29.59 | 34.52 | 34.52 | 41.42 | 27.61 | 1.38 |

values with a laboratory kneader (Brabender Plastograph, Brabender GmbH & Co. KG, Germany).^{16,17}

The mixture was produced first by melting the thermoplastic. After reaching a constant torque, the elastomeric powder and the peroxide were added and mixing was resumed until a constant torque was reached again. A significant increase of torque became apparent when adding the elastomeric powder. Finally, the SAP was added, which went hand-in-hand with a further increase of torque. After 10 min of mixing time the polymer blend was removed from the kneader, cooled down to room temperature, and afterwards granulation was carried out. During each trial, the mixing temperature was 180°C, which was lower than the degradation temperatures of the elastomeric powder and the SAP used.

Standard DIN EN ISO 527-2 Type 1A tensile test specimens and cylinder specimens (10 mm height, 10 mm diameter) were prepared through injection molding (Battenfeld BA 600-125 CDC, Germany), exhibiting the following parameters: 160°C (zone 3), 190°C (zone 2), 220°C (zone 1), 210°C (nozzle), 30°C (mold temperature), 40 cm³ (shot volume), 0.5 MPa (spec. back pressure), 80 MPa (max. injection pressure), 3 mm (nozzle diameter). Prior to being used for the further investigations, the specimens were stored at 25°C and 50% relative air humidity for 48 h.

Characterization

The mechanical properties of the materials were determined by a tensile test. Testing was performed using the standard DIN EN ISO 527-2 specimens at a temperature of 20°C. Five samples were tested for each compound. Tensile tests were carried out using a Zwick 1474 apparatus (Zwick GmbH & Co. KG, Ulm, Germany). Test speed was 100 mm min⁻¹ at a temperature of 23°C for the determination of tensile strength and elongation at break.

For the investigation of the swelling properties, the free swelling capacity (FSC value) was measured. For that purpose cylindrical samples (10 mm high, 10 mm diameter) were used. To determine the FSC value, the samples were placed in the swelling medium and free swelling was allowed. The mass of the samples was determined gravimetrically at specific times of swelling. For analysis, the relative increase of mass was calculated as defined by eq. (1). Additionally, the diameter and height of the test samples were measured.

$$\begin{aligned} \text{rel. increase of mass} &= \frac{m_{\text{swollen}} - m_{\text{dry}}}{m_{\text{dry}}} \\ &= \frac{m_{\text{liquid}}}{m_{\text{dry}}} [\%] \end{aligned} \quad (1)$$

with m_{swollen} : swollen mass of sample, m_{dry} : dry mass of sample, m_{liquid} : mass of liquid that was absorbed by the sample.

Thus a relative increase of mass of 100% equates to a doubling of the sample mass. For each compound three samples were measured. The accuracy of measurements was $\pm 5\%$ relative to the measured value.

The surface structure was examined using scanning-electron microscopy (SEM). Prior to analysis, all samples were sputtered with a gold-palladium coating. The investigations were carried out with a Leo 1530 device (Carl Zeiss NTS GmbH, Oberkochen, Germany).

RESULTS AND DISCUSSION

Mechanical properties of the materials

The material represents a polymer compound of nonpolar (elastomeric powder and thermoplastic) and polar (superabsorbent polymer) components.

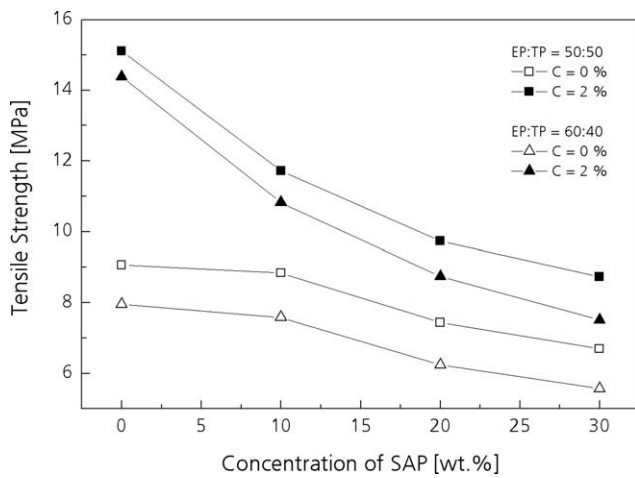


Figure 2 Tensile strength versus SAP concentration by variation of the EP : TP ratio and use of compatibilizer (C).

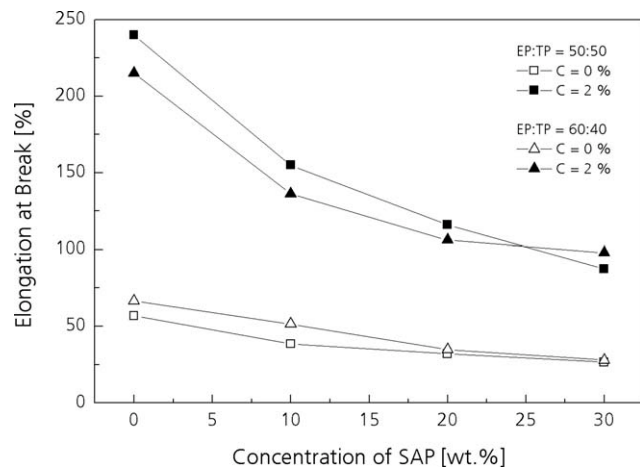


Figure 3 Elongation at break versus SAP concentration by variation of the EP : TP ratio and use of compatibilizer (C).

Figures 2 and 3 show the tensile strength and the elongation at break of the material as function of the SAP by variation of the EP : TP ratio and use of the compatibilizer.

The compatibilizer significantly improves the mechanical properties of the material. In compounds based on elastomeric powder of NR/SBR and polyolefines, organic peroxides are known as compatibilizers between the elastomeric powder and the polyolefines.^{18,19} As described by Sonnier et al. and Wießner et al. the thermally induced decomposition of the peroxide produces radicals that can initiate the building of macroradicals at the surface of the elastomeric powder and the polyolefine and therefore a copolymerization between the elastomeric powder and the polyolefine. This leads to a co-cross-linking at the rubber-polypropylene interface by grafting of polypropylene macromolecular chains onto the particle surface and thus to the improvement of the mechanical properties. The mechanical properties of the material were also influenced by the amount of the thermoplastic in the matrix. By increasing the amount of thermoplastic from a ratio of EP : TP = 60 : 40 to a ratio of EP : TP = 50 : 50 and parameters otherwise kept constant higher tensile strengths and elongations at break were measured.

The addition of SAP reduces the mechanical properties of the material. On one hand, this can be explained by the hydrophilic nature of the SAP. Therefore it cannot be embedded optimally into the matrix (EP and TP) which is hydrophobic. On the other hand, the SAP (polyacrylate) is very hard and brittle, and thus does not contribute to elastify the matrix. For concentrations of SAP from 20 to 30 wt % the elongations at break were nearly the same for the samples with a ratio of EP : TP = 60 : 40 and a ratio of EP : TP = 50 : 50 on the different levels of compatibilizer. It is to assume that in this region the

SAP increases the affinity for crack extension due to its mechanical embedding into the matrix and therefore leads to comparable values of elongation at break.

Swelling properties

Depending on the compound parameters of EP : TP ratio and the concentration of SAP, the swelling properties (relative increase of mass) of the materials can be controlled. Figure 4 shows the relative increase of mass as function of the swelling time by variation of the EP : TP ratio (by use of compatibilizer) and the concentration of SAP by swelling in deionized water.

The SAP leads to a significant influence on the swelling properties of the material. Overall, SAP concentrations in the range from 20 to 30 wt % produced a significant swelling effect. The SAP concentration of 30 wt % produced the largest relative

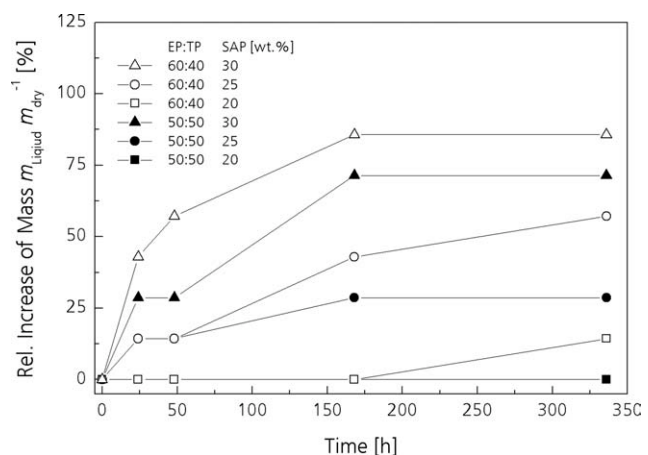


Figure 4 Relative increase of mass versus time by variation of the EP : TP ratio (by use of compatibilizer) and the concentration of SAP.

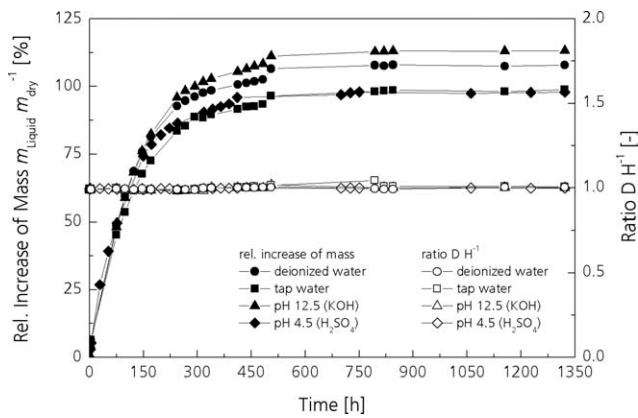


Figure 5 Relative increase of mass and $D H^{-1}$ ratio versus swelling time with different swelling media, ratio of EP : TP = 60 : 40 (by use of compatibilizer), concentration of SAP = 27.5 wt %.

increases of mass and quickly reached constant values at the same time. For the SAP concentrations of 20 wt % and 25 wt %, there was a delay in the swelling that took place. To achieve a swelling, the swelling strength induced by the swelling pressure has to compensate the elastic restoring force of the material. Thus with low SAP concentrations, the time to build up a sufficiently high swelling strength is longer than with high SAP concentrations.

For the samples with a low amount of thermoplastic (ratio of EP : TP = 60 : 40), the highest values of the relative increase of mass were yielded. Because

of a low amount of thermoplastic, the samples with the ratio of EP : TP = 60 : 40 display lower mechanical strength and can thus be stretched more easily and can be swollen to higher values. For the SAP concentrations of 20 wt % and 25 wt %, there was no difference in the relative increase of mass by varying the EP : TP ratio for swelling times up to 168 h and 48 h, respectively. Up to these times, the swelling strength is not high enough to result in different values for the relative increase of mass. After that swelling times, the samples with a low amount of thermoplastic (ratio of EP : TP = 60 : 40) showed a better swelling behavior as described above.

To investigate the suitability of the material for use in the field of sealing technology, swelling studies were carried out in different swelling media such as the following:

- Deionized water.
- Tap water.
- An alkaline solution that correspond to the liquid in the pores of concrete (KOH with pH of 12.5).
- A sulphuric acid solution that correspond to a solution strongly corrosive to concrete (H_2SO_4 with pH of 4.5).

These swelling media have established themselves within the context of testing sealings for use in the field of civil engineering.²⁰

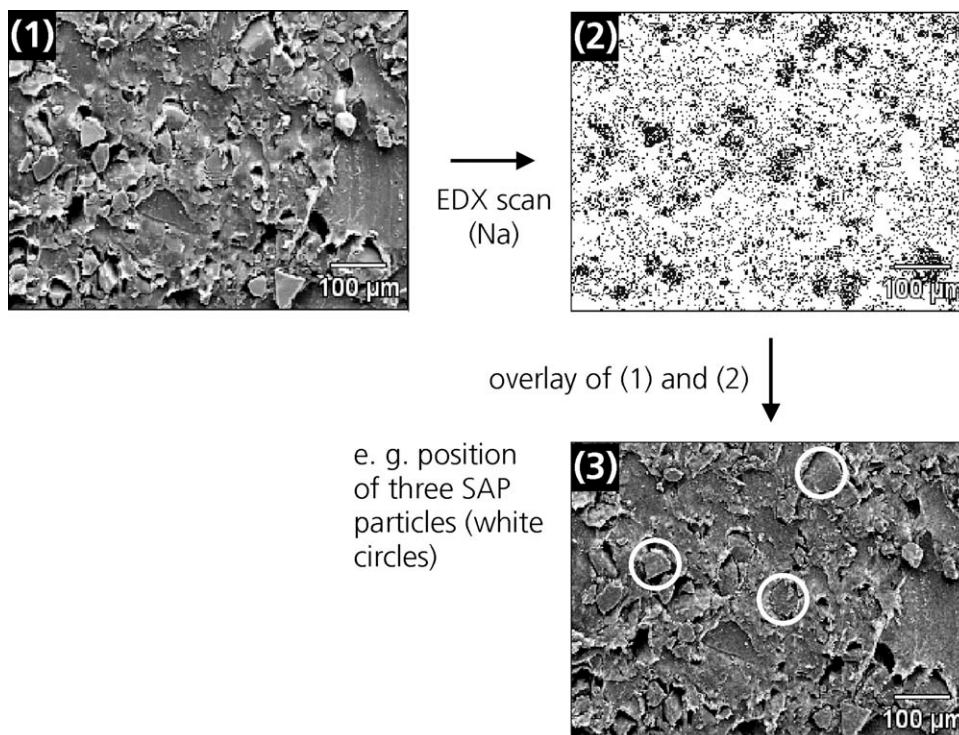


Figure 6 SEM picture of the dry sample surface (1); EDX X-ray spectrum scan (2); overlay of both analyses and exemplarily marked positions of SAP particles (3).

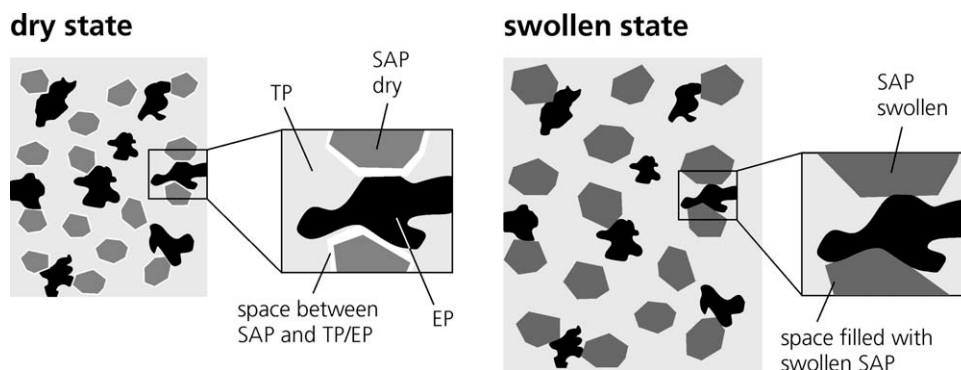


Figure 7 Material structure in principle.

Figure 5 shows values of the relative increase of mass and the ratio height-to-diameter ($D H^{-1}$) of cylindrical material samples as function of time by variation of the swelling media.

The swelling investigations on the cylinder samples confirmed an isotropic swelling behavior. For all swelling times and different swelling media diameter-to-height ratios of 1.0 were obtained for all samples. Asymptotically, the samples reached the maximum values of the relative increase of mass, which at the same time also represents the equilibrium value. Relative increases of mass of up to 120% were yielded. The material samples reached the swelling equilibrium after approximately 450 h.

Because of the ions contained in the solution and the resulting osmotic effects, lower values for the relative increase of mass were reached in the sulphuric acid solution and the tap water than in the deionized water and the KOH solution.^{21,22} For swelling in the KOH solution, the values of the relative increase of mass nearly reached the values of the deionized water and/or partly exceeded them (see Fig. 5). This effect can be explained by neutralization of the SAP by the KOH. The SAP still has free acid groups that are neutralized by contact with the KOH and contribute to an increasing swelling performance of the SAP and thus of the material as a whole.

Morphological study

The distribution and the positions of the individual components in the compound are of high significance explaining the material transport processes that take place within the material.

Scanning-electron microscope images were made to analyze and visualize the component distribution, and in parallel, an EDX X-ray spectrum scan of the corresponding sample surface was recorded. As the SAP is present in the form of sodium acrylate and the remaining material components do not contain sodium, the positions of the sodium-containing par-

ticles were marked in the EDX scan, thus visualizing the position of the SAP. Figure 6 shows the result of the analysis that was obtained at nitrogen cooled sheared edge of a shouldered test bar in dry state.

Based on the SEM analyses, a proposal for the structure of the material was developed. This proposal is shown in Figure 7. Nearly all particles exiting the material at the sample surface are SAP particles. Channels and holes are present between the SAP particles and the surrounding matrix (EP and TP). Therefore, it is assumed that the liquid transport into the sample takes place mainly along interface of the SAP particles and the matrix. Inside the material, the liquid might be transported by diffusion through the material matrix as well as along the interfaces between SAP and the matrix. In interaction with already existing swelling models²³ these qualitative results can contribute to clarify the material transport processes taking place. This is the subject of current studies.

CONCLUSIONS

Swellable materials were successfully developed on the basis of an elastomeric powder (EP), a thermoplastic (TP), and a superabsorbent polymer (SAP). The use of a compatibilizer was investigated. The mechanical and swelling properties of the materials were examined as function of the concentrations of the components. Maximum values for the relative increase of mass of 120% were obtained. The materials displayed the best swelling properties at high concentrations of SAP and high concentrations of EP. The best mechanical parameters were achieved with low SAP concentrations and low EP concentrations. The materials displayed isotropic swelling when placed in water (deionized water and tap water) as well as in acid and alkaline liquids.

The positions of the SAP particles within the material were determined. The thermoplastic and the elastomeric powder form a material matrix, in which SAP particles are embedded mechanically. The

liquid transport is assumed to take place through diffusion in the material matrix and along the SAP/material matrix interfaces.

The materials obtained can be used for the development of new, high quality self-repairing sealing systems, and thus a good way for the use of recycled elastomers in the form of elastomeric powders can be offered.

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