

Processing of polyurethane rubbers made from polyether polyester carbonate polyol with bound CO₂

Abstract

Polymers that use fewer resources can make an effective contribution to more sustainable rubber products. Polyether ester carbonate urethane rubbers (PECU) are such polymers. The comprised polyol consists of approx. 20% CO₂, which is copolymerised as carbonate and thus reduces both the carbon footprint and the use of fossil resources. However, as the resulting rubbers have unique properties (e.g. viscosity), mixing and further processing are subject of current investigations. The processability of rubber mixtures and further processing into foams, extrudates or into injection moulded parts has been successfully demonstrated.

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Introduction

Sustainability is one of the greatest challenges the rubber industry is currently facing. The fact that there are no broad recycling methods for rubbers make sustainable polymers and an efficient use of resources even more vital. The Institute for Plastics Processing (IKV) is currently working on a project on Resource efficient lightweight design in elastomer applications tackling these challenges. One of the main approaches are sustainable polymers. One project partner has developed a polyurethane rubber that incorporates carbon dioxide bound in the polymer backbone which results in a lower carbon footprint [1,2].

Polyether ester carbonate polyol-based urethane rubbers (PECU)

Using carbon dioxide as a raw material can lead to a lower use of fossil resources while also decreasing the production-related emissions of carbon dioxide into the atmosphere (lower product carbon footprint, PCF) [2]. This approach is used in a new kind of rubber wherein the polyol is a polyether ester carbonate polyol (PEC) with a carbon dioxide weight content of approx. 20 % [3]. Two types of rubber have been produced at technical scale. One is polymerised with hexamethylene diisocyanate (HDI, marked as PECU-H) and the second is made from methylene diphenyl diisocyanate (MDI, marked as PECU-M). Figure 1 reveals some structural context.

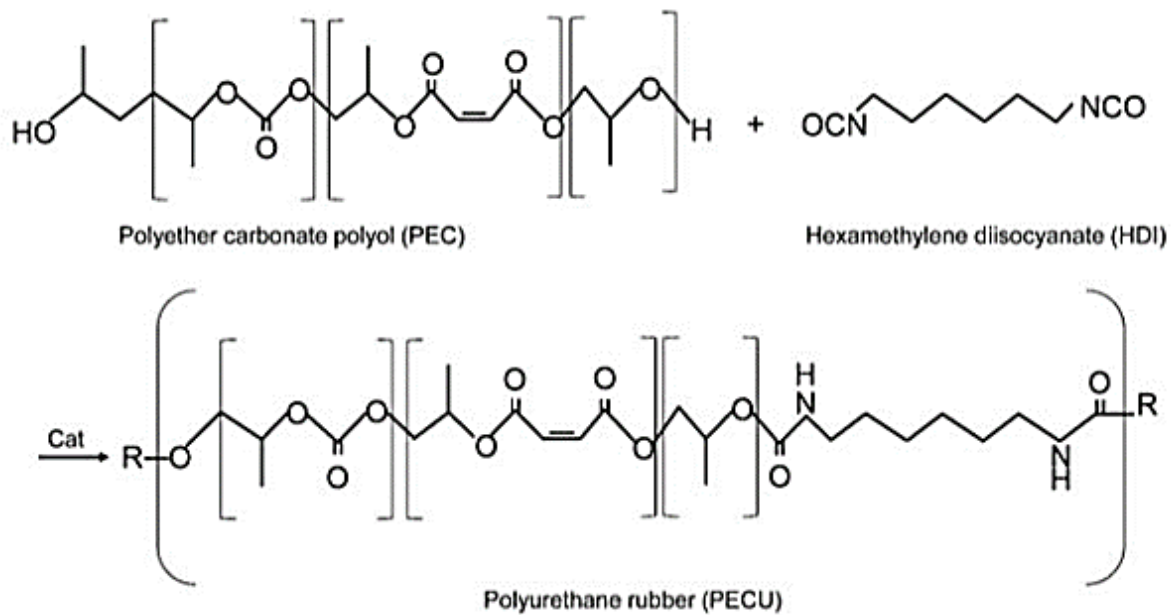


Figure 1: Reaction of PEC and HDI [6]

Since the stoichiometric ratio of diisocyanate to polyol, regarding their molar content of isocyanate and OH-groups, affects the properties of the resulting rubber, the *iso/ol*-ratio was varied in earlier studies [4,5,6]. A lower surplus of diisocyanate leads to sticky and viscous polymers, while a higher surplus results in less ductile polymers with a high tendency of crosslinking. The PECUs used for this study have an *iso/ol*-ratio of 1.06 (or a 6 % surplus of isocyanate). By current observations, these PECUs are stable and have a shelf life of several months that theoretically enable an industrial use. However, suitable formulations, mixing conditions and processing parameters still need to be investigated for the production of elastomers.

Therefore, the compounding of the rubber as well as its processing via extrusion, injection moulding and foaming were investigated by IKV and W. Köpp GmbH & Co. KG.

Mixing of PECU compounds

One of the main challenges of current PECU-rubbers is finding suitable recipes and mixing strategies. Whereas earlier polymers with lower *iso/ol*-ratio tended to liquify over time, current PECUs and especially HDI-types show signs of pre-curing in the raw polymer core [4]. Cutting bales of PECU-H in half, the different states of the inner core and the surfaces become apparent in Figure 2. PECU-M does not show any significant layers. All layers were investigated towards their physical properties to investigate the creation of different layers and the differences between both rubbers.



Outer layer

Inner layer

Outer layer

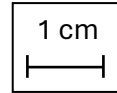


Figure 2: Cross section of a bale of PECU-M (top) and PECU-H (bottom) [Image: IKV]

In order to determine further curing or melting of already present crystalline phases, they were characterised by means of Differential Scanning Calorimetry (DSC). However, these measurements did not reveal significant differences between the two layers in a range from 25 °C to 200 °C. Moreover, no phenomena were identified indicating a relevant degree of crystallinity in PECUs. Low-temperature DSC measurements were carried out to determine changes in glass transition temperature due to potential crosslinking, branching, different molecular weight or near-order phenomena (see Figure 3).

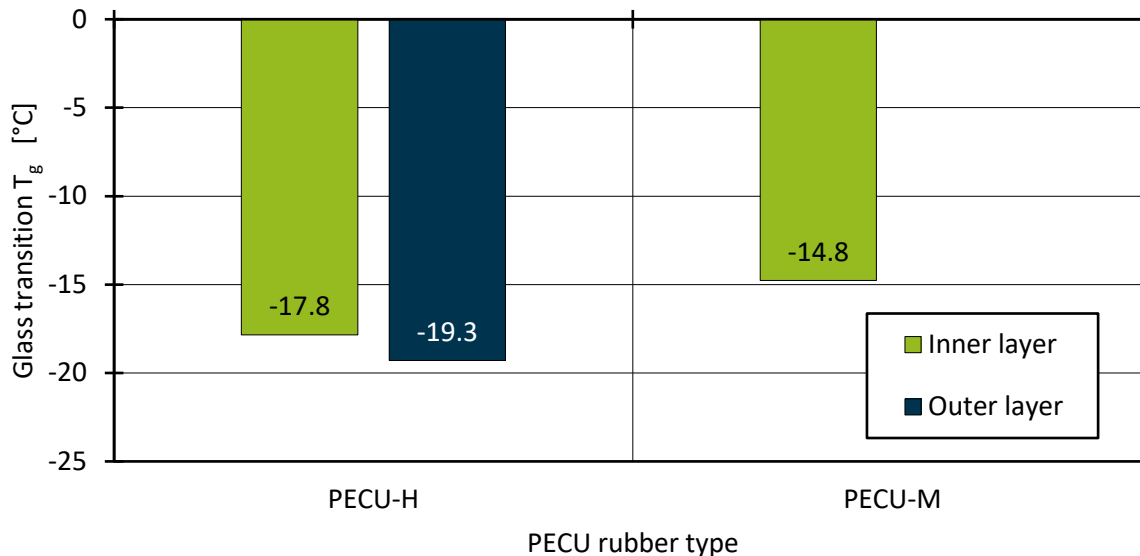


Figure 3: Glass transition temperatures (T_g) of PECU rubbers

The lower T_g of the outer layer of a PECU-H bale reflects its higher ductility and lower brittleness compared to the inner layer. The effect can be due to a higher crosslink density or higher degree of pre-curing in the inner layer caused by a different temperature-time-history. Despite its higher glass transition temperature, PECU-M with its different chemical composition is ductile.

Even though there is no detectable caloric effect in DSC curves for temperatures above 150 °C, a temperature sweep with the rubber process analyser reveals a significant decline of complex viscosity above 150 °C as seen in Figure 4. The measurement was carried out using an RPA 2000 by Montech Werkstoffprüfmaschinen GmbH, Buchen, at 1.667 Hz and an angle of 7 %.

The nondetectable thermodynamic, yet substantial rheologic effect may indicate a significant decrease of crosslink density. This effect has yet to be further characterised. In particular, the most effective reversibly crosslinking moieties have not been identified yet. Some considerations on underlying chemistry and mechanisms have been summarised in [7].

The observed temperature-dependent change in viscosity also influences the mixing process. Mixing studies show, that a first mixing step at high temperatures of 160 °C leads to a softening and plastification of the PECU-H polymer that allows incorporation of carbon black. In a secondary mixing step at a maximum of 120 °C the additional chemicals like silica and foaming agents are added. A suitable recipe for PECU-H is shown in Table 1 and 2. The mixing processing is done according to the mixing instruction in Table 3.

Component	p/hr
COPU11 – 111 (PECU-H)	100
Print Carbon Black	40
Polyglycol	2
Amid Wax	2
Chain Extender	0.5
Process Aid	0.5
Silica	2

Table 1: Recipe for PECU-H pre-batch [8]

Component	phr
PECU MB	147
ADCA	13
Silica	85
Silica Coated	15
Plasticizer Oil	45
Surfactant	2
Amid Wax	2
Silane Coupling Agent	1.5
Polyglycol	2
Hydrolysis Stabiliser	3
Urea	1.55
ZnO	1.04
Peroxide 1	0.35
Peroxide 2	1.20

Table 2: Recipe for PECU-H compound [8]

Step 1: Pre-Batch				
Phase:	Target temperature:	Speed:	Time:	Remarks:
	°C	U/min	min	
1	> 130 °C	65	5	Add all components except process aid
2	> 160 °C	65	6	Cleaning ram
3	< 100 °C	20	4	Add process aid
Step 2: Final Batch				
1	< 80 °C	65	1	Add all components except peroxides
2	100 °C	65	4	Cleaning ram
3	110 °C	65	5	Degassing
4	< 100 °C	65	2	Add peroxides

Table 3: Mixing instructions for PECU-H compound [8]

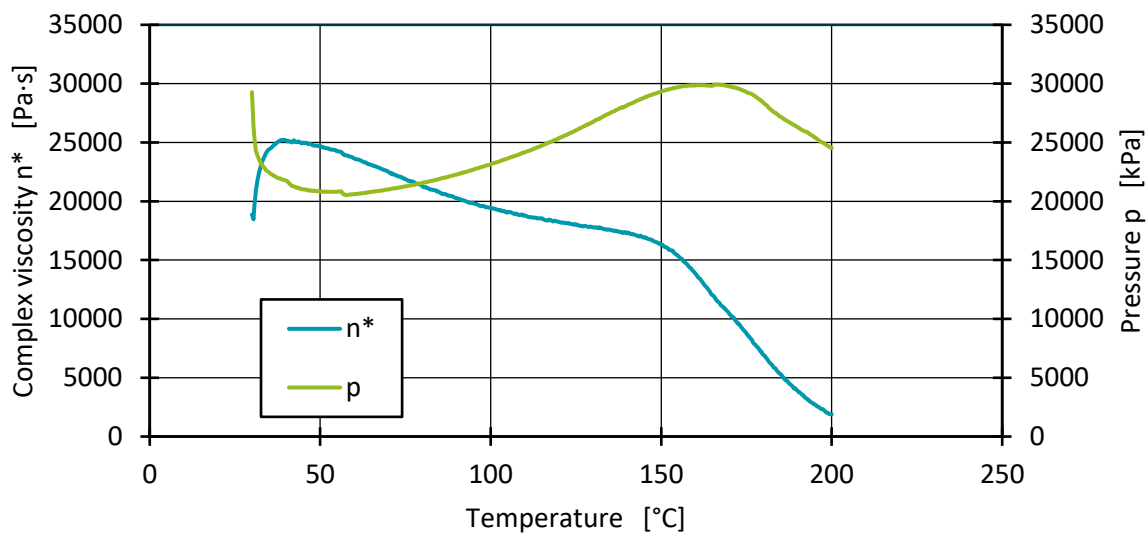


Figure 4: Complex viscosity and pressure of PECU-H as a function of temperature

Using the high-temperature mixing step along with the stated recipe allows to achieve a good dispersion of the fillers. The finished compound has a viscosity (ML(1+4)100°C) of approx. 30 MU for the PECU-H compound coming from a polymer viscosity of approx. 125 MU at 150 °C. Due to the steep decline of viscosity at 150 °C, a testing of the raw polymer at lower temperatures (e.g. ML(1+4)100°C) is not possible.

Extrusion

In the course of the development of recipe and mixing instructions, extrusion trials were carried out for selected PECU-H compounds, using a 40 mm rubber extruder with a length of 10 D. According to the suitable higher temperatures during mixing mentioned above, a barrel and screw temperature of 80 °C was chosen. For stable feeding, the feed roller temperature was set to 40 °C. A 6 mm round die was chosen as a first approach. Early batches made with non-fitting mixing conditions showed a low surface quality due to the weak dispersion and big polymer particles as seen in Figure 5.



Figure 5: Round extrudate from early batches showing insufficient mixing [Image: IKV]

Adjusting the recipe and compounding instructions to the conditions shown in Table 1 and 2 leads to a better dispersion and a smoother surface. All extrudates have an almost perfectly smooth surface. In conclusion, PECU compounds are very suitable for extrusion at the analysed process point as long as a good dispersion is assured in the mixing process. However, the used compound has a high tendency for die swell. For example, a round strip produced with a 6 mm die (11 mm in length) has a resulting diameter of 12 mm, resulting in a die swell of 100 % regarding the diameter. In order to investigate the surface quality and swelling for other extrudate geometries, two more complex profile geometries were extruded. Figure 6 shows a T-shaped profile and a sealing profile with smaller lips. When comparing the cross-section of the T-profile to the die in Figure 7, the swelling is clearly visible.

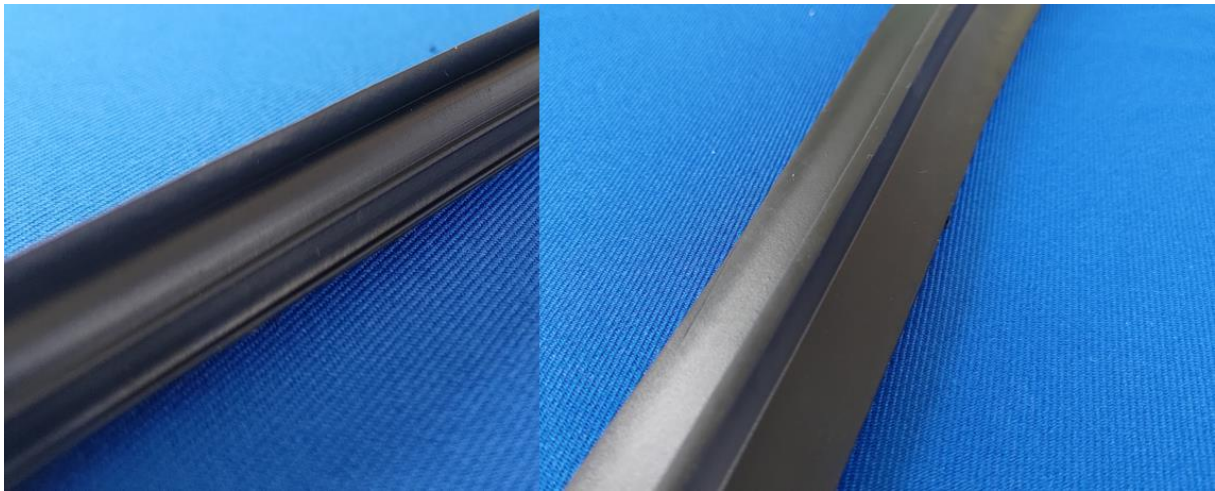


Figure 6: Various profiles made of PECU-H compound [Image: IKV]

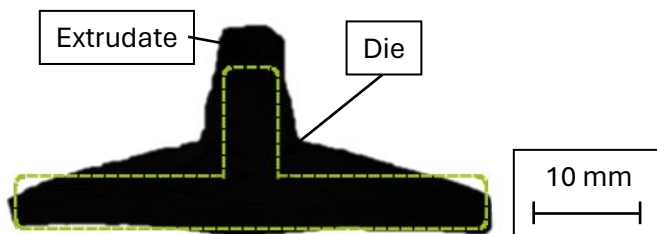


Figure 7: Cross section of a T-profile with visible die swell [Image: IKV]

Injection moulding

Due to the relatively low viscosity of the compound, it is potentially suitable for extrusion and foaming as well as injection moulding. For validation, injection moulding trials were carried out on an LWB Steidl injection moulding machine of the type VSEFE 3000/2000 s Performance. A two-cavity mould for plates of the dimension 80 x 80 x 2 mm³ was used to be able to prepare tensile rods from the parts (Figure 8). The specimens were then tested on a Zwick Roell Z100 machine for their tensile strength and elongation at break. Most parts have a visible impurity in the middle area just past the gate, which is subject to further investigation. However, as shown in Figure 9, this does not influence the tensile tests.



Figure 8: Injection moulded plate with visible impurities [Image: IKV]

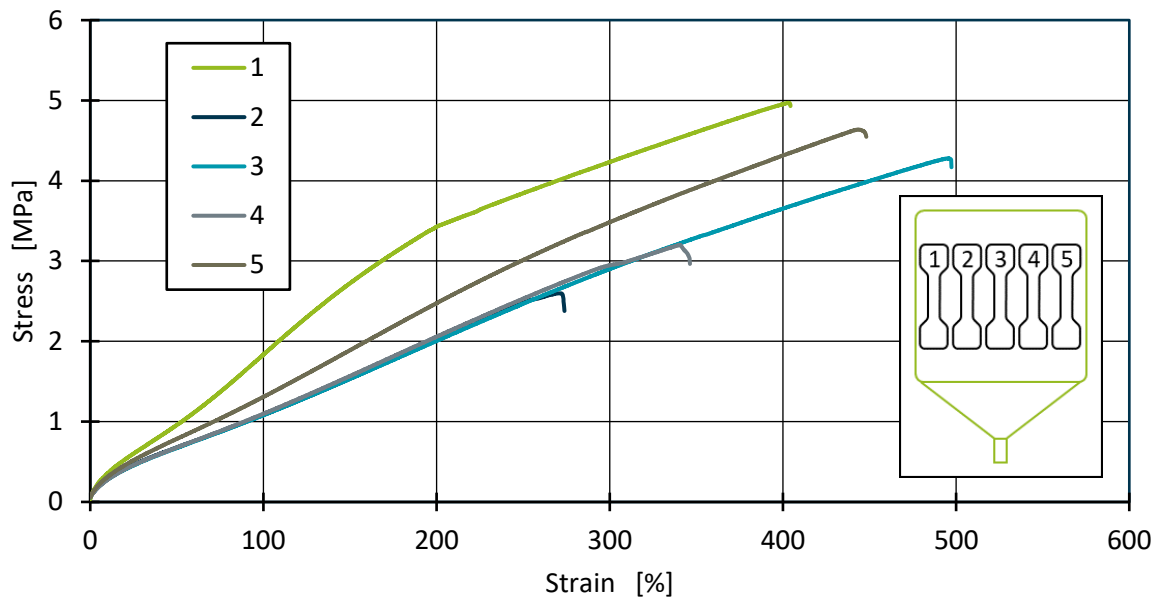


Figure 9: Tensile strength of PECU-H rubber. Tensile rods taken from left (1) to right (5)

The tensile rods taken from the middle of the plate have a very constant stiffness of 1 MPa although the elongation at break varies from 280 % to almost 500 %. It is noticeable that the tensile rods taken from the edge of the plates have higher tensile strength and stiffness due to their higher orientation caused by the higher shear rates.

PECU foams

As the foamability of rubbers is viscosity-dependent and viscosities in the range of 20-60 MU (ML(1+4)100 °C) are preferred, a comparison of the Mooney viscosities of PECU-M and PECU-H compounds is necessary in advance. Final Mooney viscosities of PECU-M would range between 10-15 MU compared to 25-30 MU achievable with PECU-H. Therefore, PECU-H is better suited for foaming and was used in the following trials.

Having established a successful mixing strategy, the resulting batches were foamed with two different blowing agents. The first was an azodicarbonamide (ADCA) with a particle size of 5-6 µm. As a second blowing agent a microsphere type was used. The starting temperature of expansion is between 120 °C and 140 °C with a particle size range of 26-36 µm.

The foaming trials were based on foaming elastomeric bun foam, achieved by a two-stage process with a pre-curing step and a main foaming step. The batches behave similar to standard (e.g. EPDM) bun foam recipes.

First, the trials with ADCA as blowing agent were carried out. After the first step, an adiabatic nucleation was achieved with a growth of approx. 20 % to 30 % in volume. In the first step, the compound block was kept in a closed mould under pressure in a hydraulic press for 35 min with heating platens keeping the temperature at 140 °C (Figure 10). The block was then placed in a hot air oven at 150 °C for 30 min to grow to the final size. The achieved density was approximately 140 kg/m³.



Figure 10: Final block of PECU-H foam [Image: Köpp]

Figure 11 shows the bun foam under the microscope. A unique cell structure was achieved in combination with a final density in the range of commercially viable products (100-175 kg/m³). A full-scale testing is currently done to prove the capabilities of the product.

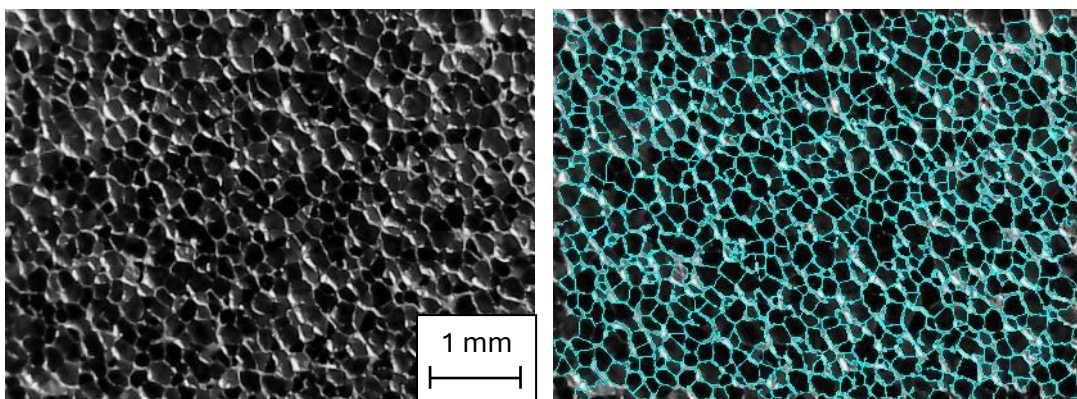


Figure 11: PECU-H bun foam with azodicarbonamide, average cell size: 0.207 (+/- 0.068) mm [Image: Köpp]

Corresponding trials with microspheres are part of future investigation. In this case, the foaming suitability of microspheres was investigated by foaming rubber sponge rings based on a one step pressureless foaming in a mould. The batch behaved similar to standard (e.g. EPDM) rubber sponge foaming recipes. Achieved density was approx. 500-600 kg/m³. The surface of the rings is already visually acceptable but shows that the flowing capabilities of the batch need further improvement. Rubber sponge parts foamed with microspheres show improved hardness compared to analogous recipes foamed with ADCA. As can be taken from the visual analysis in Figure 12, the picture is showing a bimodal cell size distribution.

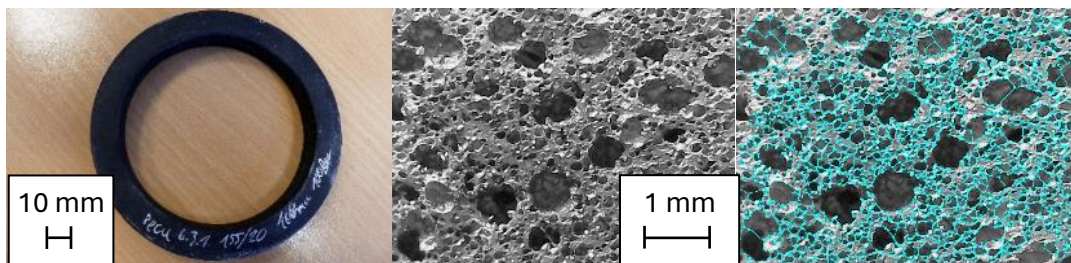


Figure 12: PECU-H foamed with microspheres, average cell size: 0.166 (+/- 0.097) mm [Image: Köpp]

This results in a rather large deviation on the cell size distribution although there are only a few cells showing the larger size. Different from Figure 10 showing the bun foam result foamed with ADCA, the foaming with microspheres does not lead to a mixing of foaming gas with the rubber matrix, as the spheres capsule their gas inside. Unless there is a mechanism such as a reaction with the shell material, that leads to a failure of some shells, it can be assumed that the large cells are created by a second foaming gas. As PECU comprises a set of different moieties prone to decomposition into *inter alia* carbon dioxide at elevated temperature, in particular via reactions triggered by water as a reaction partner, it is plausible to assume that some of these moieties could react with water carried by the fillers to create excess CO₂ gas leading to the larger cells. In the bun foam shown in Figure 11 the small quantity of CO₂ would mix with the N₂ created by the azodicarbonamide and not show up as a separate cell or different cell size.

The curve shown in Figure 4 is measured on the solitary rubber not containing any filler. An observation supporting a formation of excess gas in absence of excess water introduced (e.g. by insufficiently dried fillers) is that the change in

complex viscosity shown in Figure 4 is coherent with the commencing formation of gas bubbles (Figure 13). Further analysis may reveal a conclusive answer to this question.

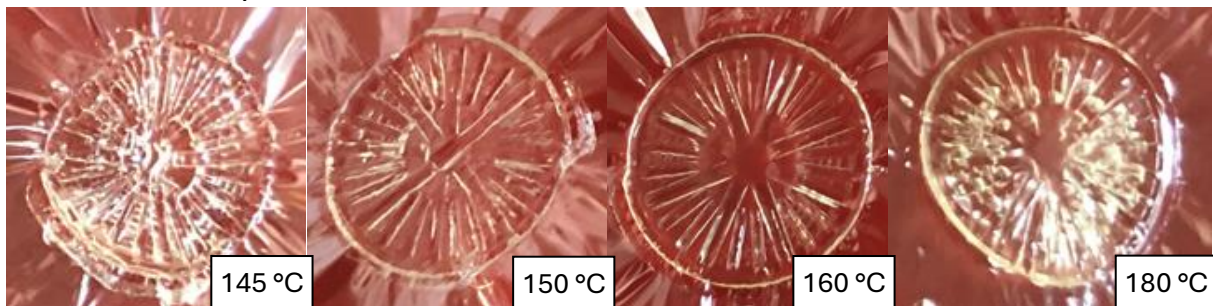


Figure 13: MDR specimens of PECU-H after testing at various temperatures [Image: Köpp]

Conclusion

Based on the two-step mixing with a first mixing step at high temperatures it is possible to mix PECU compounds that can be processed with commonly known technologies like extrusion, extrusion foaming, rubber sponge foaming, elastomeric bun foaming and injection moulding. Processing windows are similar to those known for other rubbers.

Foaming with ADCA results in a bun foam with unique cells structure, foaming with microspheres in rubber sponge products results in a bimodal cell size distribution. The source of the excess gas forming the larger cells is still unknown. Potential routes to these cells via a formation of CO₂ may *inter alia* be a reactive decomposition of intermediately (re)forming isocyanate groups or decarboxylation mechanisms of carbonate or ester functions of the polymer backbone. In addition, a two-stage foaming process with a pre-curing step and a main foaming step, as developed for foaming with ADCA, is to be tested for foaming with microspheres.

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