A new approach to the structure–properties relationship evaluation for porous polymer composites

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Abstract

In proposed study the effect of the composition and structure of polyurethane/ground rubber (PUR/GR) composites on the mechanical behavior was evaluated. The structure–properties relationship was studied for PUR matrices with different polarity, porosity and mechanical properties. The morphology of PUR/GR composites was expressed by two structural parameters—interspace filling and interspace volume. Experimental data of mechanical testing were fitted by power-law functions containing mentioned structural parameters whereas exponents of these parameters reflect differences in mechanical properties and chemical composition of PUR matrices. Obtained equations describe the mechanical behavior with respect to the structure and morphology of porous PUR/GR composites consisting of one filler and different PUR matrices. Proposed study suggests new approach to the description of the relationship between mechanical behavior and structure of porous composite materials.

Keywords Polymer composite · Reinforcement · Porosity · Mechanical properties

1 Introduction

In last few decades an effort of researchers is focused on the study of the structure–properties relationship for polymeric and composite materials. These activities are practiced for the prediction of material properties according to the material composition and for the preparation of tailor-made materials with predictable properties. As presented in our study, the porosity is one of the parameters affecting (positively or negatively) the properties of natural and synthetic materials such as deformation strain, degradation rate, density, heat conductivity, etc.

Generally, porosity may occur in both one-component (e.g. polyurethane foams, metals, ceramic) and multi-component materials (e.g. wood, concrete, mineral castings). Recently, many researchers have

attempted to examine the effect of porosity on material behavior, especially for one-component materials such as ceramics [1–11], natural materials [12], sintered metals [1, 9, 13–15] and polymers [1, 16]. The main effort has been developed in the field of mechanical properties mostly represented by elastic modulus and strength. A lot of published relationships between porosity and mechanical properties have been proposed for one-component materials in the form of linear [1–3, 6–8, 12, 15], exponential [1, 2, 7, 8, 10], power [1, 2, 5, 7–9, 11, 13, 14, 16–18] and logarithmic functions [15]. The effect of porosity in one-component polymeric materials is well examined issue. Drozdov and Christiansend reported the decrease of Young's modulus with the increasing extent of porosity for different thermoplastic foams [19]. The similar relation between

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porosity and hardness of thermoplastic polyurethanes was evidenced by Prasad et al. [20].

Except of one-component materials, multi-component materials (composites) have been also under interest of researcher's community. Hong-Liang et al. has developed the Halpin–Tsai model which is applicable for composites containing short fibers [21] while Griffith's model can be applied for the description of the fracture behavior of concrete representing multi-component porous material [15, 22]. The effect of the porosity on the mechanical behavior of polymer composites is under the interest of many researchers. For example, Hakim et al. [23] reported the influence of porosity on the interlaminar fracture behavior in carbon-fiber-reinforced polymer composites. Specifically, the increase of porosity led to the decrease in both interlaminar fracture toughness and thermal conductivity. In addition, the relationship between fracture mechanism and mechanical properties was described and affected by porosity. On the other hand, some properties can be improved by inducing porosity especially in the electronic [24, 25] or medical applications [26].

According to cited articles, the influence of structural parameters on mechanical properties is usually studied only for certain type of materials with similar chemical composition. For this reason, there are many individual expressions with an absence of universal solution for the determination of the relationship between structural parameters and mechanical properties of composite materials. In contrast, the objective of this work is to approach the experimentally obtained universal relationship between the structure and mechanical behavior of porous filled polymer composites. Proposed approaching is based on the structure–property relationship for one-component materials given by Eq. (1)

$$z = z_m \cdot (1 - n)^b \quad (1)$$

where z is mechanical property of porous material (e.g. elastic modulus E , strength σ , etc.), z_m is mechanical property of nonporous material, n is porosity and b is an empirical constant.

In accordance with our previously published work [27], interspace filling parameter (n_p) was included in our concept as a key parameter defining the amount of PUR matrix filling the volume between GR particles. n_p can be calculated according to Eq. (2)

$$n_p = \left(1 - \frac{n}{n + v_m} \right) = \left(1 - \frac{n}{n + \frac{v_{m(t)}}{1 + \frac{n}{1-n}}} \right) \quad (2)$$

where v_m is volume fraction of matrix and $v_{m(t)}$ is volume fraction of matrix in theoretical nonporous material with the same composition. This parameter can be expressed also for one-component material as $(1 - n)$.

Combination of Eqs. (1) and (2) results in the Eq. (3) calculating mechanical properties of porous composites:

$$z_c = z_m \cdot n_p^b \quad (3)$$

where z_c and z_m represent mechanical properties of porous composite and nonporous matrix, respectively. Exponent b can be derived by fitting of experimentally measured data. Since the relation between exponent b and mechanical properties of nonporous matrix was found to be more or less indicative, new structural parameter—interspace volume $(1 - v_f)$ —was included for more precise description of mechanical behavior of porous composites. $(1 - v_f)$ represents the volume of material filled by matrix and porosity and can be calculated according to Eq. (4)

$$1 - v_f = n + v_m = n + n \cdot \frac{n_p}{1 - n_p} = n \cdot \left(1 + \frac{n_p}{1 - n_p} \right) \quad (4)$$

where v_f is volume fraction of filler.

The structural parameters n_p and $(1 - v_f)$ seem to be key part in proposed research for better linkage between the structure and properties of composites. With using mentioned structural parameters and experimentally derived exponents, mechanical properties (i.e. tensile modulus, ultimate tensile strength, strain and energy need for ultimate strength achievement) can be predicted and linked to the structure and composition of multi-phase composites. Proposed model can be applied for the prediction of mechanical behavior of porous composite materials regarding the mechanical properties of individual components (matrix, fibers, filler, additives, etc.). Based on the obtained relationships, material properties could be tailored depending on the composition and material architecture. Moreover, porosity can be also induced at varied level as suggested by Bhat et al. [28] who induced different porosity level in carbon fiber reinforced epoxy resin resulting in different mechanical properties. Recently, this approaching is important for more extensive research on the light-weight materials with application in the space or automotive industry. Experimentally derived equations describe porous composite materials on the macroscopic level which make them independent on the pore size and nature.

2 Experimental

2.1 Materials

The isocyanate pre-polymer (Unixin PU4223CS, Lear, s.r.o., Czech Republic, methylene-di-phenyl di-isocyanate, 6.9 wt% of -NCO groups, $M_n = 690$ g/mol) was used for the preparation of PUR matrix via curing with (i) distilled water, (ii) glycerol (Penta Chemicals, Czech Republic) and (iii) castor oil (Fichema, Czech Republic). Linseed oil (Fichema, Czech Republic) was used for plasticization of selected PUR cured with castor oil. Di-butyltin di-laureate (Lear, Czech Republic, DBTL) was used as catalyst.

The ground rubber recycled from car tyres (RPG Recycling s.r.o., Uherský Brod, Czech Republic), limestone, iron (Pkchemie, Czech Republic) and quartz (Millisil W12, Provodínské písky a.s., Provodín, Czech Republic) were used as filler. Ground rubber was supplied in 3 fractions with different particles size distribution (R_2 —the greatest, R_1 —medium and R_0 —the lowest). All fillers were composed of randomly-shaped particles. The shape of inorganic filler was defined by scanning electron microscope Tescan MIRA3 (Fig. 1). Particles size distribution of different filler was determined by laser analyser HELOS (H2568) & RODOS and is depicted in Fig. 1. The particles size distribution of rubber fraction R_2 was determined by sieve analysis where the particles size > 800 μm was determined (the diameter of more than 50% of particles greater than 2.5 mm). Pycnometric density measurement was performed with following results: 1.18 g cm^{-3} (all

rubber fractions), 2.65 g cm^{-3} (quartz), 2.68 g cm^{-3} (limestone) and 7.03 g cm^{-3} (iron).

2.2 Preparation of samples

PUR matrices with different concentration of PU4223 CS pre-polymer (P) and curing agents were used for the preparation of PUR composites (Table 1). PUR pre-polymer was cured by water (W), glycerol (G), castor oil (CO) or by combination of G and CO. In the case of the PU4233 CS/CO combination, linseed oil (LO) was added as a plasticizer to prepare PUR matrix with different mechanical properties. Different inorganic fillers including SiO_2 (Si), CaCO_3 (Ca) and Fe (Fe) were particularly applied for the modification of mechanical properties and porosity of PUR matrices prepared with the same pre-polymer/curing agent ratio. Prepared matrices were filled with different volume fractions of ground rubber (R_0 , R_1 , R_2) according to Table 2. The porosity is neglected for all samples, e.g. with respect to the volume content of filler.

First, the pre-polymer, curing agent(s), catalyst and eventually plasticizer were intensively homogenized. Then the required mass of filler or fillers mixture (including inorganics and rubber) was added and carefully homogenized. Thus prepared mixture was loaded into molds (120 × 24 × 12 mm) covered with polyethylene foil for improved separation and the curing was performed under ambient conditions. Prepared specimens were weighted and their dimensions were measured.

Fig. 1 Particle size distributions and SEM images of filler particles

Table 1 Chemical composition of PUR matrices (P—PU4223 CS; curing agents: W—water, G—glycerol, CO—castor oil; plasticizer: LO—linseed oil; fillers included in matrices: Si—SiO₂, Ca—CaCO₃, Fe—Fe)

Designation	PU4223 CS (vol%)	Curing agent (vol%)	Others (vol%)	δ^a (—)	DBTL ^b (wt%)
P ₉₉ –W ₁	99	1 (W)	—	0.68 ^c	0.1
P ₉₅ –G ₅	95	5 (G)	—	1.22	0.03
P ₈₀ –G ₂₀	80	20 (G)	—	5.79	0.03
P ₈₅ –G ₅ –CO ₁₀	85	5 (G) + 10 (CO)	—	1.55	0.03
P ₆₅ –CO ₃₅	65	35 (CO)	—	0.87	0.1
P ₄₉ –CO ₂₆ –LO ₂₅	49	26 (CO)	25 (LO)	0.87	0.1
P ₃₃ –CO ₁₇ –Si ₅₀	33	17 (CO)	50 (Si)	0.87	0.1
P ₃₃ –CO ₁₇ –Ca ₅₀	33	17 (CO)	50 (Ca)	0.87	0.1
P ₃₃ –CO ₁₇ –Fe ₅₀	33	17 (CO)	50 (Fe)	0.87	0.1
P ₇₂ –G ₁₈ –Ca ₁₀	72	18 (G)	10 (Ca)	5.79	0.03

^aReflecting OH/NCO molar ratio^bBased on the weight of PU 4223 CS^cFor this purpose H₂O represents two OH groups**Table 2** Summary of prepared composites (differences in individual concentrations are 10 vol%)

Matrix	Filler (vol%)		
	R ₀	R ₁	R ₂
P ₉₉ –W ₁	20–90	20–90	20–90
P ₉₅ –G ₅	20–90	20–90	20–90
P ₈₀ –G ₂₀	20–80	20–90	20–90
P ₈₅ –G ₅ –CO ₁₀	20–90	20–90	20–90
P ₆₅ –C ₃₅	20–90	20–90	20–90
P ₄₉ –CO ₂₆ –LO ₂₅	20–90	20–90	20–90
P ₃₃ –CO ₁₇ –Si ₅₀	20–70	20–70	20–80
P ₃₃ –CO ₁₇ –Ca ₅₀	20–80	20–80	20–90
P ₃₃ –CO ₁₇ –Fe ₅₀	20–80	20–80	20–80
P ₇₂ –G ₁₈ –Ca ₁₀	20–80	20–90	20–90

2.3 Characterization methods

Pycnometer method was applied for the specification of the filler densities in acetone. This method was used also for P₉₉–W₁ matrix embodying high porosity. Different measurement procedure was used for the other non-filled PUR matrices having low value of closed porosity. Density of porous material was derived from weight (8–18 g) and volume of samples as a difference of ethanol amount added into a narrow-necked vessel in the presence/absence of the sample. Each measurement was carried out three times.

Porosity was determined by confocal laser scanning microscopy (CLSM, Lext OLS 3000, Olympus) from the analysis of fracture area in optical mode. The porosity was evaluated from 10 scans. Thus obtained porosity was used to calculate the density of theoretically nonporous matrix from the density of real porous matrix.

Tensile properties were evaluated by universal static materials testing machine (ZWICK Z10 ROELL) under the strain rate 30 mm min^{−1}. The main interest was focused on tensile modulus (E), ultimate strength (σ_{Fmax}), ultimate strain (ϵ_{Fmax}) and specific energy need for ultimate strength achievement (A_{Fmax}). Tensile modulus was determined from the linear part of tensile curve in the strain range 0.05–0.25% and A_{Fmax} was calculated as an integral area below the tensile curve according to Eq. (5):

$$A_{Fmax} = \sum (\epsilon_n - \epsilon_{n-1}) \cdot \frac{\sigma_n + \sigma_{n-1}}{2}; n \in \langle 1; n_{Fmax} \rangle \quad (5)$$

where σ_n , ϵ_n and σ_{n-1} , ϵ_{n-1} express the stress and strain in two neighboring points lying on stress–strain curve. Index n expresses the order of the point on the curve and n_{Fmax} is the highest point on tensile curve corresponding to σ_{Fmax} . A_{Fmax} unit is derived from the unit of σ_{Fmax} according to Eq. (6) because ϵ_{Fmax} is dimensionless:

$$\sigma_{Fmax} = \left[\frac{N}{m^2} \right]; N = \frac{J}{m} \rightarrow A_{Fmax} = \left[\frac{J}{m^3} \right] \quad (6)$$

3 Results and discussion

3.1 General relationship between structure parameters and mechanical properties of filled composites

The determination of mechanical properties of individual components of prepared composites is important for the evaluation of composites behaviour as well as structural parameters as mentioned above. Therefore the pure PUR matrices without GR were prepared in the

Table 3 Mechanical properties (Young modulus E , ultimate strength σ_{Fmax} , ultimate strain ϵ_{Fmax} and specific energy need corresponding to ultimate strength achievement A_{Fmax}), density of theoretical nonporous matrix ρ_t and whole porosity n_m of PUR matrices

Designation	E (MPa)	σ_{Fmax} (MPa)	ϵ_{Fmax} (%)	A_{Fmax} (kJ·m ⁻³)	ρ_t (g·cm ⁻³)	n_m (%)
P ₉₉ -W ₁ (more porous)	1.4 ± 0.3	0.56 ± 0.05	94 ± 9	321 ± 14	1.10 ^a	57 ± 7
P ₉₉ -W ₁ (less porous)	4.1 ± 0.1	2.7 ± 0.3	82 ± 12	1400 ± 400	1.10 ^a	16 ± 2
P ₉₅ -G ₅	13 ± 2	4.7 ± 0.1	140 ± 40	4100 ± 700	1.12 ^b	9.5 ± 0.7
P ₈₀ -G ₂₀	4.8 ± 0.3	1.75 ± 0.08	340 ± 20	3700 ± 300	1.15 ^b	10 ± 1
P ₈₅ -G ₅ -CO ₁₀	2.3 ± 0.3	1.24 ± 0.04	100 ± 4	700 ± 50	1.05 ^b	2 ± 2
P ₆₅ -CO ₃₅	1.6 ± 0.4	0.42 ± 0.03	39 ± 4	69 ± 6	1.04 ^b	4 ± 1
P ₄₉ -CO ₂₆ -LO ₂₅	1.1 ± 0.03	0.4 ± 0.03	68 ± 8	90 ± 8	1.03 ^b	1 ± 2
P ₃₃ -CO ₁₇ -Si ₅₀	9 ± 1	2.2 ± 0.3	22 ± 1	210 ± 40	1.85 ^c	16 ± 1
P ₃₃ -CO ₁₇ -Ca ₅₀	4.9 ± 0.5	0.7 ± 0.04	20 ± 1	69 ± 9	1.86 ^c	32 ± 2
P ₃₃ -CO ₁₇ -Fe ₅₀	9.1 ± 0.6	1.09 ± 0.09	13 ± 1	70 ± 10	4.04 ^c	22.6 ± 0.5
P ₇₂ -G ₁₈ -Ca ₁₀	7.4 ± 0.8	1.93 ± 0.06	260 ± 30	3700 ± 300	1.30 ^c	16.3 ± 0.6

^aMeasured by pycnometer method^bObtained from knowledge about volume, mass and porosity^cCalculated via simple mixing equation**Fig. 2** CLSM images of P₃₃-CO₁₇-Ca₅₀ composite filled with different fractions of rubber: **a** 20 vol% R₂; **b** 20 vol% of R₀; **c** 50 vol% of R₂ and **d** 50 vol% of R₀

first phase whereas their composition was designed in order to achieve different mechanical properties and different bulk porosity. Values of mechanical properties, porosity and density of PUR matrices are listed in Table 3. It is evident that the addition of filler into the PUR matrix raises elastic modulus E depending on the nature of filler and particles size distribution. Moreover, porosity increases due to poor interfacial adhesion between matrix and filler. Narrow particles size distribution of Fe (P₃₃-CO₁₇-Fe₅₀) results in the relatively high E

and low ϵ_{Fmax} due to poor assembling of Fe particles in the intermolecular space and limitation of chain mobility. As mentioned in the Introduction, the porosity affects mechanical properties as evident for P₉₉-W₁ samples with different porosity content (Table 1). The addition of castor oil (CO) as a curing agent results in more elastic matrix as reflected by the decrease of E due to greater free volume between PUR chains.

Since PUR matrix can be generally prepared in various form such as foam, porous or nonporous bulk material, the

structure of thus prepared porous composites corresponds with the shape of filler and matrix properties (e.g., elastic modulus E , strain ε , porosity, etc.) and strongly affects mechanical properties. As shown in Fig. 2, the filler affects the material porosity and can act as a barrier for degassing. Theoretically, if the concentration of filler particles is high enough, the porosity would decrease due to low content of vacancies and low content of matrix. Nevertheless, in this case the porosity usually increases due to inability of matrix to fill the space between filler particles. Proposed effect is demonstrated for $P_{33}\text{--CO}_{17}\text{--Ca}_{50}$ matrix filled with R_0 and R_2 rubber particles which are surrounded by vacancies (Fig. 2).

Selected mechanical properties in Table 3 were derived from tensile testing, specifically tensile modulus (E), ultimate strength (σ_{Fmax}), ultimate strain (ε_{Fmax}) and energy need corresponding to ultimate strength achievement (A_{Fmax}). Mechanical properties-PUR composition combination can be fitted by simple equation in the form of cubic power function:

$$z_c = z_m \cdot n_p^b \cdot (1 - v_f)^c \quad (7)$$

where z is the selected mechanical property, z_c and z_m represent the same property for composite and nonporous matrix, respectively. Coefficients b and c were derived from the fitting measured data according to Eq. (7) regarding

Table 4 Mechanical properties of theoretically nonporous matrices obtained by fitting of composites mechanical properties according to the Eq. (7)

Matrix	E (MPa)	σ_{Fmax} (MPa)	ε_{Fmax} (—)	A_{Fmax} (kJ m ⁻³)
$P_{99}\text{--}W_1$	5.30	3.38	1.25	2871
$P_{95}\text{--}G_5$	19.38	5.17	1.19	3377
$P_{80}\text{--}G_{20}$	5.17	1.49	5.72	6920
$P_{85}\text{--}G_5\text{--CO}_{10}$	1.98	1.02	1.62	1004
$P_{65}\text{--CO}_{35}$	2.02	0.42	0.38	111
$P_{49}\text{--CO}_{26}\text{--LO}_{25}$	1.19	0.29	0.50	83
$P_{33}\text{--CO}_{17}\text{--Si}_{50}$	14.09	4.50	0.22	435
$P_{33}\text{--CO}_{17}\text{--Ca}_{50}$	13.46	1.28	0.19	167
$P_{33}\text{--CO}_{17}\text{--Fe}_{50}$	18.53	1.70	0.14	153
$P_{72}\text{--G}_{18}\text{--Ca}_{10}$	6.48	1.62	3.41	5320

Fig. 3 Linear fitting of plot between properties of porous composites containing $P_{99}\text{--}W_1$ matrix filled by different fractions of rubber including E (a), σ_{Fmax} (b), ε_{Fmax} (c) and A_{Fmax} (d) and expression $(n_p^b \cdot (1 - v_f)^c)$ —data fitted according to power Eq. (7)

the highest coefficient R^2 for linear function derived from the plot between z_c and $n_p^b \cdot (1 - v_f)^c$ (Fig. 3). All slopes (z_m) obtained by Eq. (7) fitting are shown in Table 4.

Values of n_p and $(1 - v_f)$ of unfilled nonporous matrix equal to 1. Therefore, the axis x value for nonporous matrix equals to 1. Then the slope of linearized function should be equal to the value of selected property for pure nonporous matrix. However, the Eq. (7) can be modified also for porous matrix and nonporous composite as summarized in Table 5.

The Eq. (7) represents fitting of measured data but does not describe material behavior. Therefore, exponents b and c were substituted by functions derived from logarithmic fitting (Figs. 4 and 5) and included in Eqs. (17)–(18) and (20)–(21) providing connection with individual mechanical properties where subscripts m and c represent mechanical properties of nonporous matrix and composite, respectively. Exponents d , e and f , g were extracted from logarithmic fitting in Figs. 4 and 5, respectively. Equation (7) is then changed into several following relationships including (13)–(14) and (16)–(17):

Table 5 Modification of Eq. (7) for porous/nonporous matrix/composite

Material	Relationship	Value ranges of			Equations
		n_p	$1 - v_f$	$n_p^b \cdot (1 - v_f)^c$	
Porous composite	$z_c = z_m \cdot n_p^b \cdot (1 - v_f)^c$	$(0 ; 1)$	$(0 ; 1)$	$(0 ; \infty)$	(8)
Nonporous composite	$z_c = z_m \cdot (1 - v_f)^c$	$\langle 1 \rangle$	$(0 ; 1)$	$(0 ; \infty)$	(9)
Porous matrix	$z_c = z_m \cdot n_p^b$	$(0 ; 1)$	$\langle 1 \rangle$	$(0 ; \infty)$	(10)
Nonporous matrix	$z_c = z_m$	$\langle 1 \rangle$	$\langle 1 \rangle$	$\langle 1 \rangle$	(11)
Powder filler	$z_c = 0$	$\langle 0 \rangle$	$\langle 0 ; 1 \rangle$	$\langle 0 \rangle$	(12)

Fig. 4 Logarithmic fitting of plots between parameter b and E_m (a), $\sigma_{m,Fmax}/S_{m,rel}$ (b), $\epsilon_{m,Fmax}$ (c) and $\sigma_{m,Fmax}$ (d): $y = d + e \cdot \ln(x)$

Fig. 5 Logarithmic fitting of plots between parameter c and $E_m \cdot \delta$ (a), $\sigma_{m,Fmax} \cdot \delta / S_{m,rel}$ (b), $\epsilon_{m,Fmax}$ (c) and $\epsilon_{m,Fmax}$ (d): $y = f + g \cdot \ln(x)$

$$E_c = E_m \cdot n_p^{d+e \cdot \ln E_m} \cdot (1 - v_f)^{f+g \cdot \ln(E_m \cdot \delta)} \quad (13)$$

where δ is OH/NCO molar ratio in matrix before curing and should be sufficient for relative matrix polarity expression. The δ value is not different for polymeric and composite matrix based on the same PUR. The reason could be the encapsulating of inorganic particles in the basic PUR matrix. Polarity of matrix should serve as the adhesion coefficient since the chemical origin of filler was the same (only rubber). It has to be mentioned that some PUR matrices were cured with the excess of -OH groups resulting in the excess of unreacted functional groups. The ratio of reactive groups was used in this role with the assumption that all PUR matrices exhibit approximately the same polarity when the concentration of -OH groups is neglected:

$$\sigma_{c,Fmax} = \sigma_{m,Fmax} \cdot n_p^{d+e \cdot \ln \left(\frac{\sigma_{m,Fmax}}{S_{m,rel}} \right)} \cdot (1 - v_f)^{f+g \cdot \ln \left(\frac{\sigma_{m,Fmax} \cdot \delta}{S_{m,rel}} \right)} \quad (14)$$

where $S_{m,rel}$ is the integral area (values in the range 0–1) lying under the tensile curve of nonporous matrix and the relationship for its calculation (Eq. (15)) was derived from the basic relationship given by Eq. (6):

$$S_{m,rel} = \frac{A_{m,Fmax}}{\sigma_{m,Fmax} \cdot \epsilon_{m,Fmax}} = \sum \frac{\epsilon_n - \epsilon_{n-1}}{\epsilon_{m,Fmax}} \cdot \frac{\sigma_n + \sigma_{n-1}}{2 \cdot \sigma_{m,Fmax}}; n \in \langle 1; n_{Fmax} \rangle \quad (15)$$

Values of mechanical properties in Eq. (15) were derived from fitted data in Table 4, since it was not possible to prepare absolutely nonporous matrix. The area below tensile curve of nonporous matrix was used for improving the fitting of exponent b and c in the case of $\sigma_{c,Fmax}$ calculation (Eq. (14)). This is the only difference in relationships describing E and σ_{Fmax} which could be caused by the same $S_{m,rel}$ value for all E measurements. The constant $S_{m,rel}$ value (approx. 0.5) is caused by linearity of the initial stage of tensile curve which is used for the determination of E . Therefore, the $S_{m,rel}$ was excluded from the Eq. (13).

Remaining relationships are dedicated to ultimate strain and specific energy required for ultimate strength achievement:

$$\varepsilon_{c,F \max} = \varepsilon_{m,F \max} \cdot n_p^{d+e \cdot \ln \varepsilon_{m,F \max}} \cdot (1 - v_f)^{f+g \cdot \ln \varepsilon_{m,F \max}} \quad (16)$$

$$A_{c,F \max} = A_{m,F \max} \cdot n_p^{d+e \cdot \ln \sigma_{m,F \max}} \cdot (1 - v_f)^{f+g \cdot \ln \sigma_{m,F \max}} \quad (17)$$

3.2 Advanced relationships between structure parameters and mechanical properties of filled composites

General discrete relationships do not distinguish the origin of porosity, specifically whether the porosity occurs during the preparation of PUR matrix or after the addition of filler. Equations (13)–(17) can be modified by substituting the data for nonporous matrices (slopes of data fitting according Eq. (13), see also Fig. 3 and Table 4) by measured data of real porous matrices (E_{mn} , $\sigma_{mn,F \max}$, $\varepsilon_{mn,F \max}$, $A_{mn,F \max}$ and $S_{mn,rel}$ in Table 3). Instead of $S_{m,rel}$ values, $S_{mn,rel}$ represents porous matrices (calculated by Eq. (15) from data in Table 3). The interspace filling of composite (n_p) can be divided by $(1 - n_m)$, where $(1 - n_m)$ equals to n_p for unfilled matrix (see n_m values in Table 3). The d , e , f and g values were taken from Eqs. (13)–(14) and (16)–(17) (accurate values shown in the Figs. 4 and 5 in relations). Calculation of E_c , $\sigma_{c,F \max}$, $\varepsilon_{c,F \max}$ and $A_{c,F \max}$ (composites based on porous matrix) is then given by Eq. (18)–(21). Modified equations were used to recalculate the data that had been measured

for improved accordance between measured and calculated data. Then the linear dependences of measured data on the recalculated were created separately for each pair of composite samples based on one PUR matrix and chosen property. Obtained slopes served as the extent of accordance between recalculated and measured data. Thus obtained values of slopes are shown in Table 6 for all measured data.

$$E_c = E_{mn} \cdot \left(\frac{n_p}{1 - n_m} \right)^{d+e \cdot \ln E_{mn}} \cdot (1 - v_f)^{f+g \cdot \ln (E_{mn} \cdot \delta)} \quad (18)$$

$$\sigma_{c,F \max} = \sigma_{mn,F \max} \cdot \left(\frac{n_p}{1 - n_m} \right)^{d+e \cdot \ln \left(\frac{\sigma_{mn,F \max}}{S_{mn,rel}} \right)} \cdot (1 - v_f)^{f+g \cdot \ln \left(\frac{\sigma_{mn,F \max}}{S_{mn,rel}} \right)} \quad (19)$$

$$\varepsilon_{c,F \max} = \varepsilon_{mn,F \max} \cdot \left(\frac{n_p}{1 - n_m} \right)^{d+e \cdot \ln \varepsilon_{mn,F \max}} \cdot (1 - v_f)^{f+g \cdot \ln \varepsilon_{mn,F \max}} \quad (20)$$

$$A_{c,F \max} = A_{mn,F \max} \cdot \left(\frac{n_p}{1 - n_m} \right)^{d+e \cdot \ln \sigma_{mn,F \max}} \cdot (1 - v_f)^{f+g \cdot \ln \sigma_{mn,F \max}} \quad (21)$$

The classification of porosity origin also assumes different values of d and e parameters and then different b parameter for different fillers. General parameter z_{mn} in the Eq. (18) (i.e., E_{mn}) also includes porosity of matrix and exponent b including parameters d and e with different values than those for z_m from Eq. (13) (i.e., E_m). Values of these parameters should be universal for individual mechanical properties of all porous materials that are homogeneous on macroscopic scale according to Eqs. (22)–(25). When different values of d and e are assumed for different cause of porosity, they can be assumed to be different also for different filler. However, only rubber as a filler was used in this study, this assumption will be under interest in the future work.

$$E_{mn} = E_m \cdot (1 - n_m)^{d+e \cdot \ln E_m} \quad (22)$$

$$\sigma_{mn,F \max} = \sigma_{m,F \max} \cdot (1 - n_m)^{d+e \cdot \ln \left(\frac{\sigma_{m,F \max}}{S_{m,rel}} \right)} \quad (23)$$

$$\varepsilon_{mn,F \max} = \varepsilon_{m,F \max} \cdot (1 - n_m)^{d+e \cdot \ln \varepsilon_{m,F \max}} \quad (24)$$

$$A_{mn,F \max} = A_{m,F \max} \cdot (1 - n_m)^{d+e \cdot \ln \sigma_{m,F \max}} \quad (25)$$

Table 6 Accordance results between real data and data calculated by Eqs. (18–21)

PUR matrix	E	$\sigma_{F \max}$	$\varepsilon_{F \max}$	$A_{F \max}^a$
P ₉₉ –W ₁ (more porous)	1.10	1.12	0.90	1.80
P ₉₉ –W ₁ (less porous)	0.98	0.91	1.12	1.18
P ₉₅ –G ₅	0.96	0.91	0.72	0.87
P ₈₀ –G ₂₀	0.95	0.85	1.06	0.84
P ₈₅ –G ₅ –CO ₁₀	0.91	0.90	1.09	0.91
P ₆₅ –CO ₃₅	1.08	1.02	1.07	0.97
P ₄₉ –CO ₂₆ –LO ₂₅	1.08	0.78	0.80	0.55
P ₃₃ –CO ₁₇ –Si ₅₀	0.99	1.00	0.98	0.42
P ₃₃ –CO ₁₇ –Ca ₅₀	0.98	0.96	0.99	0.41
P ₃₃ –CO ₁₇ –Fe ₅₀	1.05	0.89	1.28	0.35
P ₇₂ –G ₁₈ –Ca ₁₀	0.79	0.85	0.89	0.66

Slopes values belong to linear functions going throw beginning and containing dependences of real data on those calculated. Each value serves for one property and composites based on one matrix. Total accordance is equal to 1

^aLow accordance usually in cases of low $A_{F \max}$ values of used matrices

included in matrix) should be the next step. However, it is impossible to fit the data for porous matrices as well as for porous composites due to only one value of porosity for each matrix (porosity was a property of matrix). Only $P_{99}-W_1$ matrix was prepared in two types with different porosity caused by water and affected by (un)excision of bubbles arising from the surface during curing. This lack of experimental data required a change of approach according to Eq. (26) which generalizes Eqs. (22)–(25):

$$z_{mn} = z_m \cdot (1 - n_m)^b \quad (26)$$

In Eq. (26) (comparable with Eqs. (1) and (2)), z_m is only one unknown variable while z_{mn} and n_m are measurable. Individual mechanical properties for nonporous matrix (z_m) were derived from data fitting according to Eqs. (13)–(17) valid for composites. Then the exponent b can be expressed from Eq. (26) as the last unknown variable. Obtained b values have been plotted against the z_m values (Fig. 6) in similar way as shown in Fig. 4 to obtain the general d and e values for Eqs. (22)–(25). Except of structural parameters, humidity of filler could affect the data scattering. Specifically, isocyanate groups of pre-polymer are highly reactive towards humidity and thus the structure and mechanical properties of PUR composites could be affected by humidity of added filler used without drying. Accordingly, z_m values of porous composites derived from the logarithmic fitting of porous composites (Fig. 3, Table 4) do not fit absolutely with measured z_{mn} values for porous PUR matrix without the influence of filler addition.

4 Conclusions

This study is focused on the description of the mechanical behavior of porous PUR composites filled with rubber filler. Proposed relationships are dedicated to tensile modulus (E), ultimate strength (σ_{Fmax}) and strain (ϵ_{Fmax}) and specific energy need (A_{Fmax}). Derivation of the relationships for porous filled composite was performed in two steps. First, exponential parameters were experimentally determined from data fitting using structural parameters called interspace filling and interspace volume and looking for exponents suitable for the best data fitting in discrete situations (the same property, the same composition beyond the rates of components). The second step included an effort to describe a meaning of powers obtained in the first step. It means the fitting of powers by logarithmic functions. Obtained relationships do not generally describe the role of filler in porous composite, since only the ground rubber was used as the filler for all composites. Accordingly, the use of different types of filler could lead to description of d , e , f and g members placed in exponent dependencies. However, proposed relationships enable probably an addition of infinite amount of filler types but they do not describe the influence of different types of filler absolutely. The reason is the addition of only rubbery fillers into PUR matrices. In future works it is necessary to find exact meaning of all members in structure–properties relationships for different systems. Suggested relations seem to be independent on the type of porosity (open and enclosed pores, different pore size and distribution, etc.).

Fig. 6 Dependences of parameter b from Eq. (22) on E_m (a) and parameter b from Eq. (23) on $\sigma_{m,Fmax}/S_{m,rel}$ (b). In the plots, there are shown only points except outliers

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

Appendix

Advanced relationship between structure parameters and mechanical properties of filled composites: n-component system

According to Eqs. (18)–(21) and their extensions represented by Eqs. (22)–(25), each mentioned property of porous composite can be determined with respect to the origin of porosity. Creation of proposed relationships is the key to the complex relationships, which could determine mechanical properties of n-component porous composite. The Eqs. (18) and (22) can be accompanied with this assumption resulting in Eq. (27). Equation (28) serves as its specification:

$$E_{2n} = E_{1n} \cdot \left(\frac{n_{p2}}{1 - n_1} \right)^{d_2 + e_2 \cdot \ln E_{1n}} \cdot (1 - v_{f2})^{f_2 + g_2 \cdot \ln (E_{1n} \cdot \delta)} \quad (27)$$

where

$$E_{1n} = E_1 \cdot (1 - n_1)^{d_1 + e_1 \cdot \ln E_1} \quad (28)$$

In the Eqs. (27) and (28), there is a lot of subscripts representing amount of phases in n-component system (1 = matrix, 2 = two-component composite, n = for n-component composite). If the number is added by letter n , the member value is valid for porous system. Also combination nn is possible (for n-component porous system). The members including porosity and interspace filling do not use subscript n in case of porosity occurrence, because porosity occurrence is directly determined by their values.

For n-component composite, the Eq. (27) turns into Eq. (29) valid for E_{nn} :

$$E_{nn} = E_{n-1,n} \cdot \left(\frac{n_{pn}}{1 - n_{n-1}} \right)^{d_n + e_n \cdot \ln E_{n-1,n}} \cdot (1 - v_{fn})^{f_n + g_n \cdot \ln (E_{n-1,n} \cdot \delta)} \quad (29)$$

The same type of relationship can be obtained for other properties:

$$\sigma_{nn,F \max} = \sigma_{n-1,n,F \max} \cdot \left(\frac{n_{pn}}{1 - n_{n-1}} \right)^{d_n + e_n \cdot \ln \sigma_{n-1,n,F \max}} \cdot (1 - v_{fn})^{f_n + g_n \cdot \ln \left(\frac{\sigma_{n-1,n,F \max} \cdot \delta}{S_{n-1,n,rel}} \right)} \quad (30)$$

$$\varepsilon_{nn,F \max} = \varepsilon_{n-1,n,F \max} \cdot \left(\frac{n_{pn}}{1 - n_{n-1}} \right)^{d_n + e_n \cdot \ln \varepsilon_{n-1,n,F \max}} \cdot (1 - v_{fn})^{f_n + g_n \cdot \ln \varepsilon_{n-1,n,F \max}} \quad (31)$$

$$A_{nn,F \max} = A_{n-1,n,F \max} \cdot \left(\frac{n_{pn}}{1 - n_{n-1}} \right)^{d_n + e_n \cdot \ln \sigma_{n-1,n,F \max}} \cdot (1 - v_{fn})^{f_n + g_n \cdot \ln \varepsilon_{n-1,n,F \max}} \quad (32)$$

Equations (29)–(32) should serve for the system containing 1 matrix (binder) and $n-1$ kinds of filler. δ should express relationship between the last included filler and binder component of matrix (Eqs. (29)–(32)). If the objective amount of porosity is not changed by the n th filler addition, then is valid the equality $n_{pn} = 1 - n_{n-1}$. It leads to simplification of the Eqs. (29)–(32).

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