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POLYMER BASED COMPOSITES WITH INTERPENETRATING NETWORKS STRUCTURE

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Abstract. Preparation and properties of composites consisting of two continuous interpenetrating phases, at least one of them is the polymer phase, are presented. Three different kinds of such composites are discussed: polymer-polymer (PVC-PMMA), polymer-mineral (PMMA-gypsum) and polymer-metal (PVC-Wood alloy). Composites were prepared by filling the porous matrix made of one component with other component in the liquid state which was then solidified by polymerization (PMMA) or cooling (Wood alloy). The obtained composites were characterized mainly by mechanical testing, *e.g.* elasticity modulus, flexural strength and Brinell hardness. In some cases other measurements, such as microscopic and electrical, were also carried out. It was found that obtained composites possess many interesting properties. The introduction of the second component into the matrix pores as a rule increases the mechanical properties by few times, even if its content is relatively small.

Keywords: composite, poly(methyl methacrylate), poly(vinyl chloride), mechanical properties.

1. Introduction

Due to a number of interesting properties classical interpenetrating polymer networks (IPNs) defined as networks created by two or more polymers, which are at least partially interlaced on a molecular level but not covalently bonded to each other, attracted much attention during the last decades. For this reason such IPNs were a subject of numerous papers and monographs [1, 2]. Interpenetrating structures on a larger scale than the molecular one can be created in systems comprising at least two continuous phases, such as some semicrystalline polymers, immiscible polymer blends within the phase inversion range of components or various composites including porous materials with open pores. The first two categories, including additionally ionomers and block copolymers (thermoplastic elastomers), are often referred to as thermoplastic IPNs [3]. Such systems consisting of two or more bicontinuous (co-continuous), interlaced 3D networks are often prepared by melt blending of incompatible polymers in proper amounts to obtain the phase bicontinuity. Another preparation method of such co-continuous structures also applied in this work for creation of PVC-PMMA system, makes use of porous matrix with open pores made of one polymer component, which is then filled with the second component in a liquid form, *e.g.* as a monomer. This principle can be also applied for preparation of other bicontinuous systems of IPNs pattern, such as polymer-ceramics [4-7] or ceramics-metal [5]. The same principle was also applied in this work for preparation of two other IPNs systems, *i.e.* gypsum-PMMA and PVC-Wood alloy by intrusion of MMA prepolymer into gypsum porous matrix and liquid Wood metal into porous PVC matrix. The method of Wood alloy intrusion was also used to study the cement pore structure [8]. It should be also noted that gypsum and low melting metal alloys were also used as fillers for polymers to obtain systems with quite different structure and properties [9, 10].

2. Experimental

IPNs composites PVC-PMMA, gypsum-PMMA and PVC-Wood alloy were prepared using the following materials:

- powder of suspension PVC Polanvil S-67 HBD supplied by Anwil Company (Poland)
- gypsum powder ($CaSO_4 \cdot H_2O$) supplied by Dolina Nidy Ltd (Poland)
- Wood alloy supplied by Innovator Ltd (Poland)

Typical properties of Wood alloy compared with other materials are given in Table 1 [10].

Table 1

Comparison of Wood alloy properties with other materials

Property[1)]	Water	Gal	Mercury	NaK[2)] alloy	Wood[3)] alloy
density, g/cm^3	1.00	6.10	13.60	0.87	9.60
melting temperature, K	273	303	234	261	343
boiling temperature, K	373	2478	630	1057	1873
heat conductivity, W/(m·K)	0.6	28.0	7.8	25.3	18.0
heat capacity, J/(kg·K)	4181	373	140	1154	172
viscosity, mPa·s	0.85	1.96	1.55	0.47	3.3
electrical resistivity, Ω·cm	$1.82\cdot10^{7}$	$1.4\cdot10^{-5}$	$9.6\cdot10^{-5}$	$4.1\cdot10^{-5}$	$4.3\cdot10^{-5}$

Notes: [1)] properties are related to the liquid state in a temperature close to the melting point; [2)] eutectic 22 % Na, 78 %; [3)] eutectic 50 % Bi, 27 % Pb, 13 % Sn and 10 % Cd.

Porous PVC matrices in the form of discs (4 mm thickness, 32 mm diameter) used for preparation of PVC-PMMA and PVC-Wood alloy IPNs composites were fabricated by sintering the PVC powder. The sinter density was adjusted by changing the weighted amount of PVC powder poured into the mold. The powder in the mold was initially densified by vibration, and then put into an oven at 443 K for 20 min. Hereafter the mold was closed and hold for 15 min under pressure for cooling at room temperature.

Gypsum matrices were prepared by mixing gypsum powder with assumed amount of water (water/gypsum ratios: 0.6:1, 0.8:1, 1:1). The gypsum-water mixture was put into silicon molds (80×30×30 mm) for 3 days. Obtained samples were dried at room temperature.

To obtain the composites with IPNs structure the prepared matrices were impregnated (infiltrated) with liquid PMMA prepolymer or liquid Wood metal under conditions established in preliminary tests. Prepolymerization of methyl metacrylate was carried out under the addition of 2 % benzoil peroxide and microwave irradiation (power 90 W) during 10 min at 333 K [11]. The prepolymer was introduced into the pores of gypsum or PVC matrices and polymerized. In the case of gypsum 5 % addition of *g*-methactyloxypropyl-trimetoxysilane was applied to improve wettability and adhesion between components. The prepolymer infiltration was performed in an autoclave at room temperature. Prior to infiltration the air was evacuated and the sample poured with prepolymer. The increase of external pressure facilitates the filling of the pores. After 60 min (gypsum) or 15 min (PVC) the infiltrated sample was removed from the autoclave and put into an oven for final polymerization at 323 K within ca. 24 h.

The infiltration of PVC matrix with Wood alloy was carried out in a special pressure autoclave made of steel at 353 K. The proceeding (somewhat similar to the previous case) was described elsewhere [12].

The prepared matrices and IPNs composites were characterized by various methods, *e.g.* mercury porosimetry and SEM (pore structure), mechanical and thermal measurements. The results of the study are presented below.

3. Results and Discussion

3.1. Gypsum-PMMA Composites

Three kinds of gypsum matrices for water/gypsum ratios: 0.6:1, 0.8:1 and 1:1 were prepared. The pore structure was determined by mercury porosimetry as well as density and water uptake measurements. It was found that for increasing the water/gypsum ratio the mean pore diameter and the total pore volume (porosity) increase. Simultaneously, it was observed that the content of closed pores becomes smaller. Such pores appear especially in the system prepared for the lowest water/gypsum ratio. The obtained results including mechanical tests for both gypsum matrices and gypsum–PMMA composites are summarized in Table 2.

It can be seen from Table 2 that gypsum matrix prepared with addition of small water amount has the smallest mean pore diameter and the lowest content of open pores (determined by mercury porosimetry). It leads to the low water uptake of both gypsum matrix and composite. However, mechanical properties are better for composites with matrices characterized by high gypsum/water ratio. This statement is valid probably not only for flexural strength but also for compression strength. This property for composites could not be measured as it exceeded the value (ca. 23 MPa) resulting from the maximal load of the testing machine.

3.2. PVC–PMMA Composites

Fig. 1 shows a typical pore size distribution curve obtained for the sintered PVC matrix with 20 % porosity by means of mercury porosimetry.

Table 2

Characteristics of gypsum–PMMA composites with IPNs structure

Gypsum/water ratio	Mean pore diameter, nm	Open pore content, %	Density, g/cm^3		Water uptake, %		Flexural strength, MPa		Compression strength, MPa
			matrix	comp.	matrix	comp.	matrix	comp	matrix*)
1:0.6	95	40.0	0.99	1.17	38.2	15.3	4.2	11.6	7.7
1:0.8	115	52.2	0.88	1.13	51.2	25.5	3.5	12.2	6.7
1:1.0	135	55.2	0.82	1.08	64.3	34.4	2.8	13.1	3.4

Note: *) gypsum–PMMA composites do not break under compression stress < 23 MPa.

Table 3

Characteristics of PVC–PMMA composites with IPNs structure

Porosity range, %	Mean density, g/cm^3	Water uptake, %		Brinell hardness, MPa		Dynstat impact strength, kJ/m^2		Dynstat flexural strength, MPa	
		matrix	comp.	matrix	comp.	matrix	comp.	matrix	comp.
16–20	1.12	7.1	3.2	39.2	-	0.35	-	2.55	-
21–25	1.05	7.3	3.4	37.8	56.2	0.27	0.85	2.37	8.29
26–30	0.99	7.6	3.7	37.1	55.8	0.42	0.81	2.17	8.05
31–35	0.94	7.7	3.8	36.9	55.6	0.35	0.79	1.99	7.71
36–40	0.88	7.9	4.0	-	55.2	-	0.73	-	7.51

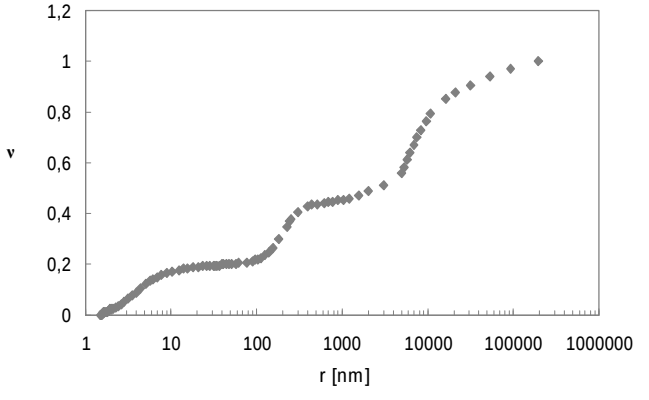

Fig. 1. Dependence of cumulative relative pore volume on pore radius

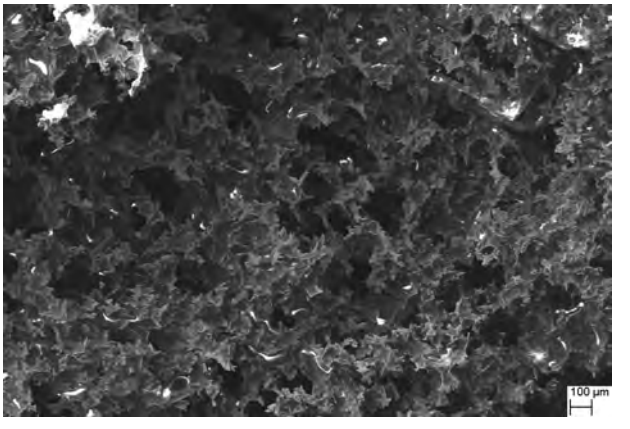

Fig. 2. SEM micrograph of the metal network in PVC–Wood alloy IPNs composite

It can be seen that the pore structure is characterized by a trimodal pore size distribution with maxima at ca. 5, 200 and 1000 nm. The first two kinds of pores result probably from the porous grain structure of the suspension PVC, while the largest pores are the empty space between sintered PVC grains. The existence of the smallest pores can be treated as advantageous to obtain good adhesion between components because they make possible the mechanical anchoring of the liquid component introduced into the porous matrix.

It follows from Table 3 that the composites have a reduced water uptake and remarkably improve mechanical properties in comparison with initial sintered matrix. They somewhat decrease with increasing porosity of the PVC matrix.

3.3. PVC–Wood alloy Composites

Fig. 2 presents the SEM micrograph of the porous structure of the metal network. The structure was visualized after PVC extraction from the composite with cyclohexanone.

It can be easily seen that the alloy phase creates a 3D structure giving rise to assume the ultimate structure of the whole composite as the IPNs structure.

Table 4 summarizes the properties of the investigated PVC–Wood alloy composites.

Table 4

Characteristics of PVC–Wood alloy composites with IPNs structure

Alloy content (porosity), vol %	Vicat temperature, K		Brinell hardness, MPa		Dynstat impact strength, kJ/m^2		Dynstat flexural Strength, MPa	
	matrix	comp.	matrix	comp.	matrix	comp.	matrix	comp.
10	369	366	63	73	1.4	1.5	14.5	15.8
20	365	363	55	62	0.8	1.6	11.5	18.1
30	356	357	40	53	0.5	1.5	3.4	17.9

It follows from Table 4 that the presence of Wood alloy lowers somewhat the Vicat temperature. This is probably due to the low melting point of this alloy. Mechanical behavior of the composites is apparently better than that of the corresponding matrices. The properties decrease somewhat with increasing alloy content (matrix porosity). However, the relative property changes caused by the alloy addition are the most advantageous for matrices with the highest porosity, especially for pore volume fraction of 30 %.

It should be also noted that the composites behave as typical conductors. Electrical resistivity of the composite containing 20 vol % Wood alloy is equal to $4.2 \cdot 10^{-5}$ Ω·m, which is characteristic of conducting materials. Electromagnetic shielding effectiveness of the same composite is also quite well and equals to 65–90 dB.

4. Conclusions

In summary, different composites consisting of two continuous interpenetrating phases were examined. It was found that the second component which is intruded into pores of matrix increases the mechanical properties a few times. Mechanical properties of all composites vary with the filler content. For PVC-Wood's alloy composites great improvement in strength is observed at high-metal percentages. Also gypsum-PMMA composites show increment in flexural strength value when PMMA content is higher. Significant is the fact that PVC–metal composites conduct electrical current well and exhibit electromagnetic shielding capabilities. It is evident that the metal phase is continuous and conducting paths are formed. Network (phase) structure was in addition confirmed by scanning electron microscopy.

Acknowledgements

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ПОЛІМЕРНІ КОМПОЗИТИ ІЗ ВЗАЄМОПРОНИКНОЮ СТРУКТУРОЮ

Анотація. *Вивчено одержання і властивості композитів, що складаються з двох суцільних взаємопроникних фаз, одна з яких принаймні, є полімерною. Розглянуто три різних види таких композитів: полімер-полімерні (ПВХ-ПММА), полімер-мінеральні (ПММА-гіпс) і полімер-металеві (ПВХ-сплав Вуда). Приготування композитів відбувалось заповненням пористої матриці одного компонента іншим компонентом в рідкому стані, яку потім затверджували внаслідок полімеризації (ПММА) або охолодженням (сплав Вуда). Визначено характеристики отриманих композитів: модуль пружності, міцність на вигин і твердість за Брінеллем та деякі мікроскопічні та електричні вимірювання. Встановлено, що отримані композити характеризуються оригінальними властивостями. Показано, що введення другого компонента, навіть при малому його вмісті, в пори матриці, підвищує в декілька разів механічні властивості виробу.*

Ключові слова: *композит, поліметилметакрилат, полівінілхлорид, механічні властивості.*