

Producing and Mechanical Testing of Urea-Formaldehyde Resin Foams Reinforced by Waste Phosphogypsum

Krasimira Georgieva, Yordan Denev

Abstract—Many of thermosetting resins have application only in filled state, reinforced with different mineral fillers. The co-filling of polymers with mineral filler and gases creates a possibility for production of polymer composites materials with low density. This processing leads to forming of new materials – gas-filled plastics (polymer foams). The properties of these materials are determined mainly by the shape and size of internal structural elements (pores). The interactions on the phase boundaries have influence on the materials properties too. In the present work, the gas-filled urea-formaldehyde resins were reinforced by waste phosphogypsum. The waste phosphogypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is a solid by-product in wet phosphoric acid production processes. The values of the interactions polymer-filler were increased by using two modifying agents: polyvinyl acetate for polymer matrix and sodium metasilicate for filler. Technological methods for gas-filling and recipes of urea-formaldehyde based materials with apparent density 20-120 kg/m^3 were developed. The heat conductivity of the samples is between 0.024 and 0.029 $\text{W/m}^\circ\text{K}$. Tensile analyses were carried out at 10 and 50% deformation and show values 0.01-0.14 MPa and 0.01-0.09 MPa, respectively. The apparent density of obtained materials is between 20 and 92 kg/m^3 . The changes in the tensile properties and density of these materials according to sodium metasilicate content were studied too. The mechanism of phosphogypsum adsorption modification was studied using methods of FT-IR spectroscopy. The structure of the gas-filled urea-formaldehyde resins was described by results of electron scanning microscopy at three different magnification ratios – x50, x150 and x 500. The aim of present work is to study the possibility of the usage of phosphogypsum as mineral filler for urea-formaldehyde resins and development of a technology for the production of gas-filled reinforced polymer composite materials. The structure and the properties of obtained composite materials are suitable for thermal and sound insulation applications.

Keywords—Gas-filled thermosets, mechanical properties, phosphogypsum, urea-formaldehyde resins.

I. INTRODUCTION

THE low-density polymeric foams have a long history in their development. The materials made from chemically foamed rubber dated in the years prior to World War II and soon possessed significant civilian applications [1]. In a few years, polyurethane (PU) and polystyrene foams became strong performance platforms to deliver a variety of products in packaging industries [2]. There is a wide choice of disperse

or fibrous inorganic and polymeric fillers in solid phase which can be used as reinforcement materials in polymer foams producing process. [3]. A recent market research report indicated a steady growth in consumption to exceed 50 billion lb. by 2019 [4]. The thermosetting polymer took place as construction polymeric materials and they are a good base for development of new polymeric composite materials [5], [6]. Foamed plastics are special class of expanded materials with a cellular structure and can be produced in a great variety of densities, ranging from 0.1-1.6 kg/m^3 to over 960 kg/m^3 [7].

The most important part of external building insulation in construction industry is the thermal insulation materials with varied composition and structure [8]. Organic thermal insulation material has the advantages of excellent heat-insulating property, low density and cheap price; on the other hand it is the combustible material with poor fireproofing [9].

The use of insulation materials has increased, both in terms of buildings being insulated and in the minimum values of insulation required by the national regulations [10].

The main and only synthetic polymer, independent from the oil industry is urea-formaldehyde resin. The urea-formaldehyde polymeric foams are produced by different technologies usually without using of high pressure forming [11]-[14]. The wide spectrum of available methods in producing technologies is determined by resin properties, chemical nature of blowing agent, size and distribution of cells and material requirements [15]. The foaming process and hardening of thermoset composites can be performed at room or higher temperature. In many plastic foams detergents for better components distribution and foam stabilizing are used [16]. The usage of surface active compounds makes possible to obtain materials with good distribution of reinforcing agent and obtaining of open- and closed-cells with desired size. Many different types of blowing agents [17] are known and every of them have specific usage. At relatively low gas content the pores have spherical shape and higher package density respectively. The polymeric foams incorporating higher gas content have non-uniform structural behavior and their pores have multi-layered shape.

The co-filling of polymers with mineral filler and gases creates a possibility for production of polymer composites materials with low density. During the years many literature sources describe different developed foam materials produced from urea-formaldehyde resin [18]-[21]. The reinforcement of thermosets with mineral filler leads to forming of multiphase systems with specific interactions on the phase boundary

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polymer-filler [22]. Many authors also discussed the mechanical properties of reinforced urea-formaldehyde resins [23]-[26].

The aim of present work is to study the possibility of the usage of phosphogypsum as mineral filler for urea-formaldehyde resins and development of a technology for the production of gas-filled reinforced composite materials (polymeric foams). The mechanical properties, structure and thermal coefficient values of obtained composite materials prove that they are suitable for thermal and sound insulation applications.

II. MATERIALS AND METHODS

A. Experimental Materials

The urea-formaldehyde resin, phosphoric acid (H_3PO_4), sodium metasilicate (Na_2SiO_3), ammonium carbonate ($(NH_4)_2CO_3$) and polyvinyl acetate were obtained by Bulgarian production plants. The blowing agent was dodecyl benzene sulfonic acid (DBSA) supplied by Merck. The phosphogypsum was provided by Agropolychim Plant (Devnya, Bulgaria). The phosphogypsum is a waste solid by-product of the H_3PO_4 production which forms up when decomposing Kola apatite in reaction with sulfuric acid [27], [28]. The chemical composition of the phosphogypsum samples (calculated for the dry product) in (%) is shown on Table I.

TABLE I
 CHEMICAL COMPOSITION OF WASTE PHOSPHOGYPSUM

Component	Content, %
CaO	39-40
SO ₃	56-57
P ₂ O ₅ (total)	1.1-1.2
P ₂ O ₅ (in water)	0.5-0.6
P ₂ O ₃	0.5-0.6
F	0.3-0.4

B. Formulation for Producing of Foam Composites

In Table II developed compositions for producing of urea-formaldehyde resin (UFR) composite foams are listed.

TABLE II
 COMPOSITIONS OF UFR SUSPENSION AND FOAM FORMING SOLUTION

Ingredient	Content, wt. %
UFR	100
Water	50
DBSA	7.2
$(NH_4)_2CO_3$	1.1
H_3PO_4 (65 %)	6.12
Water	15.56
Glycerol	1.5
Phosphogypsum	0 – 100
Polyvinyl acetate emulsion	0 – 100

C. Technology for Modification of phosphogypsum with Na_2SiO_3

The first preparation step in the surface modification process was initial phosphogypsum treating to neutral pH due

to its residual acid content. The main parts of solution for modification were 100 wt% phosphogypsum and 500 wt% water. These components have been mixed in glass reactor and rapidly stirred. Then relevant quantities of Na_2SiO_3 were added at continuous mixing. The mixing process carried out for around 1 hour in the presence of diluted HCl for controlling of pH in range of 4-5. Polysilicic acid was formed from Na_2SiO_3 in these conditions and on the phosphogypsum surface the new particles were observed. Prepared modificates were neutralized by NaOH and remained in the reactor for several hours. The treated phosphogypsum was filtered and dried. The presence of crystallization water in phosphogypsum was undesirable in plastic reinforcement and conversion of phosphogypsum dihydrate to hemihydrate at 150 °C for a few hours in laboratory dryer was held.

D. Preparation of UFR Foams

H_3PO_4 , DBSA, glycerol, water, $(NH_4)_2CO_3$ and phosphogypsum were placed in 500 ml reactor and the obtained mass was foamed at 350 rpm. UFR, diluted with 50% water, was added to form foam and the mixture was homogenized for 10 min. The foamed suspension was transferred into a desired shape container where after 1.5-2 hours at room temperature final hardening occurred. The produced UFR foam was dried 4 days with gradually increasing the temperature up to 60 °C.

E. UFR Foam Testing Methods

The mechanical properties of UFR foams, reinforced with phosphogypsum were studied in static conditions [29]. The compressive strength of the studied materials was carried out according to specifications of standard ISO 604 on INSTRON 4020 machine.

The apparent density of the produced foam materials was obtained according the specifications of standard ISO 844.

The FTIR spectra of samples were registered using a Bruker Tensor 27 FTIR Spectrometer. Potassium bromide plates of powder samples both untreated and treated by sodium metasilicate (SMS) were prepared and analyzed by 32 scans at a resolution of 4 cm^{-1} in the wavenumber range of 4000-400 cm^{-1} . Sample plates were directly investigated and collected spectra were processed with OPUS 6.5 software.

Scanning electron microscopy (SEM) images were taken according to specifications of standard ISO 16700:2016 to study the cells size and distribution in the prepared urea-formaldehyde composite foams.

The heat conductivity was determined according to specifications of standard ISO 8302.

III. RESULTS AND DISCUSSION

The mechanical characteristics of phosphogypsum reinforced UFR foams were studied as a function of different factors such mineral filler-polymer interactions, phosphogypsum content effect, curing process and structure of the polymeric foams. Acidic type catalysts such as phosphoric, hydrochloric, and sulfuric acid or some hydrolysable salts such as ammonium chloride can be used as resin hardeners. As

phosphogypsum contains some H_3PO_4 content, an approach to foam hardening by acid amounts ranging from 1 to 10 wt% has been investigated.

The study on the mechanical properties of UFR foams focused on their compressive strength. The static compressive strength mainly determines the usage possibilities of polymeric foams as thermal and sound insulation materials in building construction industry. The mechanical properties of UFR foams produced with modified filler always improved when compared to that of foams, produced with untreated phosphogypsum. In our previous studies phosphogypsum was treated with different components in order to improve the filler-to-polymer bonding [30], [31]. Best results were obtained using SMS and in the present work phosphogypsum was treated with this coupling agent. The results for compressive strength of UFR phosphogypsum reinforced foams are presented on Figs. 1 and 2.

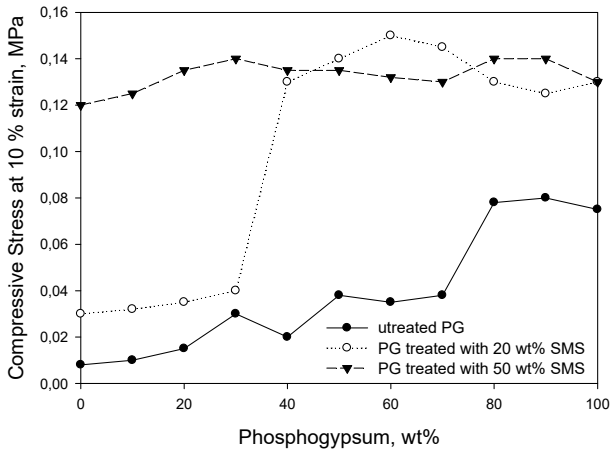


Fig. 1 Effect of phosphogypsum content on compressive stress at 10% strain of UFR foams

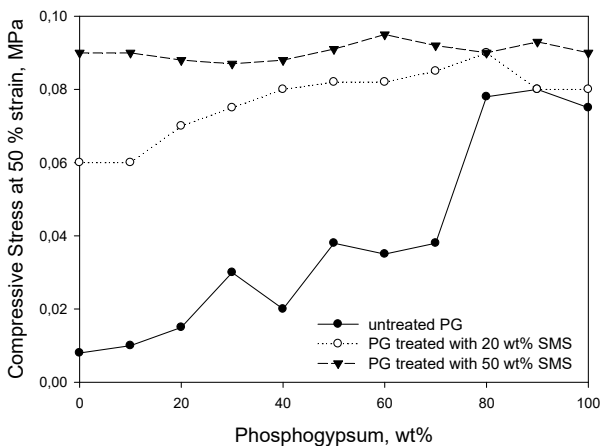


Fig. 2 Effect of phosphogypsum content on compressive stress at 50% strain of UFR foams

Figs. 1 and 2 describe the effect of various concentrations of mineral filler (PG) on the UFR foams compressive stress at 10 and 50% strain. It is obvious that compressive strength extremely increased as the concentration of the PG increased.

The compressive stress at 50% strain was relatively stable once the PG modification ratio reached 20 and 50% concentration of SMS. The compressive stress at 10% strain increased from 0.008 to 0.082 MPa for the untreated phosphogypsum and from 0.082 to 0.113 MPa for treated phosphogypsum. The compressive stress at 50% strain increased from 0.008 to 0.075 MPa for the untreated phosphogypsum. The same characteristic has values from 0.06 to 0.082 MPa for the phosphogypsum treated with 20 wt%. The most promising foam was obtained to be UFR composite with 20 wt% SMS and reinforcement rate of 60 wt% phosphogypsum.

In our previous works, surface modification of phosphogypsum with polyethylene glycol, SMS and carboxymethyl cellulose was described [30], [31]. Different concentrations of coupling agent show that mechanical strength increased. When treated phosphogypsum was introduced, physical interactions between the macromolecules and coupling agent molecules were obtained on the surface of phosphogypsum particles. In this work SMS as coupling agent was chosen [32]. SMS has a strong alkaline character, and when the pH was increased to 5.5, silicic acid was formed. The sodium metasilicate was adsorbed on the phosphogypsum surface during its subsequent polymerization to polysilicic acid under the same conditions [33]. When surface modification was completed a hybrid filler consisting of treated phosphogypsum and polysilicic acid particles occurred.

The relatively low strength of the resulting UFR foams can be increased by treating of the resin with a polyvinyl acetate emulsion. Polyvinyl acetate emulsion adhesive has been widely used due to its good bonding performance and environmentally friendly properties [34]. The mechanical results for the polyvinyl acetate emulsion effect on the compressive strength of UFR foams are shown on Fig. 3.

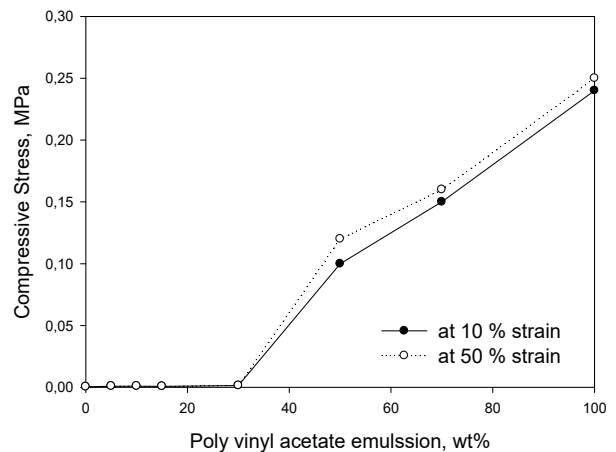


Fig. 3 Effect of polyvinyl acetate emulsion on the compressive stress at 10 and 50% strain of UFR foams

The reinforcement was carried out with 50 wt% phosphogypsum and coupling agent content polyvinyl acetate (PVA) varied up to 100 wt%. When PVA emulsion has reached 100 wt% the stress at 10% strain increased to 0.24

MPa. As seen on Fig. 3, the compressive stress both at 10 and 50% strain stay unchanged to 30 wt% PVA emulsion. When PVA content reaches 40 wt% the compressive strength rapidly increases to 0.24 MPa.

The weight and density of the materials in the building construction industry have significant importance in their usage [35]. The reinforcement of polymer by mineral fillers which have density of 2500-2800 kg/m³ causes significant increase in composite materials total density. This disadvantage can be overcome by incorporating of gas-cells in the polymer matrix. By this way the apparent density of the developed polymer composite materials can be regulated to desired values close to the density of the raw polymer.

Fig. 4 describes the effect of the mineral filler content (PG) on the apparent density of obtained UFR foams.

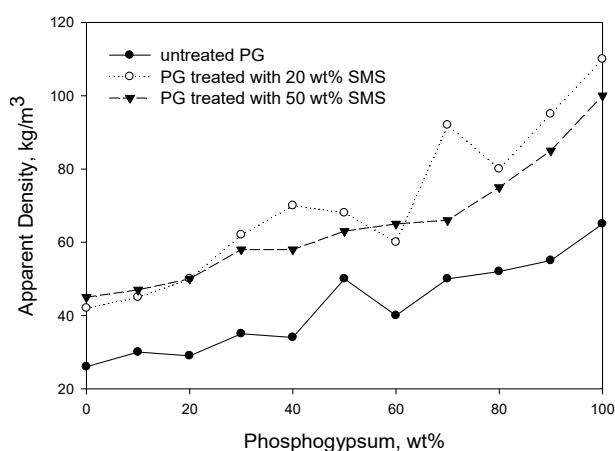


Fig. 4 Effect of phosphogypsum content on the UFR foam apparent density

The developed receipt of the compositions gave possibility for producing of foam composite materials with very low apparent density. The essence of the developed method consists of preliminarily foaming of ingredients which leads to producing of fine and stable foam following by adding of UFR suspension reinforced by phosphogypsum. This process was carried out at rapidly stirring.

Foaming capacity represents the ratio of foam volume and resin volume [36]. In the developed technology, DBSA was used as foaming agent and UFR hardener simultaneously. DBSA has a very high foaming capacity of 60-70 and shows foam stability for around 600 s. The apparent density of UFR foams was studied as a function of phosphogypsum content which varied from 10 to 100 wt%. Depending on the mineral filler fraction the apparent density gradually increased from 25 to 60 kg/m³ and from 40 to 110 kg/m³ for untreated and treated phosphogypsum respectively.

The effect of added PVA emulsion on the apparent density of UFR foams was studied too and the results are shown on Fig. 5. Regardless of the strong increase in foam strength according to PVA emulsion content, the apparent density also increases considerably.

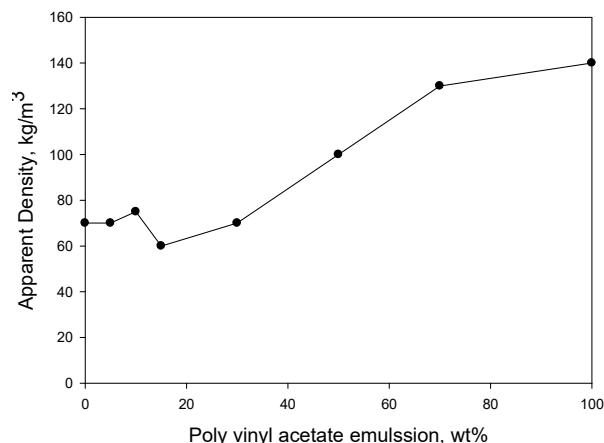


Fig. 5 Effect of PVA emulsion on the UFR foam apparent density

Because of the higher PVA emulsion density [37], the resulting apparent density of the UFR foams reached values up to 140 kg/m³. The results shown on Fig. 5 clearly prove that desired low density can be obtained only with PVA emulsion content below 50 wt%.

The main potential usage of the UFR foams as thermal insulation material in the building construction industry was proposed. The calculated heat conductivity values of the UFR foams samples are between 0.024 and 0.029 W/m²K and they confirm that UFR reinforced foams are suitable for application of foams as insulation materials.

In recent years some analysis techniques such Fourier Transform infrared spectroscopy (FTIR) and SEM have been widely used to study the surface and interface between coupling agents and mineral fillers [38]. FTIR is probably the most widely used analytical tool and it is often used to characterize the new peaks accompanied with coupling agent-filler interactions after the surface modification of inorganic fillers [39].

It was reported in [40] that SMS in the presence of H₃PO₄ could also transform to polysilicic acid on the surface of filler, so the amount of adsorbed coupling agent changed with storage time.

The single IR spectra of phosphogypsum SMS are shown on Fig. 6. The collected IR spectra for treated phosphogypsum with different concentrations of SMS are presented on Fig. 7. All registered spectra were processed for elimination of water content and CO₂ as well as the baseline of each spectrum was corrected.

The characterization of treated phosphogypsum by the FTIR spectroscopy clearly proves that despite the presence functional groups, chemical REACTION BETWEEN FORMED polysilicic acid and unreactive calcium sulfate not occurred.

The existence of cyclic structural motifs in the SMS was confirmed by the presence of band in the spectrum with a maximum at 3623 cm⁻¹ [41], [42].

An absorptive-water region was found at 3441 cm⁻¹ and bending vibration bands that induced by the H₂O appear at 1637-1639 cm⁻¹. The absorption bands at 1102-1116 cm⁻¹ are

caused by the asymmetric vibration of SO_4^{2-} existed in cm^{-1} are also induced by the bands in SO_4^{2-} [43]. phosphogypsum. The bending vibrations at around 602-669

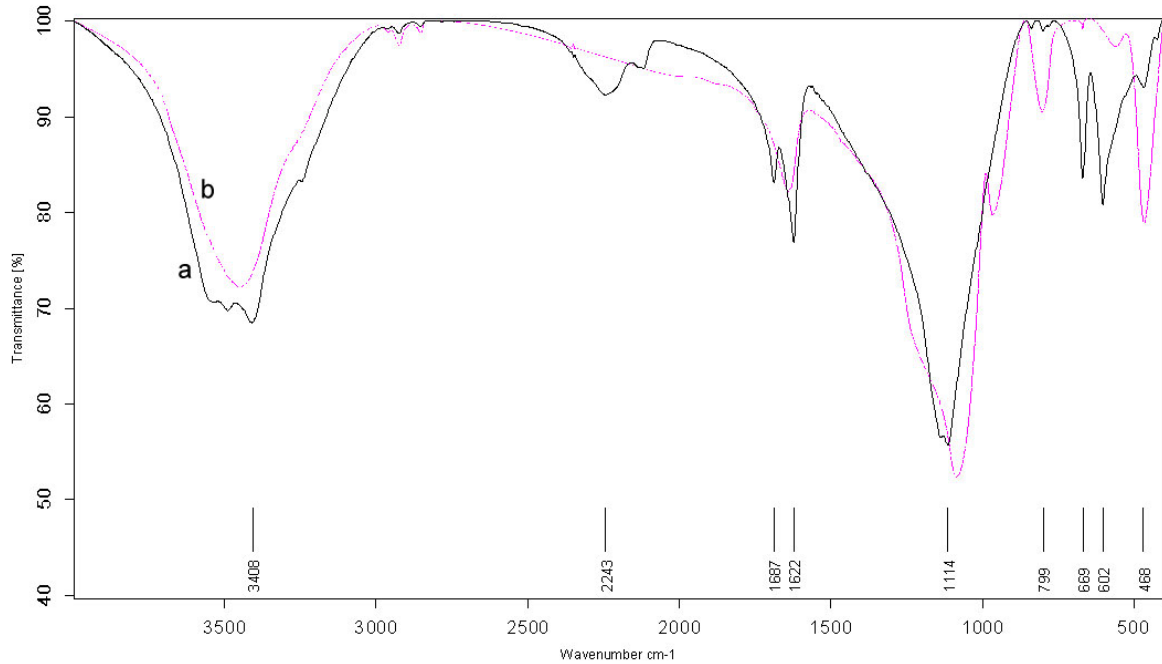


Fig. 6 Infrared spectra of the source compounds (a – phosphogypsum; b – SMS)

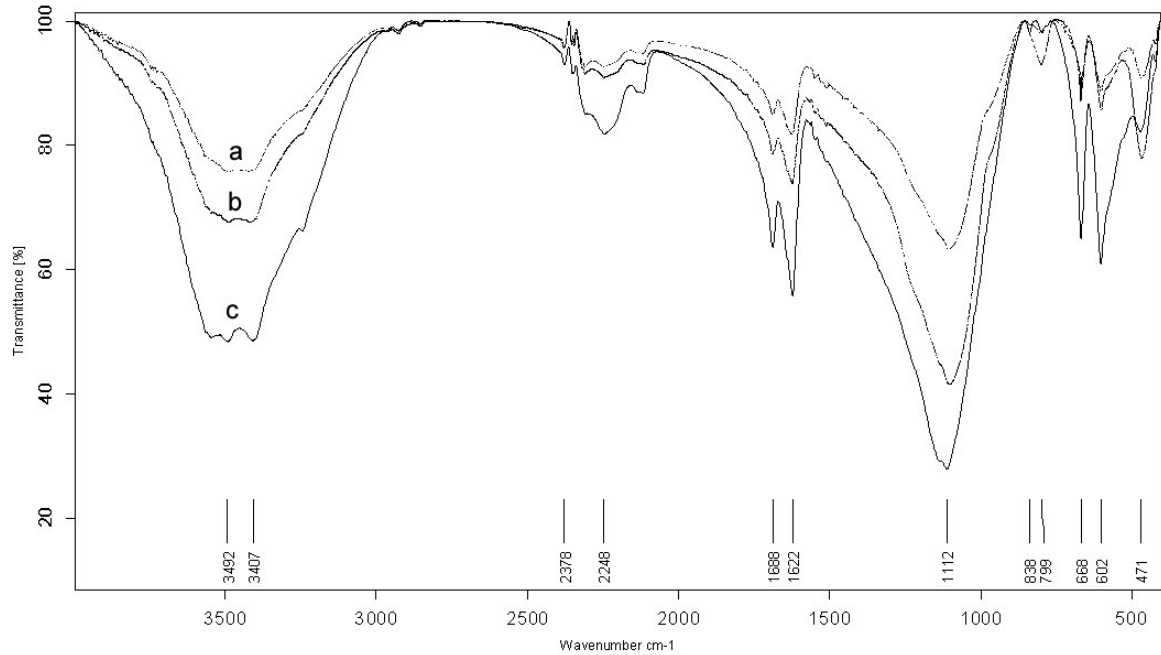


Fig. 7 Infrared spectra of the obtained phosphogypsum/ SMS modificates (a – PG + 5 wt % SMS; b – PG + 20 wt% SMS; c – PG + 50 wt % SMS)

As shown in Fig. 7 the intensity of bands associated with polysilicic acid increases in the same manner as SMS content.

For morphological studies, a SEM was used to reveal the pores distribution in reinforced thermoset composites together with information concerning the nature of the bond between the filler and matrix [44]. The structure of the foam depending

on the phosphogypsum content was examined by SEM at three magnification ratios – x50, x150 and x500.

Cellular structure of urea-formaldehyde composite foam materials is presented on Fig. 8.

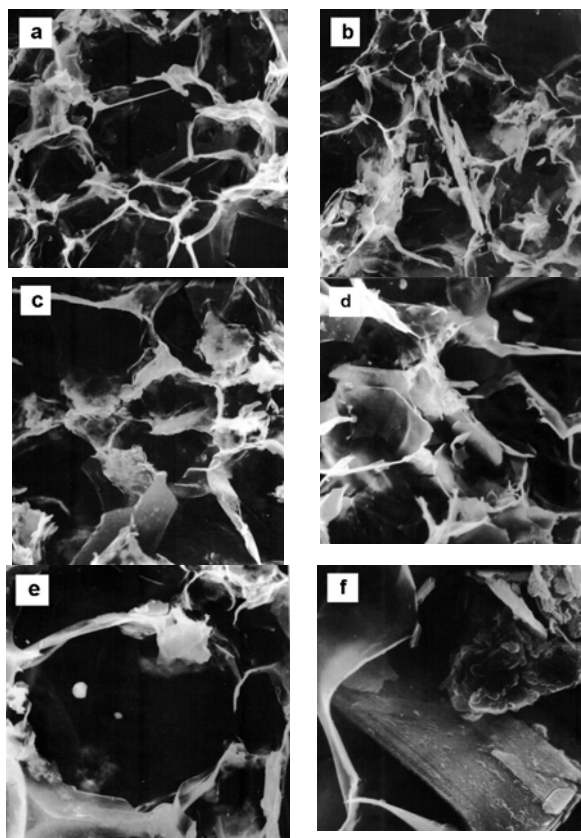


Fig. 8 SEM microphotographs of UFR foams at different magnification ratios (a, b – x50; c, d – x100; e, f – x500)

SEM microphotographs show the shape, size and distribution of open-cells and closed-cells at the three different magnification ratios. It is clearly shown that cells possessed almost right circle shape, same average size and relatively normal distribution. Heterogeneity increased with more compacted areas as well as the average pore size decreased. The magnification x150 confirmed the seal of the structure. The cell walls became thicker with deformed shape with increasing of phosphogypsum content. At magnification x500 it can be seen that as the phosphogypsum content increases, the distances between the filler particles significantly decreases. At the same time, some of the filler particles are statistically distributed out of foam cells. This correlates with the strength characteristics of the reinforced polymeric foams. At lower phosphogypsum content a good compatibility between the polymer and filler, good uniform distribution and wetting of the resin particles were observed. At higher phosphogypsum content the wetting degree strongly decreases as larger aggregates of particles were observed. The resin content in the observed aggregates was greater and the filler particles have formed a monolithic structure. The general panoramic microphotograph at x50 magnification proved an accidental accumulation of large pores but the walls around them were strongly compacted.

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