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Comparison the structure of PVC foams with different additives

K Roman[1] and G Zsoldos[1]

[1] University of Miskolc, Institute of Ceramics- and Polymer Engineering, Miskolc-Egyetemváros, Hungary

E-mail: polkrisz@uni-miskolc.hu

Abstract: The effects of various types of fillers in the PVC structure can be determined by using Scanning Electron Microscope. By the results of microscope, the modifying effects of fillers can be examined. Due to the most common failures which can occur in the production detected from the records. At different dose of fillers the structural changes were examined. The results of SEM analysis show that the most common structural failure was caused by the mixing preparation (especially for $CaCO_3$ blends). The types of fillers influence the shape-, orientation- and open-close of foam cells. Adding fillers of different percentage changes the thickness of the cells walls and the size and orientation of the cells. Based on these tests, it is possible to determine which filler is the most suitable for the formation of regular cellular structure.

1. Introduction

In the last 20 years, polymer foams are used in many applications, such as insulation systems, furniture or decorative elements. There are numerous reasons for use this, such as good mechanical and insulating properties and the low cost. Other advantages are low density and weight; therefore easy to transport and build it. The main disadvantage is difficulty to break down, because it is made from PVC raw materials [1]. PVC processes needs different types of additives. These additives are stabilizers and co-stabilizers, lubricants, polymeric auxiliaries, plasticizers, heat resistance, pigments and fillers [2]. Based on the literature review, the mechanical properties of blends change according to different fillers [3]. The mechanical and structural properties of the foam mainly depend on the cell's morphology, such as size-, shape of cells, the wall thickness and the density of the materials [4]. It is well known that calcium carbonate fillers modify the impact properties of the polymer. Some studies were dealing with the effect of rise husks fillers of the PVC foam. The measurements, determines that the density of the non-filled foam material is lower than the foam with filler. If the filler content in the mixture is higher than the original PVC, than cells of composite were deformations. The original PVC does not include fillers ($CaCO_3$ and marble). These fillers ($CaCO_3$, marble, rise husk) are the most important additives in the PVC formulation if we wanted to change the form of structure [5]. It was observed that using surface – treated fillers in the material causes higher resistant to the external influences [6].

2. Materials and sample preparations

The raw material was the PVC from the BorsodChem Zrt. company. The component the suspension grade PVC (K value=58) and the other components of the mixture were: solid Ca-Zn based stabilizer, paraffin based external- and partial glycerol ester type internal lubricants, acrylic based processing aid 1.5 phr azodicarbonamide. The azodicarbonamid [commercial name: Tramaco] was used as a blowing agent in all mixtures.

Types of fillers [commercial name]:

1. treated ultra fine calcium carbonate [OMYA EX-H1]
2. surface treated white marble [OMYACARB 1T-AV]
3. fine uncoated precipitated calcium carbonate [Socal P3]
4. ultrafine, white and odorless precipitated calcium carbonate [Socal 31]
5. ultrafine surface treated precipitated calcium carbonate [Socal U1S2]

6. ultrafine, white and odorless coated precipitated calcium carbonate [Socal 312]

Table 1. Particle size of fillers

	OMYA EX-H1	OMYACARB 1T-AV	Socal P3	Socal 31	Socal U1S2	Socal 312
Particle size (μm)	1.7	2.0	0.18-0.24	0.24-0.35	0.07-0.13	0.045-0.090

Table 2. Formulation of the blends

PVC	Stabilizer	Lubricants	Processing aid	Bowling agent	Fillers six each
100	2.4	2	7	1.5	5;10;20

In the blends the fillers were added 5; 10; 20 phr. Five types of $CaCO_3$ and one of marble filler were used in the materials. The differences between the different $CaCO_3$ is the surface treatment and the particle size. The mixtures were made using a laboratory dry-mixer. In the mixer the temperature increased to 110 °C. Extruded sheets were made from the mixtures by a twin screw laboratory extruder. The extruder parameters were: D=30mm, L/D= 20, compression rate 1:3 and the extruder temperature set at 165°C/170°C/170°C°/175°C/175°C/180°C from hopper to die. The extruded sheets were guided trough cooling cylinders to fix thickness cylinders. The space between the cylinders was 4 mm. The densities of final sheets were about 0.7027 g/cm^3, there were only slight variations.

2.1. SEM analysis

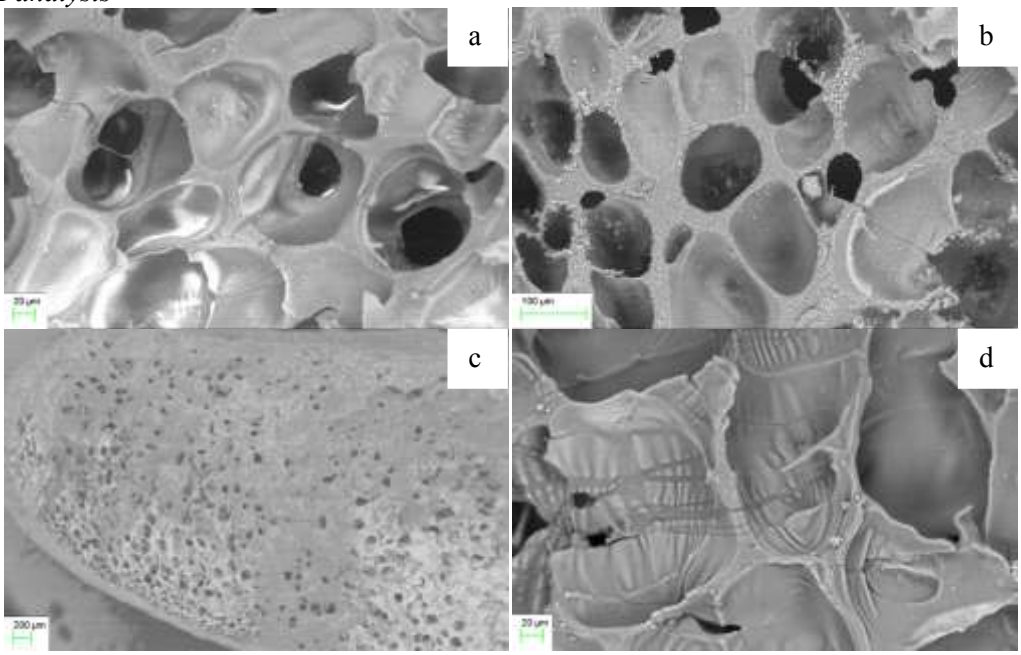

Figure 1. Failures of structure cells: a) charges; b) unloaded filler; c) glue in the cellular structure; d) membrane formation

The final structures of the mixtures were studied by Scanning Electron Microscopy. The SEM images show the fractured surface on different specimens. Furthermore the shape- and size of the cells can be tested.

Process of sample preparation [7]:

- Used liquid nitrogen to fractured the samples
- The samples must be electrically conductive. A conductive layer on the insulating materials has to be formed. The conductive layer was gold.
- The samples were fixed on a metal plate with universal glue.
- Used ZEISS SEM to observe samples, cells sizes and wall thicknesses were measured at 2 areas each

Figure 1. shows a little bright area on the surface, where the conductive layer was too thin (lach of gold), therefore the effect of reflecting electrons is visible. It was also observed that the particle sizes of $CaCO_3$ have poor dispersion in the PVC in Fig 1. b). The Fig 1. c) shows the open cells structure and the effect of glue infusion. The adhesive material migrated into the cellular structure thus destroying the whole foam structure. The phase of the specimen and the gilding formed a membranous material on the Fig 1. d). This determined that the gilding layer was too thin, so the surface charged.

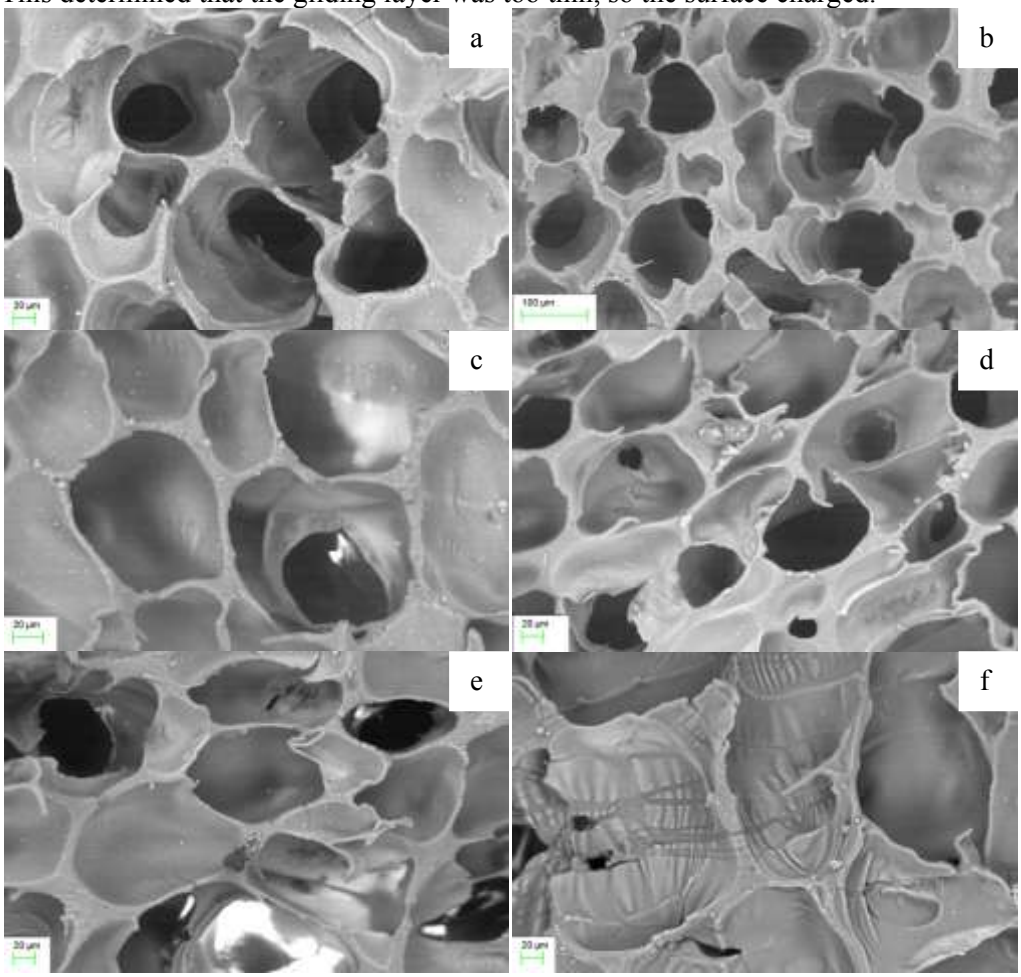

Figure 2. Scanning Electron Microscope fractured structure of several types of fillers [a - treated calcium carbonate; b - surface treated white marble; c - fine uncoated calcium carbonate; d –calcium carbonate; e - surface treated calcium carbonate ; f – coated calcium carbonate]

The Figure 2. illustrates the structural effect of various fillers. The cells shape (open and close cells) the changes in all samples. Fig 2. f) sample have much more closed cell structures than the other samples. Indicating that the fillers have modifier effect of the morphology. Based on Fig 2. it can be seen that the cells have seemingly similar density distribution in all samples. During the formation of the structure,

the machine orientation has an effect on the shape of the cells. Fig 2. a) and 2. e) shows that the various fillers further orientate the foam. In Fig. 2. c) and 2. d) it is also noticed that the surface treatment, untreated surface and the uncoated filler does not have a major effect on the form of the final structure. Fig 2. c) has different magnification 350x vs. 250x this is why the cell sizes are larger here seemingly.

The mixtures differ in the 5, 10, 20 phr dosage of marble filler. Fig. 3. shows the changes of the wall thickness and cell size by added different marble concentration. The wall thickness and the size of the cells show irregularity distribution for mixtures of 5 and 20. The smallest size of cells and also unified structure is observed in case of the mixture with 10 phr. I show only one result of mixture 1, because the other measurements gave similar results.
In case of 10 phr wall structure was equable and the cells sizes were approximately the same in the whole sample. Based on Fig. 3. for the further production and examination the 10 phr samples were used.

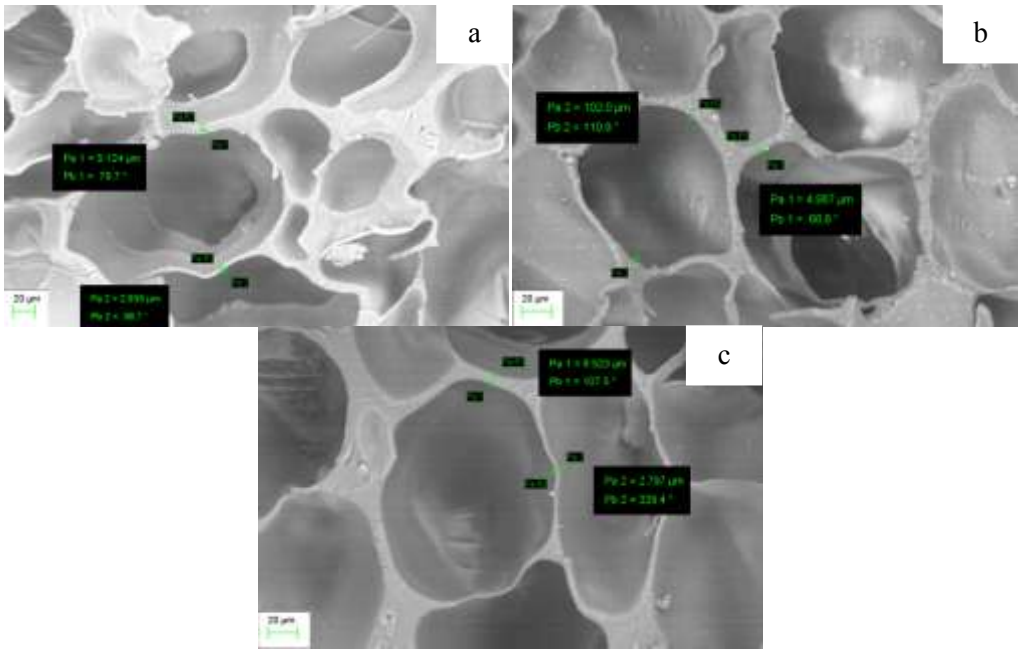

Figure 3. Effects of different dosage of marble: a) 5 b) 10 c) 20

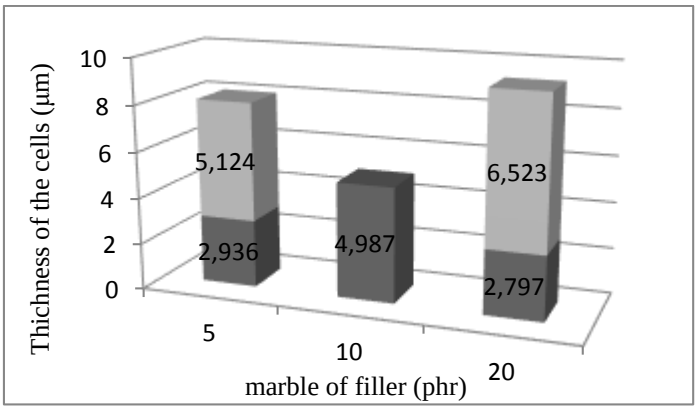

Figure 4. Thicknesses of the cell walls according to the dosage of marble

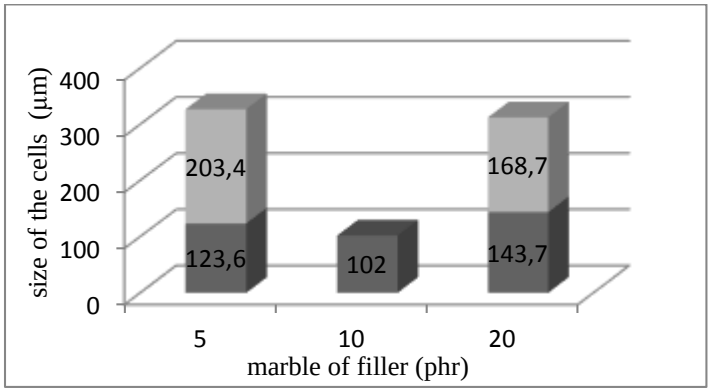

Figure 5. Size of the cells according to the dosage of marble

3. Conclusion

Several types of blends were produced with different types of fillers. In this paper the main goal was to determine the modifier effects of the $CaCO_3$ and the marble filler. Fillers greatly influence the morphology of the cellular structure. Accordingly, the prepared mixtures were tested by SEM analysis. From the SEM analysis the structure of the blend can be examined. The results of SEM examinations show that the surface treatment additive does not modify the structures. The different dose and type of fillers other changed the orientation and the shape of the cells in the structure. Furthermore, the size of the fillers more significantly affects the size and the wall thickness of the final cells. From the result of the six types of specimens I choose the marble filled for the future measurements, because despite of the small particle size of the cells. It has a more even distribution structure than the other samples. The aim of the research was formation of regular cells shape, and the apparent changes can be observed on the samples. Accordingly, certain structures can be formed, which are suitable for insulation foams.

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