The effect of calcium carbonate content and particle size on the mechanical and morphological properties of a PVC foamed layer used for coated textiles

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ABSTRACT – REZUMAT

The effect of calcium carbonate content and particle size on the mechanical and morphological properties of a PVC foamed layer used for coated textiles

Due to recent developments in composite formulations and coating technology, polyvinyl chloride (PVC)-coated textiles are becoming increasingly popular in the textile industry. The most critical properties of PVC-coated textiles are their mechanical characteristics and morphological properties because they control their cost well. This study focuses on the impact of filler diameter and content on the mechanical properties of the PVC foam layer used for coated textiles stuffed with calcium carbonate ($CaCO_3$). The mechanical properties of the PVC foamed layer (breaking load, tearing strength and elongation at break) were studied. The applied contents were found to significantly influence the mechanical properties of the PVC foamed layer. The addition of $CaCO_3$ fillers improved their mechanical properties. The results also showed that mechanical properties were enhanced using calcium carbonate with different particle sizes; the smallest particle size gave the highest mechanical resistance. The morphology of the different samples showed that the employment of calcium carbonate increases foam formation. A higher $CaCO_3$ content can deteriorate the PVC foam layer structure. Using a small filler particle diameter decreased pore sizes and ameliorated the regularity in pore size distribution.

Keywords: *coated fabric, filler, coating, PVC, $CaCO_3$, content, particle size*

Influența conținutului de carbonat de calciu și al dimensiunilor particulelor asupra proprietăților mecanice și morfologice ale unui strat de spumă PVC utilizat pentru peliculizarea materialelor textile

Datorită dezvoltării recente în compozite și tehnologia de finisare, textilele peliculizate cu clorură de polivinil (PVC) devin din ce în ce mai populare în industria textilă. Cele mai importante proprietăți ale textilelor peliculizate cu PVC sunt caracteristicile lor mecanice și proprietățile morfologice, deoarece costul este ușor controlabil. Acest studiu se concentrează asupra impactului diametrului și conținutului de umplutură asupra proprietăților mecanice ale stratului de spumă PVC utilizat pentru textilele peliculizate îmbibate cu carbonat de calciu ($CaCO_3$). Au fost studiate proprietățile mecanice ale stratului de spumă PVC (sarcina la rupere, rezistența la rupere și alungirea la rupere). S-a constatat că acest conținut aplicat influențează semnificativ proprietățile mecanice ale stratului de spumă PVC. Adiția de $CaCO_3$ a îmbunătățit proprietățile mecanice. Rezultatele au arătat, de asemenea, că proprietățile mecanice au fost îmbunătățite folosind carbonat de calciu cu diferite dimensiuni ale particulelor; cea mai mică dimensiune a particulei a dat cea mai mare rezistență mecanică. Morfologia diferitelor probe a arătat că utilizarea carbonatului de calciu crește formarea de spumă. Un conținut mai mare de $CaCO_3$ poate deteriora structura stratului de spumă PVC. Folosirea unui diametru mic de particule de umplutură a redus dimensiunea porilor și a îmbunătățit regularitatea distribuției dimensiunii porilor.

Cuvinte-cheie: *țesătură peliculizată, umplutură, acoperire, PVC, $CaCO_3$, conținut, dimensiunea particulelor*

INTRODUCTION

Coated textiles represent a highly used group of textile materials. They are used in a variety of industries, including footwear, automobiles, upholstery, and clothing. These fabrics usually consist of a topcoat, a middle coat, and backing cloth. PVC-coated textiles are easy to process, low in cost, and have a consistent appearance [1–3].

Their main components include a polymer (PVC), a stabilizer, a plasticizer, and a filler. These components are uniformly mixed to form the plastisol. The different components are important for the general behaviour of the final product. However, the filler characteristics are a key issue in determining many of the technical properties of PVC-coated textiles.

Almost 80% of the fillers used in PVC-coated materials are based on calcium carbonate Titanium dioxide is the second most used filler, approximately 12%, followed by calcined clay approximately 5%. The remains are other materials, including glass and talc [4–6]. Calcium carbonate is an adequate filler for PVC-coated materials. The specific properties of this chemical, such as its low cost of production as well as its availability, encourage industries to enhance its performance and optimize its use. Traditionally, $CaCO_3$ filler was considered an additive, and because of its reduced surface area and unfavourable geometrical features, it was used to lower the cost, increase the melt viscosity and moderately increase the modulus of the PVC final product, whereas tensile strength and deformability remained unaltered or even reduced in some situations. Recently, the particle size and shape distribution, the dispersion degree, and the filler content have been reported to affect PVC material properties when filled with calcium carbonate [7, 8]. Thus, the applications of $CaCO_3$ particles on PVC product quality are determined by several parameters, including specific surface area, morphology, size, brightness, oil adsorption, and purity. Particle morphology and size play an important role in industrial applications, and control of crystal shape and size is therefore a basic requirement from the viewpoint of applications. The impact of calcium carbonate particles was attributed to their large interfacial surface and small particle size, which create a strong adhesion between the plastisol and the filler and enhance the van der Waals interaction force between them [9–11]. Numerous studies have been carried out to correlate the calcium carbonate content and particle size with the properties of PVC materials. Sun et al. [12] showed that the impact strength and the tensile strength of PVC increase considerably with decreasing $CaCO_3$ particle size. Nakamura et al. [13] observed that the yield stress of PVC composites decreases while increasing the filler content. The effect of calcium carbonate particle size on PVC foam was studied by Azimipour et al. [14] and Demir et al. [15].

In general, ample research has been conducted using PVC plastics and composites. However, few studies have been performed to study the effects of calcium carbonate concentration and particle size on the properties of PVC layers used for the production of coated textiles. The use of calcium carbonate with a small particle size may help increase the mechanical properties of PVC-coated textiles at a lower filler level, which may result in a lower formulation cost. Developing PVC-coated textiles with lower costs and improved quality will aid industry growth.

Several properties are required to improve the practical usability of PVC-coated fabrics as textile materials. This work aims to explore the effect of calcium carbonate content and particle size on microstructural properties, breaking load, tearing strength, and elongation to break the PVC internal layer used for coated textiles.

EXPERIMENTAL PROCEDURE

Raw materials

Commercial grades of PVC, diisononyl phthalate (DINP), mixed-metal heat stabilizer, kicker, azodicarbonamide, pigment, transfer paper and poly-cotton knitted fabric base were kindly provided by the Plastiss Company (Sayada, Monastir, Tunisia). $CaCO_3$ particles with different ground micron sizes were provided by the SOFAP Company (Sfax-Tunisia).

Preparation of polymeric layer formulations

The formulations used to produce the PVC sheets (superficial and expanded layers) are shown in table 1. All the ingredients were blended using a mechanical stirrer until a homogenous mixture was obtained, with a desired viscosity level fixed by the company. To reach the desired viscosity, the amount of plasticizer was variable.

Production of PVC leather fabric

We used the transfer coating technique for the production of PVC-coated textiles. On the first coating head, the plastisol is spread on the transfer paper using a blade while controlling the thickness. The formed layer, called the skin layer or superficial layer, is then dried at 140°C for 20 seconds and cooled. On the second coating head, the plastisol is spread on the first formed layer using a blade at a given thickness. This second layer forms foam after being dried at 200°C for 80 seconds and is called the bottom layer or expanded layer. Later, the knitted poly-cotton fabric is laminated to the resulting PVC layers, and the complex thus formed is passed through the main furnace where gelling and expansion of the cellular plastisol take place. After cooling, the paper and the formed PVC-coated textile are detached and rolled up separately.

Figure 1 shows some photographs of the prepared PVC leather fabric. Figure 2 presents the coating process.

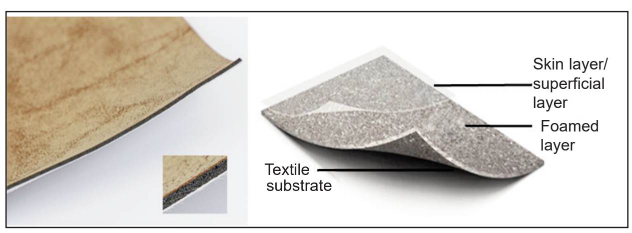

Fig. 1. PVC leather fabric

Table 1

SUPERFICIAL AND EXPANDED LAYER FORMULATIONS						
Layer	**Ingredient contents expressed as parts per hundred of resin (phr)**					
	PVC resin	**Plasticizer**	**Stabilizer**	**Calcium Carbonate**	**Kicker**	**Azodicarbonamide**
Superficial	100	X	1.5	Y	Ø	Ø
Expanded	75	Z	Ø	Y	2	4

X = (70/80/82/94/102;114); Y = (0/25/50/75/100/125); Z = (37, 5/62, 5/76, 5/90, 5/102; 114).

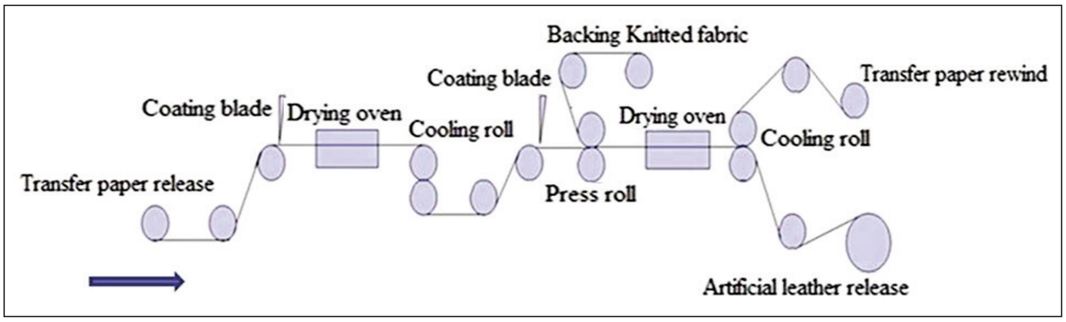

Fig. 2. Coating process

Tensile and burst tests

Tensile and burst tests were carried out according to NF EN ISO 1421-2017 standards using a testing machine (Zwich GmbH, Ulm, Germany) with a crosshead speed of 100 mm/min. Test specimens had dimensions of 50±0.5 mm in width with a sufficient length to obtain a distance of 200±1 mm between the jaws of the testing machine.

Tearing strength

The tearing strength test was performed according to NF EN ISO 4674-1-2017 using an ELMENDORF dechirometer. Tests were run in triplicate to avoid an experimental error.

Optical microscopy

The morphology and structure of the expanded PVC layers were observed using a Leica DM 500 optical microscope equipped with different objectives connected to a colour view camera and controlled by the analysis software. The materials were observed in transmission mode under different magnifications of the objective.

Scanning electron microscopy (SEM)

Detailed morphological investigations were carried out using a high-resolution FEIQ250 Thermo-Fisher ESEM with a resolution greater than 7 nm at 5–10 kV low working voltages. The cross sections of PVC foams were prepared by sharp bending and then covered by a gold layer.

RESULTS AND DISCUSSION

Mechanical properties

The effect of calcium carbonate content

Figure 3 illustrates the results of tearing strength, breaking load and elongation to break measurements

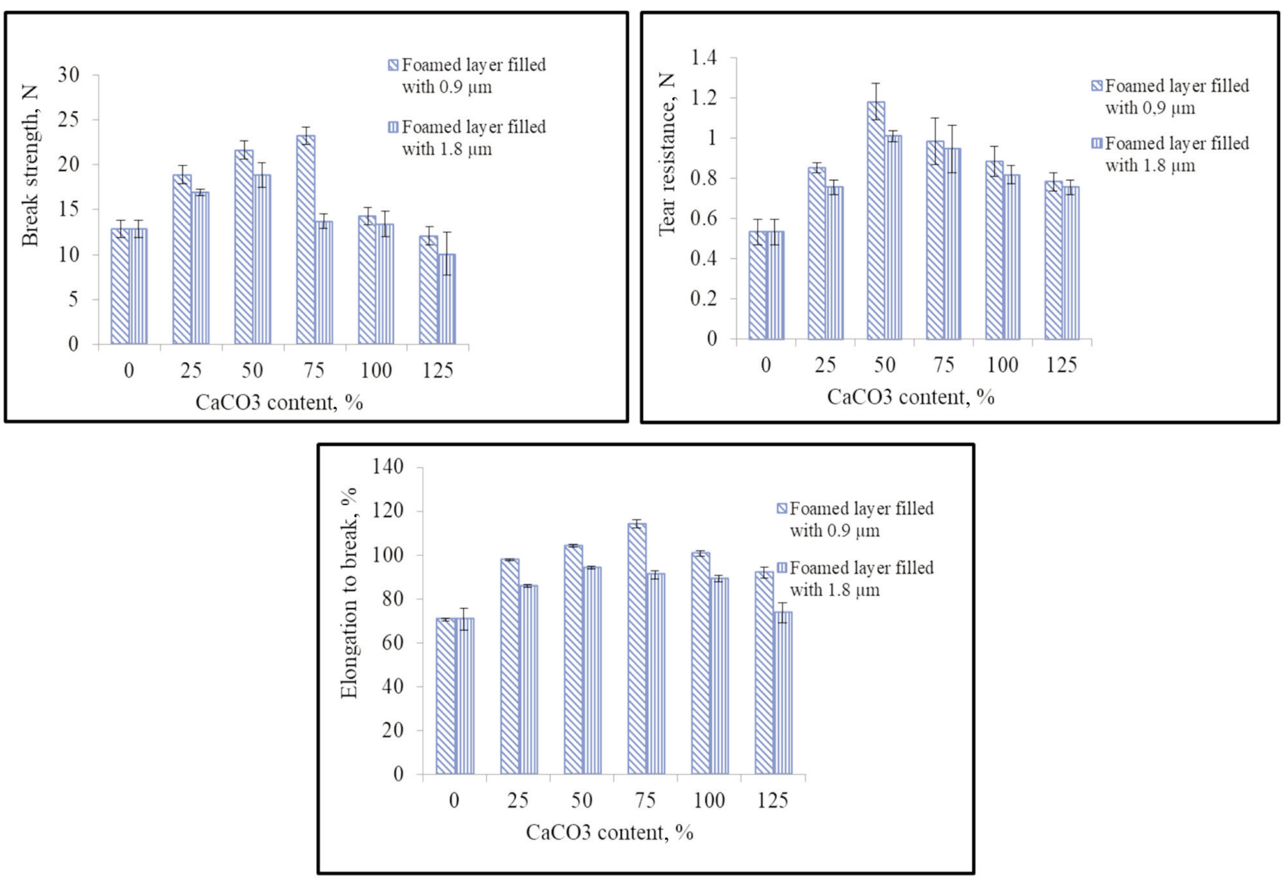

Fig. 3. Effect of $CaCO_3$ particle size and content on the mechanical properties of PVC internal layer used for coated textile

for internal layer samples at different amounts and particle sizes of calcium carbonate particles. The standard deviation of tearing strength values varies from 0.05 to 0.235, from 0.325 to 2.4 for the breaking load results and from 0.42 to 4.45 for the elongation to break measurements. The addition of $CaCO_3$ leads to an increase in the elongation at break, break strength, and tear resistance. The best results were obtained when the amounts of $CaCO_3$ reached 50 and 75%. The data suggested that the surface adhesion between $CaCO_3$ particles and the PVC matrix plays a crucial role in improving the mechanical properties of the prepared PVC layers. In fact, the stronger the interfacial adhesion is, the greater the stress moved to the $CaCO_3$ entities from the PVC matrix, leading to higher mechanical properties. However, an excess $CaCO_3$ content results in a low dispersion rate of particles in the PVC matrix. This indicates that there is an optimal amount of $CaCO_3$ to be added for the preparation of such a PVC layer. The interfacial adhesion between CaCO3 and the PVC matrix is then too weak, which causes a decrease in the breaking load, elongation to break and tearing strength of the PVC layers.

These outcomes agree with previous studies that have shown that an excess of $CaCO_3$ results in a decrease in the tensile strength of PVC and that the mechanical properties of PVC materials are influenced by the interfacial adhesion between the PVC matrix and the $CaCO_3$ particles [12–14]. Only a small amount of strain is likely to be transferred from the PVC matrix to the inorganic filler.

The effect of calcium carbonate particle size

Figure 3 also shows that the finer the filler particles are, the better the mechanical properties. The PVC layers filled with fine $CaCO_3$ have a higher elongation to break, tear resistance, and break strength.

The use of a small particle size results in an intense increase in the specific surface area of the filler particles, resulting in a rise in the interfacial contact area between the filler and the PVC matrix. The larger the interfacial contact area is, the better the transmission of stress from the PVC matrix to the filler particles, resulting in higher mechanical properties.

A literature survey shows that fine calcium carbonate particles significantly improve the mechanical characteristics of PVC matrices [12–15].

Structural properties

The effect of calcium carbonate content

The microscopic images of the PVC internal layer filled with different types of calcium carbonate particles at different contents are presented in figure 4. For the sample prepared without filler, the voids appear large, crowded, and very close to each other, and the presence of open cells is evident. These voids are a result of the foaming process, in which two main steps are included: bubble nucleation and growth. By adding the filler, the small voids start to move away from each other, the cell number increases, and closed cells are clearly observed, forming a regular pore shape and uniform structure. It can be concluded that the presence of calcium carbonate particles can promote foam formation by increasing the number of nucleation sites for bubble genesis. These outcomes have been confirmed by many researchers [12, 14, 15].

Using a content of 100% calcium carbonate can boost the liberation of decomposed gases, increase the nucleation sites and raise the total energy between the different bubbles. Therefore, there is a

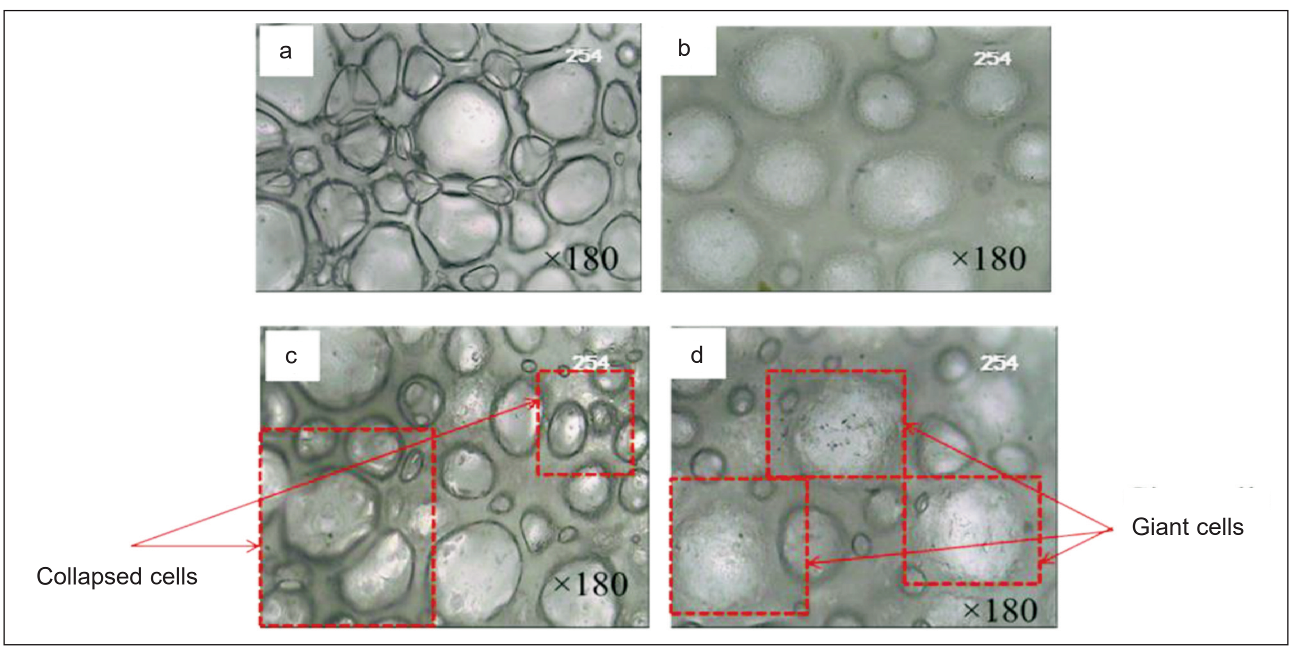

Fig. 4. Effect of $CaCO_3$ (0.9 μm) content on the structural properties of the internal layer: *a* – without filler; *b* – with 50% of $CaCO_3$; *c* – with 100% of $CaCO_3$; *d* – with 125% of $CaCO_3$

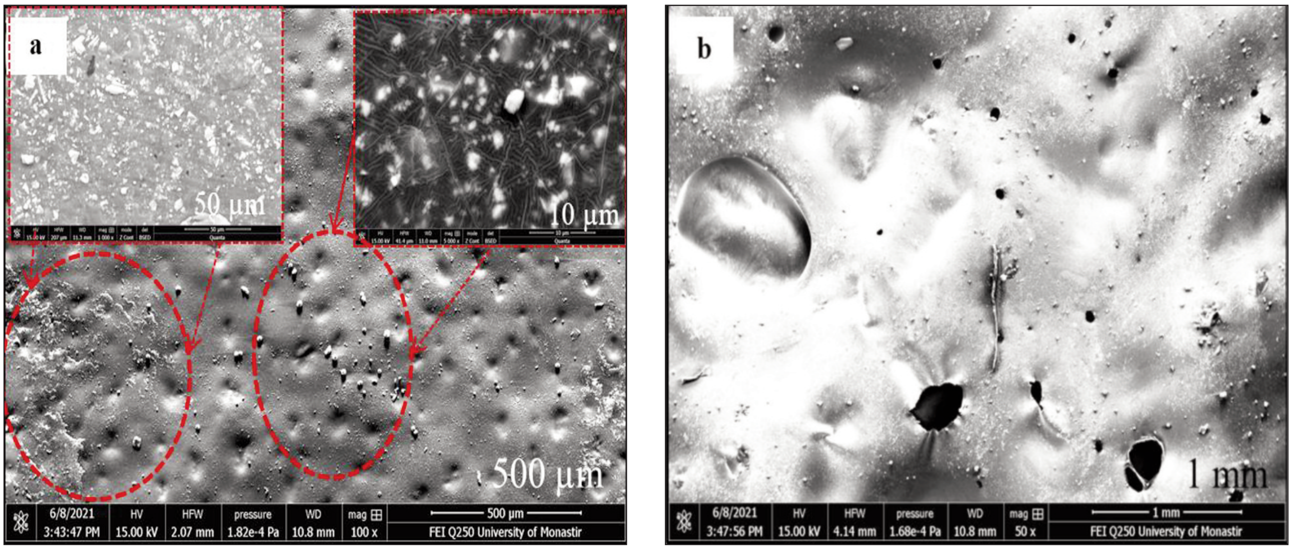

Fig. 5. SEM images of the internal layer prepared using 100% of $CaCO_3$ (0.9 µm) at different magnifications

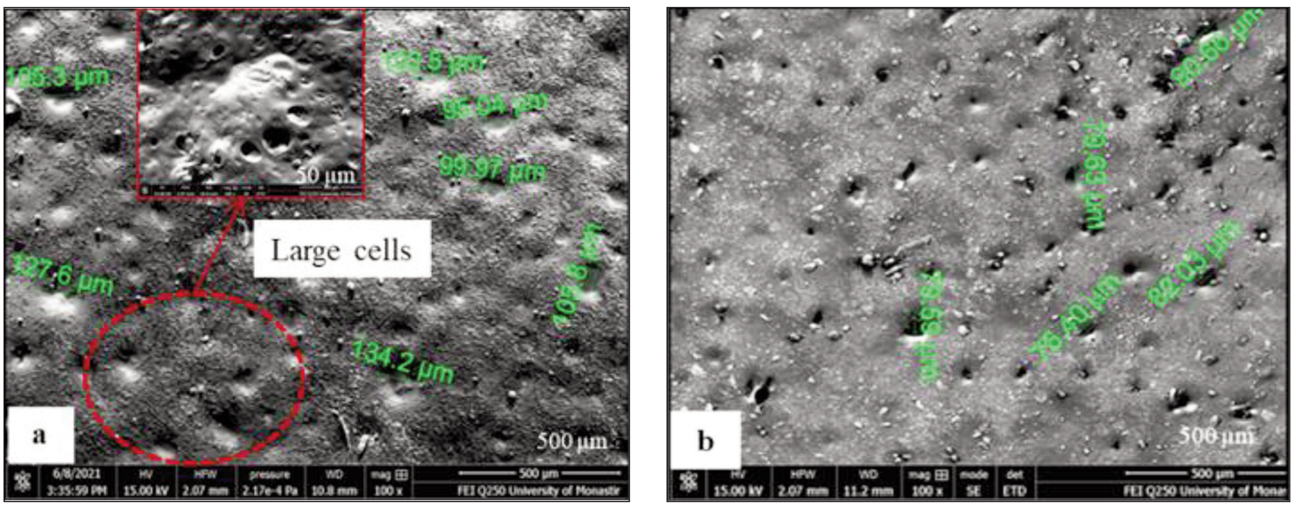

Fig. 6. SEM images of the internal layer prepared using 50% of CaCO3: *a* – 1.8 µm; *b* – 0.9 µm

higher possibility of forming collapsed cells, as observed in figure 4, *c*, which can create more gigantic cells, as evidenced in figure 4, *d*, so the foam structure begins to deteriorate.

These results confirm the poor mechanical quality previously observed for samples prepared without filler and for samples prepared with an excess of filler.

Figure 5 shows an SEM micrograph of the internal layer using 100% $CaCO_3$ (0.9 µm). From the images, it can be observed that $CaCO_3$ particles are scattered on the surface of the layer. We can also observe the irregular and rough surface of the samples. This result is due to the presence of an excess of calcium carbonate, which is poorly distributed in the PVC matrix. The poor dispersion of the filler results in poor adhesion between the PVC matrix and the filler.

Figure 5, *b* shows the appearance of microvoids and cracks, which are due to the poor dispersion of the filler. Several studies have shown that the poor dispersion of the fillers deteriorates the mechanical properties of the final materials [10–13].

The effect of calcium carbonate particle size

Figure 6 shows the pores forming the PVC foam of the internal layer. Using fine calcium carbonate particles (0.9 µm), the pores appear more uniform and smaller than those of the sample prepared using large calcium carbonate particles (1.8 µm). Using small filler particles, the liberation of the decomposed gases is better, which enhances the creation of additional nucleation sites for bubble formation, resulting in a uniform structure.

James Lee [17] confirmed these results and showed that the vast surface area of nanoparticles provides more intimate contact between the filler particles, PVC matrix, and gas, resulting in the enhancement of the foam structure and its mechanical properties.

The mechanical results are in good agreement with the morphological observations and are also in agreement with previous work by Azimipour et al. [14], who studied the effect of filler particle size on the morphological behaviour of the PVC foam.

CONCLUSIONS

This research has been conducted to investigate the effects of calcium carbonate content and particle size on the mechanical and structural properties of the PVC foam layer used for coated textile production. It is important to know that calcium carbonate is the cheapest chemical among all the others used in the production of the polymeric layers used for PVC-coated textiles.

Through various analyses, we found that both the content and particle size of calcium carbonate have strong effects on mechanical and morphological properties. In particular, the most significant effect was detected when using fine calcium carbonate particles for the production of the PVC internal layer.

The low filler concentration of calcium carbonate resulted in positive changes in mechanical and structural characteristics. However, the structure of the PVC layers becomes mechanically poor at higher filler rates.

These outcomes have been confirmed by many studies that have investigated the effect of the content and particle size of calcium carbonate on the final properties of PVC materials.

Numerous authors [17–25] have studied the effects of calcium carbonate content and particle size on the behaviour of PVC in fires; thus, the effect of $CaCO_3$ content and particle size on the thermal characteristics of PVC-coated textiles will be evaluated in subsequent work.

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