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Investigation of wettability behavior and surface topology of PVC materials used in outdoor applications

Dış mekan uygulamalarında kullanılan PVC malzemelerin islanabilirlik davranışının ve yüzey topolojisinin incelenmesi

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Investigation of Wettability Behavior and Surface Topology of PVC Materials Used in Outdoor Applications

Highlights

- *Polyvinyl chloride materials used in outdoor applications*
- *Analysis by Scanning Electron Microscope*
- *Wettability behavior*
- *Contact angle measurement*
- *Surface roughness*

Graphical Abstract

Since the behavior of wetting is related to the contact angle, the lower contact angle reasons more wetting of the material.

Table 1. Contact angle measurement values

Measurement	Sample 1	Sample 2	Sample 3	Sample 4
1	71.581 °	76.699 °	64.435 °	64.708 °
2	72.540 °	74.311 °	63.916 °	63.511 °
3	73.571 °	73.883 °	66.542 °	71.47 °
4	71.901 °	76.546 °	64.812 °	70.994 °
5	74.673 °	75.337 °	69.753 °	67.991 °
6	73.517 °	77.582 °	67.822 °	66.392 °
Average	**73±2 °**	**76±2 °**	**67±3 °**	**68±4 °**

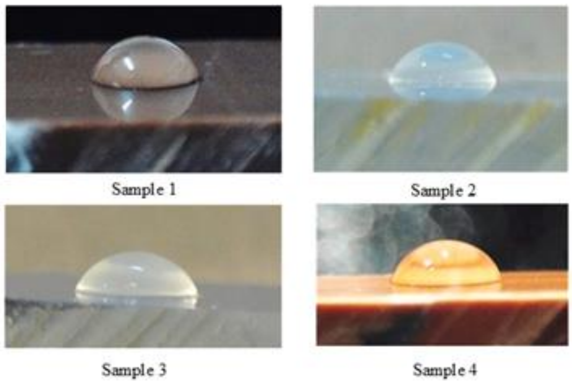

Figure. Contact angle measurements of Polyvinyl chloride samples

Aim

Investigation of wettability behavior of polyvinyl chloride materials.

Design & Methodology

Contact angle measurements were made for the wettability of Polyvinyl chloride materials used in outdoor applications today. Roughness and structural characteristics were analyzed.

Originality

The wettability, roughness, and structural characteristics of Polyvinyl chloride materials have been correlated.

Findings

It has been observed that the homogeneous structure and roughness values of Polyvinyl chloride materials affect the contact angle.

Conclusion

The contact angle measurements of the samples were made and their relations with the roughness values and SEM analyses were investigated. It is understood from the measurement results that the contact angle value is high in the samples with a small roughness value and homogeneous and smooth in SEM analysis.

Declaration of Ethical Standards

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Investigation of Wettability Behavior and Surface Topology of PVC Materials Used in Outdoor Applications

Araştırma Makalesi / Research Article

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ABSTRACT

The wettability behavior is crucial in determining the materials' applications and durability. The measurement of contact angle is utilized to assess the wettability behavior. In this study, commercially produced PVC profiles were sampled, and a contact angle measurement system, consisting of both software and hardware, was developed to measure the contact angle of the samples. The contact angle measurements were conducted by placing approximately 20 µl of MilliQ Ultra-Pure water on the samples, and each sample was measured six times, with the average being taken. A device for measuring roughness was used to determine the surface roughness of the samples, and the average roughness value was obtained from four different parts of each sample. Additionally, SEM images of each sample were taken to conduct surface and structural analyses. The correlation between roughness, SEM image analysis results, and contact angle was examined in the research study. Moreover, the wettability behavior of PVC materials was analyzed by evaluating the impact of the elements in their structure and their homogeneity on the contact angle values.

Keywords: PVC material, SEM analysis, contact angle, wettability behavior, roughness.

Dış Mekan Uygulamalarında Kullanılan PVC Malzemelerin Islanabilirlik Davranışının ve Yüzey Topolojisinin İncelenmesi

ÖZ

Islanabilirlik davranışı malzemelerin kullanım alanlarının ve servis ömrünün belirlenmesinde önemli bir parametredir. Islanabilirlik davranışını belirlemek için temas açısı ölçümü kullanılır. Bu çalışma kapsamında ticari olarak üretilen PVC profillerden numuneler alınmıştır. Numunelerin temas açısı ölçümlerinin yapılabilmesi için yazılım ve donanımdan oluşan temas açısı ölçüm sistemi geliştirilmiştir. Numunelerin üzerine yaklaşık 20 µl MilliQ Ultra-Pure su damlatılarak temas açısı ölçümleri yapıldı. Her numune için 6 kez temas açısı ölçümü yapılarak ortalaması alındı. Numunelerin yüzey pürüzlülüğü pürüzlülük ölçüm cihazı ile ölçülmüştür. Numunelerin farklı yerlerinden 4 kez pürüzlülük ölçümleri yapılarak ortalama pürüzlülük değeri elde edildi. Ayrıca her bir numunenin SEM görüntüleri alınarak yüzey ve yapısal analizleri yapılmıştır. Sonuç olarak temas açısı, pürüzlülük ve SEM görüntü analiz sonuçları arasındaki ilişki araştırıldı. Ayrıca PVC malzemelerin yapısındaki elementlerin ve homojenlik yapısının temas açısı değerlerine etkisi değerlendirilerek PVC malzemelerin ıslanabilirlik davranışı yorumlanmıştır.

Anahtar Kelimeler: PVC malzeme, SEM analizi, temas açısı, ıslanabilirlik davranşı, pürüzlülük.

1. INTRODUCTION

Polyvinyl chloride, the abbreviated name of PVC, is one of the most important products used in the chemical industry, and today, it has begun to form the basis of building materials [1]. PVC, a widely used material, is composed of two primary elements: Chlorine, derived from salt, and Ethylene, obtained from crude oil. The conversion of ethylene dichloride compound to Vinyl Chloride Monomer (VCM) gas occurs at extremely high temperatures. VCM undergoes polymerization to transform into a durable and stable powder, producing PVC in powder form. PVC, a kind of polymer, is produced in petrochemical factories and turned into desired products by adding various additives. The construction industry utilizes over half of the PVC produced globally. As a building material, PVC is inexpensive and easy to install. Among the usage areas of PVC are pipe and installation materials, window and door profiles, vinyl siding, hobby materials, electrical cables, and flooring. It is also preferred in the wastewater industry due to its flexibility and cheapness [2-5]. In addition, PVC materials have increased in applications where easy workability, high resistance to chemicals, corrosion, impact resistance, color, air tightness, and water resistance are of great importance [6-10]. PVC has become a more popular choice of construction material in various fields, leading to the replacement of traditional materials like wood, concrete, and polymer clay in recent times.

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Chlorine atoms in the monomer of PVC material are covalently bonded to carbon atoms, and a rigid polymeric material emerges due to dipolar solid interactions between the chains of these monomers [11,12]. With its low density, SiO_2-filled PVC is used in household tools, building materials, the automobile industry, and the electrical industry. Today, $CaCO_3$-filled PVC is widely used in construction materials, electrical cable coatings, food, and automobile industries, as well as building materials [13-15]. SiO_2 and glass fiber fillers increase mechanical strength, especially abrasion resistance, provide dimensional stability, and reduce thermal conductivity; they are therefore used to manufacture plastic products that will work for a long time [16]. In addition, additives such as $CaCO_3$ filling reduce the product cost, increase the mechanical strength, and decrease the thermal conductivity unless used excessively [17,18].

The wettability behavior of materials is one of the most critical factors in determining their usage areas [19,20]. To determine the wettability behavior, the contact angle (CA) is measured. Measuring the angle formed by the liquid dropped on the solid material with the solid, liquid, and air provides valuable insight into the material's wettability behavior. However, wettability behavior is affected by factors such as the surface roughness of the solid material, its pollution, the type of dripping liquid, its volume, the falling distance, the vibration, and the temperature of the environment [21].

Apart from the professional CA measurement systems used in CA measurement, contact measurement can also be performed with measurement setups to be prepared. Especially with high-resolution digital microscopes, liquid dripping syringe assembly, adjustment mechanisms, and software that can control them, desired measurements can be made.

In this study, different trademarked PVC samples with commercially available Nace code 22.23.08 were used to examine the wettability behavior of PVC materials used in the production of windows and doors. SEM images were obtained to investigate the structural properties of the samples. It was produced by designing a measurement system for the CA required to determine the wetting behavior. The CA of each sample was measured and commented on with SEM images.

2. WETTABILITY BEHAVIOR and CONTACT ANGLE

Examining wettability behavior is important in many branches of science [22]. It is used extensively in many areas, from ceramic to PVC materials [23,24]. Determination of wettability behavior is provided by CA measurement. The CA is the angle formed between the solid and liquid material [25,26]. However, the effect of the ambient air on this angle should not be forgotten. The magnitude of the cohesion forces and adhesion forces between the molecules of the liquid and solid, respectively, determines the value of the CA [27]. The CA value between a liquid and a solid is directly proportional to the magnitude of cohesion forces relative to adhesion forces. A high CA signifies weaker gravitational forces between the liquid and solid, whereas a low one signifies more vital gravitational forces. Various methods are utilized to calculate CAs, including the half angle, tangential, Young-Laplace, ellipse, and polynomial methods [28]. In addition, there are computer programs prepared for CA measurements. One of them is the ImageJ program, which is open to use. The DropSnake method available in the ImageJ program can be utilized to conduct CA measurements.

Young first explained the wettability behavior [29]. The CA between the surface of the material and the liquid drop is the most important factor explaining the wettability behavior of the material [30]. The molecules in a liquid have equal attraction towards each other in all directions when the liquid is placed on a surface. The attractive forces between the surface and subsurface molecules cause the potential energy of the surface molecules to be lower than that of those beneath it. This results in the surface molecules being drawn towards the interior of the liquid, where they form a closely packed surface layer. Consequently, the surface layer of the liquid becomes denser and more condensed. Due to the inward pull on the surface molecules, they become arranged more regularly, resulting in the liquid drop taking on a spherical shape when it is released. The energy called surface tension ensures that it maintains its spherical shape on the surface where it is dropped [31].

The relationship between CA and surface tension is given in Equation 1. This equation is called Young's Equation and forms the basis of wettability behavior [32].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}.\cos\theta \tag{1}$$

The wettability characteristics of solid materials emerge according to the value of the CA formed when the liquid drips onto the solid materials [33]. If the CA value is below 90° ($\theta<90°$), the solid material shows hydrophilic properties, and above 90° ($\theta>90°$), the solid material offers hydrophobic properties. When the CA value is zero ($\theta=0°$), complete wetting, and the CA value is $\Theta=180°$, it is understood that there is no wetting behavior [34,35].

This equation is called Young's Equation and forms the basis of wettability behavior [36]. Young's equation is used to investigate wetting behavior on smooth solid surfaces. When the surface is rough, two different wetting models are used: Cassie-Baxter (heterogeneous wetting) and Wenzel (homogeneous wetting)[37,38]. Assuming that the rough solid surface is thoroughly wetted by the liquid is a vital aspect of the Wenzel model [39].

It is implied that there is no gas present between the liquid and the surface. Roughness increases the wetting property of the solid surface [40]. When the CA equation is created for rough surfaces, the equation obtained is called the Wenzel CA. The Wenzel CA is given in Equation 3. Here, r is the roughness factor. θ_w represents the Wenzel CA, and θ_Y represents the young CA. Equation 2 clearly states that a hydrophobic surface can become more hydrophobic when roughened [41,42].

$$\cos\theta_W = r.\cos\theta_Y \qquad (2)$$

However, when the product of r.cosθ_Y exceeds 1, equation 2 becomes undefined, and the Wenzel CA (θ_w) fails for very high roughness ratios.

The Cassie-Baxter model is used on inhomogeneous rough solid surfaces [43]. This model assumes that the air is trapped in the valleys between the surface roughness [44]. Cassie – Baxter's CA is given in equation 3.

$$\cos\theta_{CB} = f_S.\cos\theta_y - (1 - f_S) \qquad (3)$$

Here, f_S represents the solid-phase friction coefficient, $(1 - f_S)$ the compressed air friction coefficient, θ_Y represents the Young CA, and θ_{CB} the Cassie–Baxter CA [45]. Cassie-Baxter model gives much more suitable results than the Wenzel model. However, studies and discussions about the CA continue, and many factors affect the angle value. The most important ones are the roughness of the solid material, its pollution, the dropping liquid, its volume, the falling distance, and the vibration and temperature of the environment.

3. MATERIAL AND METHOD

3.1. Preparation of PVC Samples

Many companies manufacture PVC doors and windows. Samples for experimental studies were obtained from 4 companies. The commercial code of the PVC samples used is Nace Code: 22.23.08. These firms are named 1, 2, 3 and 4. Figure 1 shows the PVC materials used in experimental studies.

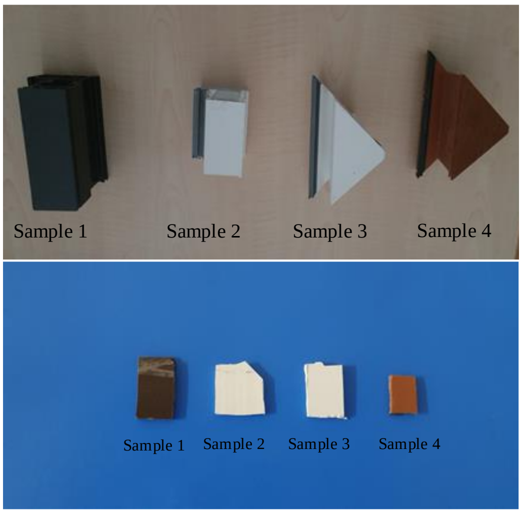

Figure 1. PVC profile samples used in experimental studies

3.2. Contact Angle Measurements of PVC Samples

The PVC samples used were subjected to a Millipore ultra-pure water cleaning process before measurements. Measurements were performed after each sample was wiped dry with 99.9% Ethanol (Merck, Darmstad, Germany). Experimental information was entered into the system's interface program. MilliQ Ultra-Pure water was put into the syringe unit on the system, and approximately 20 µl of liquid was dropped on the samples. Droplet images were taken from the sample with the interface program 10 seconds after dripping. The measurement process was repeated six times for each sample. The droplet images obtained for each sample are given in Figure 2.

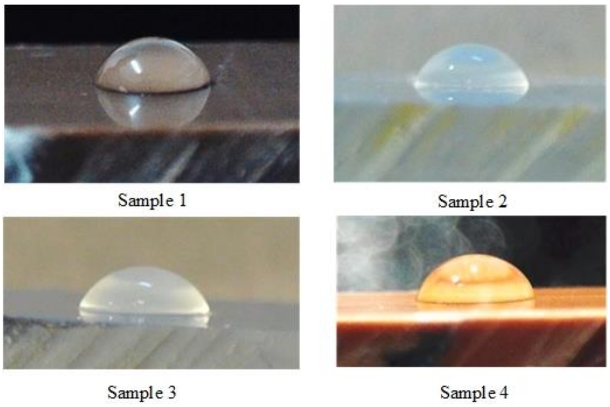

Figure 2. Droplet images on the samples

After the droplet images were obtained, CA measurements were made using the DropSnake measurement method of the ImageJ program. Figure 3 shows the CA measurements of the samples with the DropSnake measurement method.

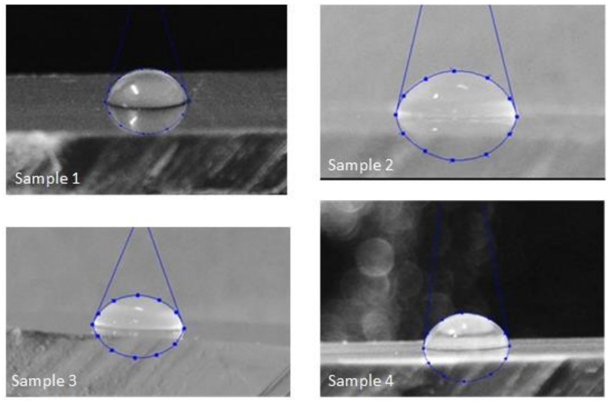

Figure 3. Measuring CAs of 4 samples with the DropSnake measurement method

3.3. Roughness Measurements

The PVC samples used were cleaned with Millipore ultra-pure water before measurements. Measurements were performed after wiping and drying with 99.9% Ethanol (Merck, Darmstadt, Germany). Mitutoyo SJ-410 Surface Roughness Tester device was used to measure the average roughness of the PVC materials.

3.4. Obtaining SEM Images of PVC Samples

SEM (Scanning Electron Microscope) images were obtained to examine the surface characteristics of the samples used. Each sample must be coated to get SEM images. PVC samples were coated with 6 nm thick gold-palladium alloy for 180 seconds. After the samples were coated, SEM images were obtained using the Carl Zeiss brand Sigma 300 VP model device.

4. RESULTS AND DISCUSSION

4.1. Contact Angle and Roughness Values Of Each Sample

CA values must be measured, which are important in determining wettability behavior. Approximately 20 microliters of MilliQ Ultra-Pure water were dropped onto each sample, and CAs were measured. CA values of the samples were measured six times and averaged. The CA measurement values are shown in Table 1.

Table 1. Contact angle measurement values

Measurement	Sample 1	Sample 2	Sample 3	Sample 4
1	71.581°	76.699 °	64.435 °	64.708 °
2	72.540 °	74.311 °	63.916 °	63.511 °
3	73.571 °	73.883 °	66.542 °	71.47 °
4	71.901 °	76.546 °	64.812 °	70.994 °
5	74.673 °	75.337 °	69.753 °	67.991 °
6	73.517 °	77.582 °	67.822 °	66.392 °
Average	**73±2** °	**76±2** °	**67±3** °	**68±4** °

The behavior of wettability is influenced by the roughness of the sample's surface. The roughness measurements of each sample obtained from PVC profile pieces were made with the Mitutoyo SJ-410 device. Measurements for each sample from different regions were made four times. The roughness measurement values are given in Table 2.

Table 2. Roughness measurement values of samples

Measurement	Sample 1	Sample 2	Sample 3	Sample 4
1	0.122	0.147	0.139	0.122
2	0.118	0.092	0.113	0.124
3	0.11	0.103	0.112	0.128
4	0.105	0.112	0.108	0.116
Average	**0.11±0.002**	**0.11±0.003**	**0.11±0.007**	**0.12±0.002**

4.2. SEM Images and EDX Graphs of Each Sample

The SEM image of each sample was obtained from two different locations of the samples. Images were enlarged 2.00 KX with an SEM device. Reference SEM images and graph EDX for sample 1 are given in Figure 6.

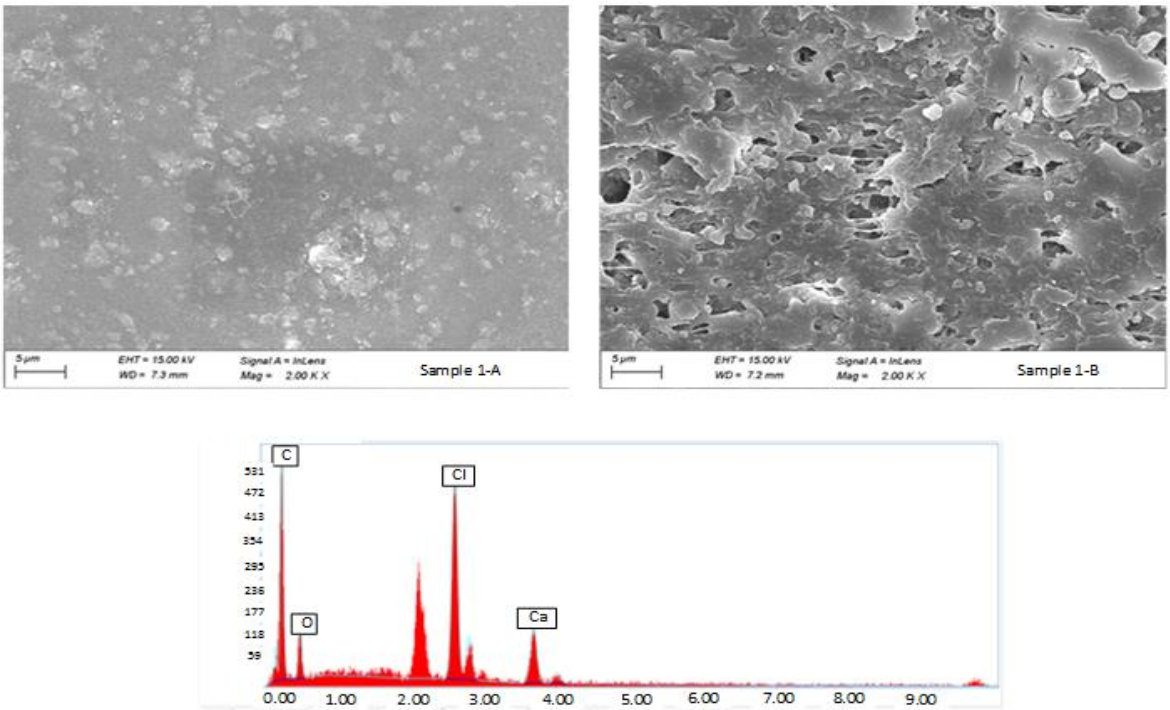

Figure 6. SEM images and EDX graph from different locations A and B of sample 1

SEM images and EDX graphs obtained from different locations of sample 2 are given in Figure 7.

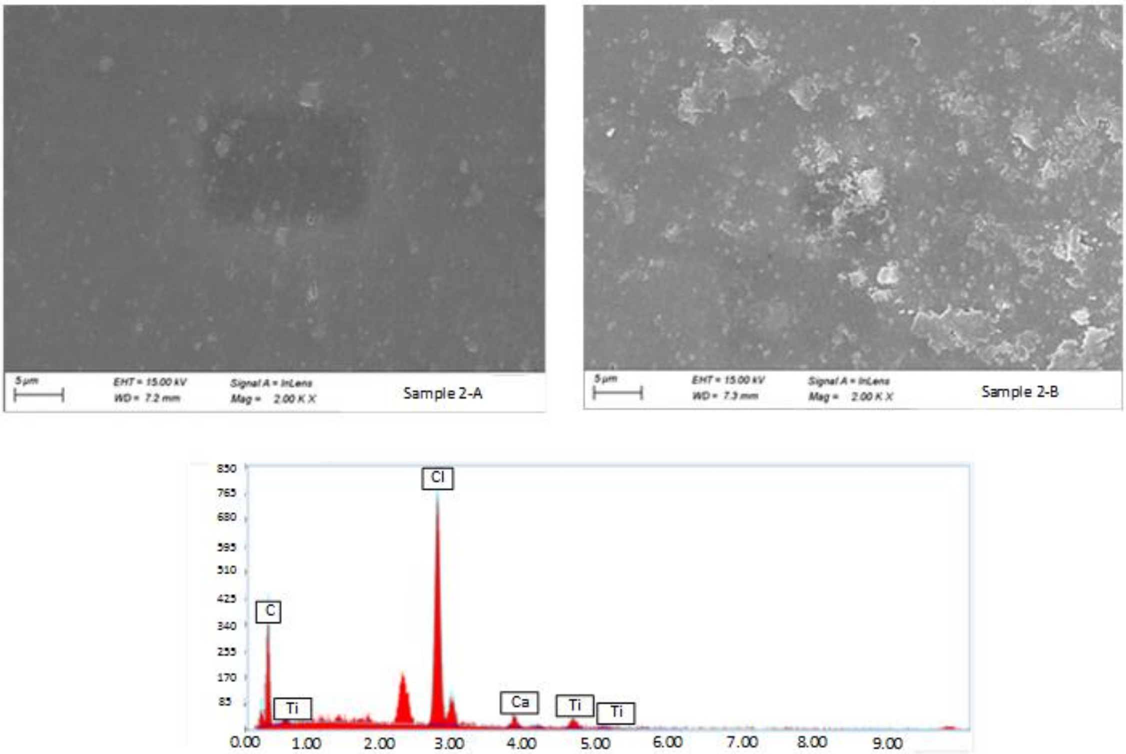

Figure 7. SEM images and EDX graph from different locations A and B of sample 2

SEM images and EDX graphs obtained from different locations of sample 3 are given in Figure 8.

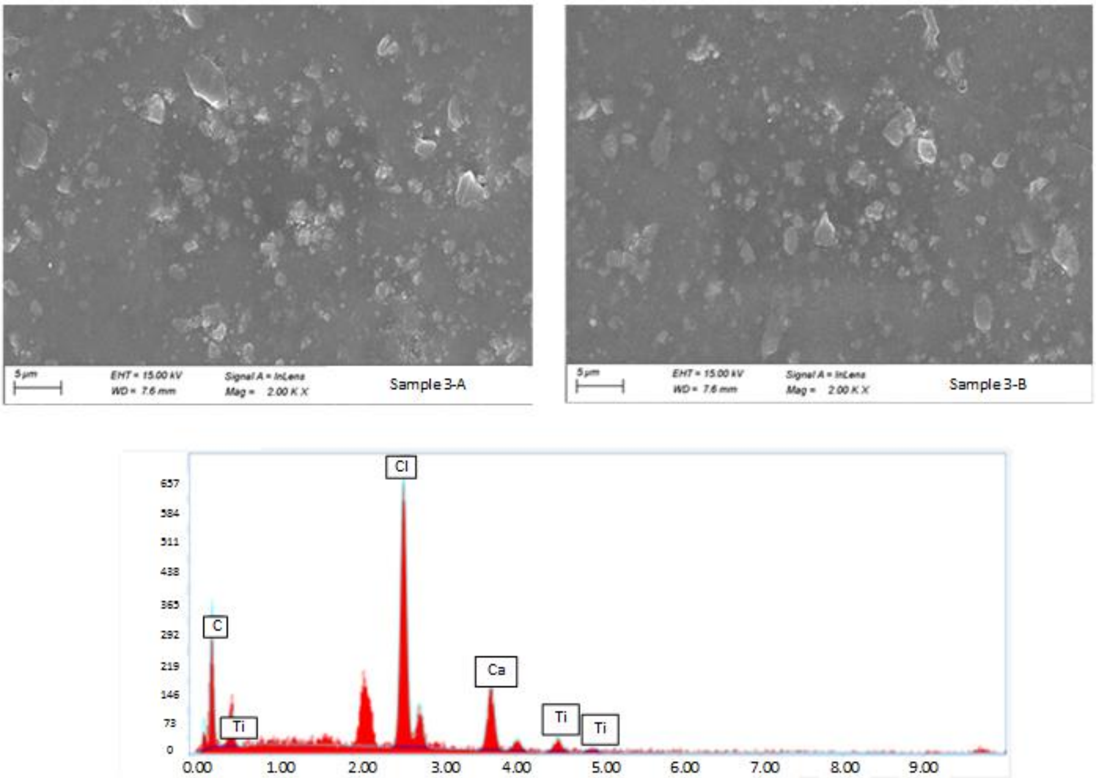

Figure 8. SEM images and EDX graph from different locations A and B of sample 3

SEM images and EDX graphs obtained from different locations of sample 4 are given in Figure 9.

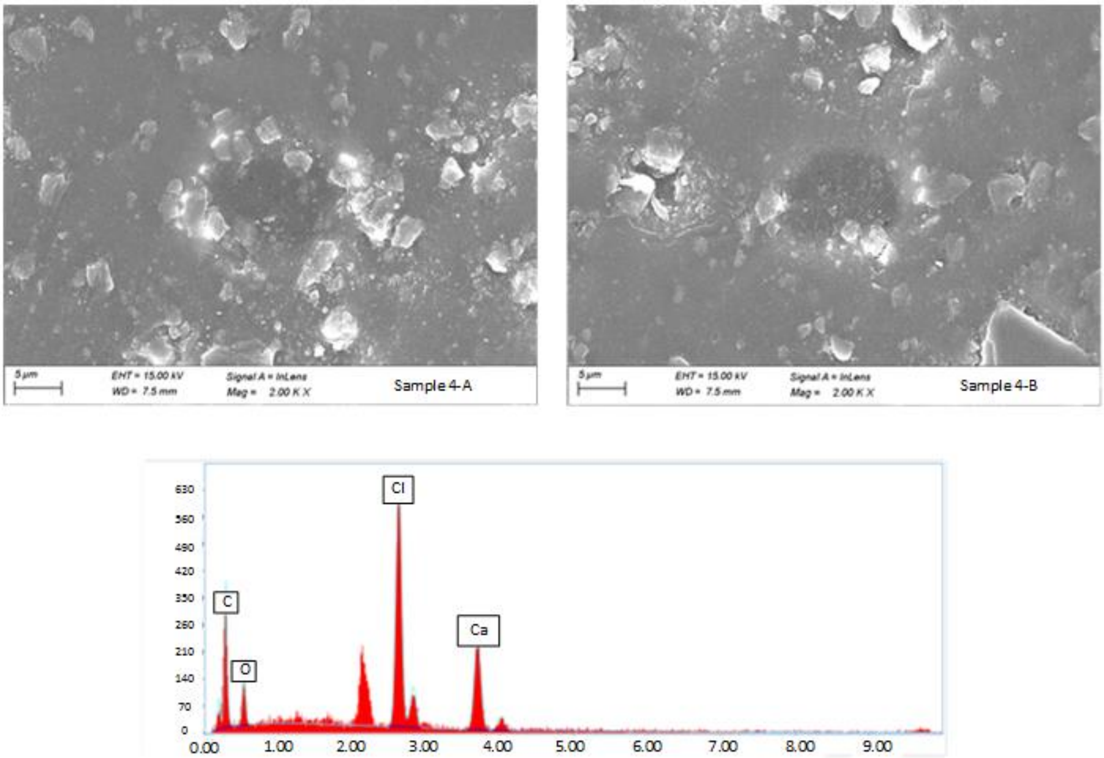

Figure 9. SEM images and EDX graph from different locations A and B of sample 4

4.3. Analysis of SEM Images and EDX Graphics of Samples

When the SEM image and EDX graph of Sample 1 were examined, 25% chlorine, 54% carbon, 9% oxygen, and 10% calcium were observed. The coating causes the cracks in the SEM images, and the surface causes the holes.

Calcium pigment and titanium oxide were used as filler in Sample 2, but calcium pigment was used too much. In the EDX graphic analysis of Sample 2, it was found that 3% Titanium, 2% Calcium, 67% Carbon, and 27% Chlorine were found in the PVC sample. It has been determined that the surface is flat, and there are no cracks or deformations. The homogeneous structure of sample 2 can be seen quite well in the measurements made from different points.

In Sample 3, calcite was used too much as a filler pigment. According to the EDX graph, it is composed of 11% calcium, 3% titanium, 25% chlorine, and 58% carbon. The surface roughness may be due to the filler pigment or high calcium level. According to the measurements from different regions, its homogeneous structure is weak. (Different zone measurement values: 18% calcium, 23% chlorine, 55% carbon) .

In the analysis of sample 4, it was observed that the surface was not flat; that is, it was rough, and there were cracks on the surface. 16% calcium, 22% chlorine, 13% oxygen, and 48.9% carbon were measured. In addition, it was understood that the homogeneous structure was weak due to measurements made from different regions. (7% calcium, 26% chlorine, 9% oxygen, and 57% carbon were measured from different zones.) The element percentages in each sample are shown in Table 3.

4.4. Discussions

In studies on PVC, Ellison and Zisman reported the CA value as 87˚ [46]. In this study, the smallest CA measurement in PVC samples was obtained as 67˚ in sample 3. This difference is not due to the cleanliness of Sample 3. Each sample was cleaned with Millipore ultra-pure water before measurements. Measurements were performed after wiping and drying with 99.9% Ethanol (Merck, Darmstadt, Germany).

It is thought that the difference is due to the additives of sample 3, especially the high calcite value, the weak homogeneous structure, and the higher roughness value than the other samples. The contact angle was measured as 76±2 ˚ in sample 2. Sample 2 is more hydrophobic with a higher contact angle than the other samples. As the contact angle increases, the hydrophobicity of the material increases. As the contact angle decreases, hydrophilic properties and wettability increase. The high wettability of materials can increase their ability to hold liquid and cause deformations.

Table 3. Percentage of elements found in samples as a result of SEM and EDX analysis

SAMPLE	Element	Atomic %	Weight %	Net Int.	Error %	R	A	F
1	C	73.95	54.20	166.20	13.93	0.9101	0.0646	1.0000
	O	9.51	9.28	50.39	19.50	0.9211	0.0923	1.0000
	Mg	0.70	1.04	34.09	17.88	0.9374	0.6117	1.0091
	Cl	11.62	25.13	643.43	3.53	0.9536	0.9383	1.0151
	Ca	4.23	10.34	160.82	6.69	0.9620	0.9246	1.0128
	C	73.95	54.20	166.20	13.93	0.9101	0.0646	1.0000
2	C	86.35	67.46	211.09	13.29	0.9157	0.0624	1.0000
	Cl	11.72	27.02	734.33	3.34	0.9570	0.9478	1.0103
	Ca	0.96	2.51	41.51	17.21	0.9649	0.9242	1.0214
	Ti	0.97	3.01	40.44	14.86	0.9698	0.9538	1.0251
3	C	81.73	58.88	173.10	13.84	0.9058	0.0646	1.0000
	Cl	12.16	25.85	639.03	3.52	0.9509	0.9409	1.0176
	Ca	4.89	11.74	176.13	6.47	0.9596	0.9236	1.0181
	Ti	1.23	3.52	42.16	14.03	0.9651	0.9373	1.0215
4	C	68.88	48.87	181.29	13.72	0.9065	0.0724	1.0000
	O	13.82	13.06	76.09	15.87	0.9178	0.0917	1.0000
	Cl	10.54	22.06	611.75	3.63	0.9513	0.9355	1.0211
	Ca	6.76	16.00	270.06	5.24	0.9600	0.9299	1.0121

4.4.1. CA–Roughness Correlation

The CAs of sample 1 and sample 2 are close to each other. Roughness values were also measured quite closely. The roughness value of sample 3 is close to the values of sample 1 and sample 2. The CA of sample 3 was measured lower than the others. It is thought that this situation arises from the additives added when producing PVC materials and the homogeneous structure of the material. Additionally, the roughness value also affects the CA. Sample 4 has high roughness and low contact angle.

4.4.2. CA – SEM Images Correlation

When the measured CA and SEM images are analyzed, the cracks in the SEM images of sample 1 are due to the coating, and the holes are due to the surface. In the SEM image of Sample 2, the surface is flat, there are no cracks, and no deformation is seen. As can be seen from the measurements taken from different points, its homogeneous structure is quite well seen. In Sample 3, from the SEM image, calcite was used too much as the filling pigment. Surface roughness may be due to the filler pigment used or high calcium levels. According to measurements made from different regions, its homogeneous structure is weak. From the SEM image of sample 4, it was observed that the surface was not flat; that is, it was rough, and there were cracks on the surface. As a result of measurements made from different regions, it was understood that the homogeneous structure was weak. It was understood from the measured values that the CA in the samples with weak homogeneous structures was lower than the others.

4.4.3. CA – EDX Graph Correlation

In Sample 2, Calcium pigment and titanium oxide were used as fillers, but too much calcium pigment was used. In Sample 3, calcite was used too much as a filling pigment. In Sample 4, it was understood that the homogeneous structure was weak as a result of measurements made from different points. CA values can be associated with the homogeneous structure with additives. The irregularity of the homogeneous structure affects the contact angle more the values measured in samples 3 and 4 show this. The CA value of the samples with higher calcite density among the additives was measured lower than the others.

5. CONCLUSION AND FUTURE WORKS

This study investigated the relationship between the structural properties of PVC materials and their wettability behavior. Samples were obtained from PVC profiles used in the market. The roughness values of each sample were measured. CA measurements were made by dropping approximately 20 µl of MilliQ Ultra- Pure water on the samples. SEM images were taken to determine the structural properties of the samples.

In the roughness measurements, it was understood that the roughness values were very close to each other and at a level that can be called smooth. However, cracks and deformations were detected in some samples in SEM image analysis. The CA measurements of the samples were made, and their relations with the roughness values and SEM analyses were investigated. It is understood from the measurement results that the CA value is high in the samples with a small roughness value and homogeneous and smooth in SEM analysis. The CA values of sample 3 and sample 4 were lower than the other samples, and it was determined that the surface roughness values were higher than that.

It has been observed that the homogeneous structure and roughness values of PVC materials affect the CA. Since the wetting behavior is related to the CA, the lower CA causes more material wetting. Since materials exposed to liquid will deform in a shorter time, it is thought that the importance of wettability is excellent in determining material life.

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DECLARATION OF ETHICAL STANDARDS

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Musa Faruk ÇAKIR: Performed the design and implementation, analyzed the results, and wrote the manuscript.

Mustafa KARHAN: A literature survey of results and revising.

Fatih ISSI: The plan for this study and help to analyze.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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