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Properties of UV-Curable Bisphenol-A Glycerolate Diacrylate Coatings Containing 1H,1H,2H,2H-Perfluorodecyl Acrylate Monomer

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Abstract: In this study, fluorine chains were bonded with covalently in epoxy acrylate system via UV light. For this purpose, five different coating samples prepared. Bisphenol-A glycerolate diacrylate (epoxy acrylate) and 1,6-Hexanediol diacrylate were used as the main coating solution. The weight ratio of Bisphenol-A glycerolate diacrylate and HDDA was determined as 7/3. As a long fluorine chain, 1H,1H,2H,2H-perfluorodecyl acrylate (PFOA) was added into the main coating solution in the ratios of 0.25 wt %, 0.50 wt %, 0.75 wt % and 1 wt %. All prepared solutions were coated on aluminum plates by 75 µm by wire wound applicator and then cured via UV dryer. Physical properties of coatings were measured by tests such as MEK rubbing test for solvent resistance, gloss 60^{o} test for brightness, cross-cut test for adhesion property and pencil hardness test for scratch resistance. Hydrophobicity was measured as static water contact angle test. The total surface energy was calculated by contact angle measurement software. In terms of mechanical properties, sheen impact test (for coating samples) and Shore - D hardness tests (for free film samples) were carried out. By examining the results of all these tests; cross-cut adhesion and gloss 60^{o} values decrease with the fluorine content. On the other hand, by the increasing within the content of the fluorine chains, Taber abrasion resistance and hydrophobicity increase significantly but sheen impact resistance and Shore - D hardness values decrease slightly. In terms of cost and overall results, the most proper and multifunctional coating seemed at 0.25 wt %.

Key words: Epoxy acrylate, 1H, 1H, 2H, 2H-perfluorodecyl acrylate, UV-curable coatings, hydrophobic surface,

1H, 1H, 2H, 2H-Perflorodesil Akrilat Monomeri İçeren UV ile Sertleşebilen Bisfenol – A Gliserolat Diakrilat Kaplamalarının Özellikleri

Özet : Bu çalışmada flor zincirleri, UV ışığı ile sertleşebilen epoksi akrilat sistemine kovalent olarak bağlandı. Bu amaçla beş farklı kaplama örneği hazırlanmıştır. Ana kaplama çözeltisi olarak Bisfenol-A gliserolat diakrilat (epoksiakrilat) ve 1,6-Heksandiol diakrilat kullanıldı. Bisfenol-A gliserolat diakrilat ve HDDA'nın ağırlık oranı 7/3 olarak belirlendi. Uzun bir flor zinciri olarak 1H, 1H, 2H, 2H-perflorodesil akrilat (PFOA) ağırlıkça % 0.25, % 0.50, % 0.75 ve % 1 oranlarında ana kaplama çözeltisi içine ilave edildi. Hazırlanan tüm çözeltiler, alüminyum plakalar üzerinde 75 µm tel sargılı aplikatör ile kaplandı ve daha sonra UV kurutucu ile sertleştirildi. Kaplamaların fiziksel özellikleri; solvent direnci MEK ovma testiyle, parlaklık 60^{o} parlaklık ölçüm testiyle, çizilme direnci kalem sertliği testiyle, yapışma özelliği çapraz-kesme testiyle yapılmıştır. Yüzeylerin hidrofob özelliği statik su temas açısı testiyle ölçüldü. Toplam yüzey enerjisi temas açısı ölçüm yazılımı ile hesaplandı. Mekanik özellikler açısından, Sheen darbe testi (kaplama numuneleri için) ve Shore-D sertlik testleri (serbest film numuneleri için) yapıldı. Bu testlerin sonuçları ele alındığında, çapraz kesme-yapışma ve parlaklık 60^{o} değerleri flor içeriğinin artması ile azaldığı gözlemlendi. Diğer taraftan Taber aşınma direnci ve hidrofobisite önemli ölçüde artmaktadır, ancak darbelere karşı dayanıklılık ve Shore-D sertlik değerleri azalmıştır. Maliyet ve genel sonuçlar açışından bakıldığında en uygun ve çok fonksiyonlu kaplama % 0.25 olduğu bulunmuştur.

Anahtar kelimeler: Epoksiakrilat, 1H,1H,2H,2H-perflorodesil akrilat, UV ile sertleşebilen kaplamalar, hidrofobik yüzey

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1. Introduction

Epoxy resins can be used in industry as durable coatings due to their high mechanical strength and good adhesion to specific substrates. Also, epoxy acrylate systems provide excellent coating properties in various applications such as kitchen cabinets, outdoor furniture, aluminum siding, and other metal products. Epoxy acrylates systems are suitable for UV curing with radical photoinitiators due to the presence of unsaturated bonds. Moreover, epoxy acrylates based on bisphenol diglycidyl ether and epoxy novolac have been widely used due to their good adhesion, hardness, and chemical resistance. But for Bisphenol-A epoxy acrylates there can be some application limitations such as yellowing, low flexibility and poor adhesion to plastic substrates. Bisphenol-A epoxy acrylates are generally used in wood, plastic, metal and paper coatings [1,4].

UV curing techniques have been becoming important in the field of coatings due to their specific characteristics such as fast drying, environmentally, solvent-free and energy saving etc. Especially, in the field of UV curing industries, epoxy acrylate derivatives have been widely used as coatings, structural adhesives and advanced composite materials [2,3]. In order to obtain hydrophobic surfaces, it should be mentioned about the properties of fluorine. We know the unique characteristics of fluorine such as so low atomic radius and having the highest electronegativity. Due to the high electronegativity, fluorines are to occur strong covalent bonding with carbons. Low free surface energy results from strong carbon-fluorine bond. In addition, as fluorine atom replaces with carbon or hydrogen, free surface energy increases. Surface tension of functional groups are arranged as follows ; $-CF_3 < -CF_2H < -CF_2 < -CH_3 < -CH_2$. Due to the hexagonal structure groups of $-CF_3$, the lowest free surface energy with all surfaces can be obtained. Moreover hydrophobic properties increase when the length of fluorine chain become longer [5,6]. PFOA has 17 fluorine atoms. Also, this chemical can be covalently bonded to an epoxy acrylate system by UV curing. In this study, epoxy acrylate containing PFOA coatings were obtained on aluminum sheets in different weight ratios of PFOA such as 0.25 wt %, 0.50 wt %, 0.75 wt % and 1 wt %. By incorporating the different ratios of PFOA into the system, the changing of physical properties of coatings, hydrophobicity, total surface energy, Taber abrasion resistance, sheen impact and Shore-D hardness values were investigated.

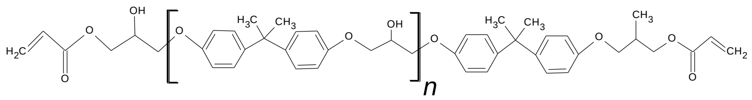
2. Material and Method

2.1. Materials

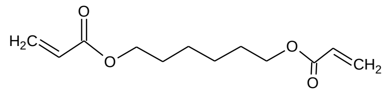
Bisphenol-A glycerolate diacrylate was used as the resin and 1,6-Hexanediol diacrylate (HDDA) was used as a reactive diluent in epoxy acrylate systems. Also, 1H,1H,2H,2H-Perfluorodecyl acrylate (PFOA) was used to obtain hydrophobic surfaces. Hydroxycyclohexyl phenyl ketone was used as the photoinitiator. These chemicals were purchased from Aldrich. Aluminum plates purchased from a local supplier were used as substrates. The chemical structures are shown in figure 1.

2.2. Preparation of UV cured epoxy acrylate coatings containing fluorine chains

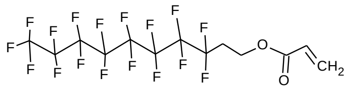
First, Bisphenol-A glycerolate diacrylate and 1,6-Hexanediol diacrylate were mixed with the photoinitiator mechanically. After the mixing for four hours, a clear and homogeneous solution was obtained. The weight ratio of Bisphenol-A glycerolate diacrylate and HDDA was determined as 7/3. 1H,1H,2H,2H-Perfluorodecyl acrylate (PFOA) was added into the coating solution and mechanically mixed in the ratios of 0.25 wt %, 0.50 wt %, 0.75 wt % and 1 wt %. All solutions were coated on aluminum plates by using 75 μm wire-wound applicator and then coated plates cured via UV dryer.



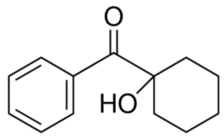
Epoxy acrylate resin



1,6-Hexanediol diacrylate



Perfluorodecyl acrylate



Hydroxycyclo hexyl phenyl ketone

Figure 1. The chemical structures of the used chemicals

2.3. Characterization of samples

Coating characteristics of the samples were tested by cross-cut (ASTM D 3359), pencil hardness (ASTM D 3363), gloss 60^o (ASTM D 2457) and MEK rubbing test (ASTM D 5402). Coating impact resistances were measured by Sheen Tubular Impact Test having 908g weight, 25" Tube with weight locking collar (ASTM D 2794). The abrasion resistance of the coatings was performed by Taber abrasion test (ASTM D 4060) where mass losses of the coatings were measured. CS10 wheels were used as abrader with 250 grams and the aluminum substrates were abraded to 50 cycles totally. Static water contact angle tests were performed on the coating samples at room temperature via using a PG-X2 Device Goniometer integrated with the image-capture software. The measurements were carried out throughout 20 seconds and one image was taken for each second. The total surface energy was calculated together with the same software. Total surface energy measurements were carried out according to ASTM D 5946. Also, in order to measure Shore-D hardness free film of each sample was prepared.

The fracture surface morphology of specimens was performed via Field Emission Scanning Electron Microscope (FESEM) Carl Zeiss Ultra Plus machine with an energy-dispersive X-ray spectroscopy (semi-quantitative EDX) analysis system. The specimens were coated with 2-4 nm of Au/Pd in an ion beam sputtering system via Quorum Q150R machine before SEM investigation.

3. Results and Discussion

Epoxy acrylate containing PFOA coating samples that were cured by UV exhibits favorable coating properties rather than the uncoated aluminum sheet. Table 1 shows the formulations of different coating samples.

Impact resistance and physical properties of coatings such as scratch resistance, the adhesion strength to the substrate, brightness, MEK solvent resistance and static water contact angle are exhibited in Table 2.

Table 1. The formulations of coatings

	Epoxy acrylate (g)	HDDA (g)	Hydroxycyclohexyl phenyl ketone (UV Photoinitiator)	Perfluorodecyl acrylate (PFOA)
S-0	7	3	0,002	0
S-0,25	7	3	0,002	0,0250
S-0,50	7	3	0,002	0,0502
S-0,75	7	3	0,002	0,0755
S-1	7	3	0,002	0,1010

The hardness of the coatings was measured by the pencil hardness test. A pencil that ranging from 6B (the softest) to 6H (the hardest) was used for determining the hardness of the coatings. The pencil which does not scratch the coating was defined as pencil scratch hardness. While S-0 sample exhibited 5H pencil hardness, the other samples exhibited 6H pencil hardness. The reason for the higher values in the scratch resistance is the increment of the fluorine content in the coating.

Table 2. Physical properties of coatings

Formulations	Cross Cut Adhesion Test	Sheen Impact Test (Inch)	MEK Rubbing Test	Pencil Hardness Test	Gloss 60^o Test	Water Contact Angle ^{o}	Total Surface Energy (mj/m^2)
S-0	5B	5	500	5H	184	66.4	41
S-0.25	5B	4	500	6H	170	88.8	32.9
S-0.50	4B	3	500	6H	162	91.2	32.1
S-0.75	3B	3	500	6H	141	93	31.4
S-1	3B	3	500	6H	135	92.7	31.5

Adhesion properties of the coatings were measured by the cross-cut test. Adhesion properties are defined from 0B to 5B. While 0B symbolized the poorest adhesion, the 5B symbolized as the excellent adhesion property. As shown in table 2, S-0 and S-0.25 samples exhibited excellent adhesion property on the aluminum substrate but S-0.75 and S-1 samples showed poor adhesion property due to the long fluorine chains in high ratio [7, 8].

Solvent resistance was measured by MEK rubbing test. This test was applied with a cotton ball which soaked in MEK, by rubbing back and forth on the surfaces over 500 times. After the test, all the coatings showed strong resistance to MEK and no solubility occurred on the coating surface.
Gloss 60◦ test were applied for brightness measurement of the coatings [9, 10]. This property is very important for decorative coatings. The amount of light reflected from a surface at a certain angle is measured in that test. Gloss value is strongly affected by surface roughness. Also, the refractive index and the topographical orientation of the microfacets affect the gloss value. When the content of long fluorine chains increases, the gloss values decreases. This could be derived from the roughness values [11].

Impact resistance of the coating samples was measured with Sheen Tubular Impact Tester. Many surface coatings are subject to the risk of damage by impact**.** That instrument consists of a graduated vertical tube mounted into a solid base. This tube acts as a guide for an impacting weight of the predetermined mass. The height from which this falls is variable. By using the locking collar, exactly the same force of impact can be produced for each test. The weight and indenter are combined and hit the panel directly. The test panel is placed on the die. The panel is held firmly by a clamping sleeve. The weight is raised to a set height and then released. The height is increased by 2.5 cm (1") intervals until coating failure is seen. The testers can be used as a pass/fail test by calculation of the impact energy (height x mass), and for the classification of the test sample.

The crack pictures of S-0 and S-0.25 samples after the Sheen test for the dropping from the height of 4 inches. Hence Sheen impact resistance value of these samples means the energy of 3-inch height. S-0 and S-0.25 samples didn’t exhibit any crack on the surfaces for the test conducting from the height of 3 inches. Cracks were observed for these samples for the height of 6 and 5, respectively. These also mean that the energy of 5 and 4 inches height for S-0 and S-0.25, respectively.

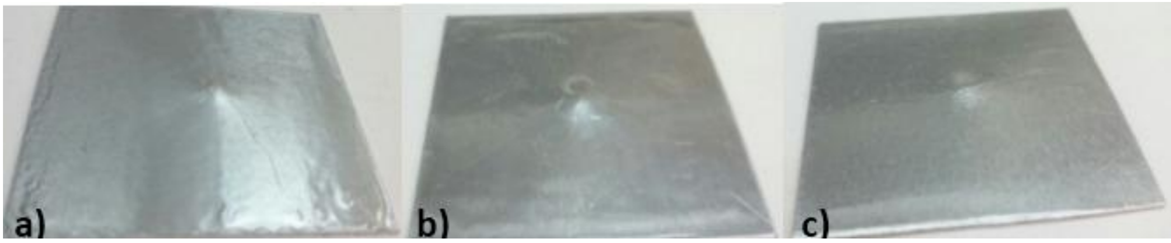


Figure 2. The crack views of a) S-0.50 and b) S-0.75 c) S-1 after Sheen Impact Test

As shown in Table 2, when the content of long fluorine chains increases, the impact resistance decrease. This decrease may be derived from the lower adhesion properties on the surface due to the long fluorine chain content.

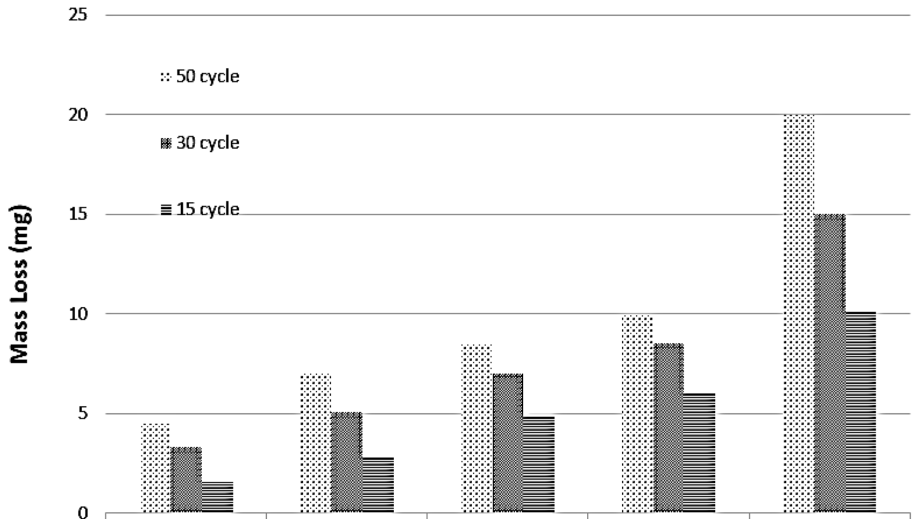
Abrasion resistance was measured by Taber abrasion tester, Abrader model CS10, the abrasive device in an interval of from 15 to 50 cycles under 250 grams weight and 72 rpm. The mass losses of all coatings are given in Figure 3. While the ratio of fluorine chains increased, coatings exhibited significantly higher abrasion resistance due to the low friction coefficient of fluorine structures. For 50 cycles of Taber abrasion test, abrasion rate decrease as % 77.5 for S-1.

The Shore-D test was used to evaluate the hardness of free film samples. The test positions for Shore-D test and graphics of the results are shown in figure 4 and figure 5 respectively. Also, the average hardness values are listed in Table 3.

Table 3. Shore-D hardness test of free films

Samples Codes	S-0	S-0.25	S-0.5	S-0.75	S-1
Shore-D Hardness Values	59	57	54	51	49

While the content of long fluorine chains in epoxy acrylate system increase, the hardness results slightly decrease. Hardness test may also provide an insight about tensile strength and Young Modulus. It is possible that Young Modulus and tensile strength results may slightly decrease with increasing the content of long fluorine chains in epoxy acrylate system.



	S-1	S-0.75	S-0.50	S-0.25	S-0
50 cycle	4,5	7	8,5	10	20
30 cycle	3,3	5,1	7	8,5	15
15 cycle	1,6	2,8	4,9	6,1	10,1

Figure 3. Taber abrasion resistance

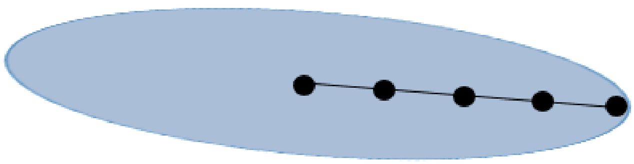


Figure 4. Shore-D hardness measurement points of free films

Many studies have shown that the fluorine chains decrease the glass transition temperature and reduce the hardness of the main structure (12).

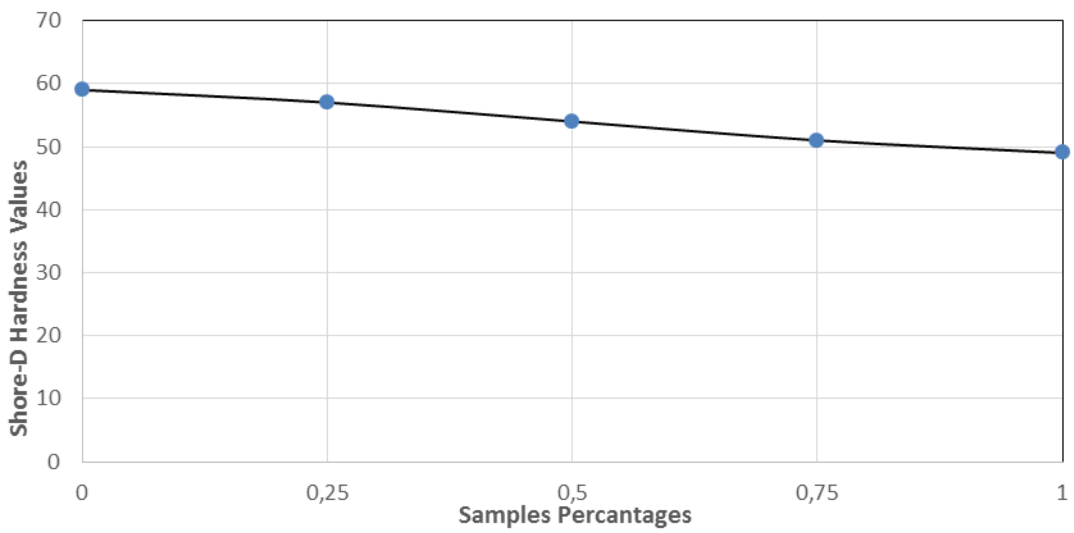


Figure 5. Shore –D hardness values of free films

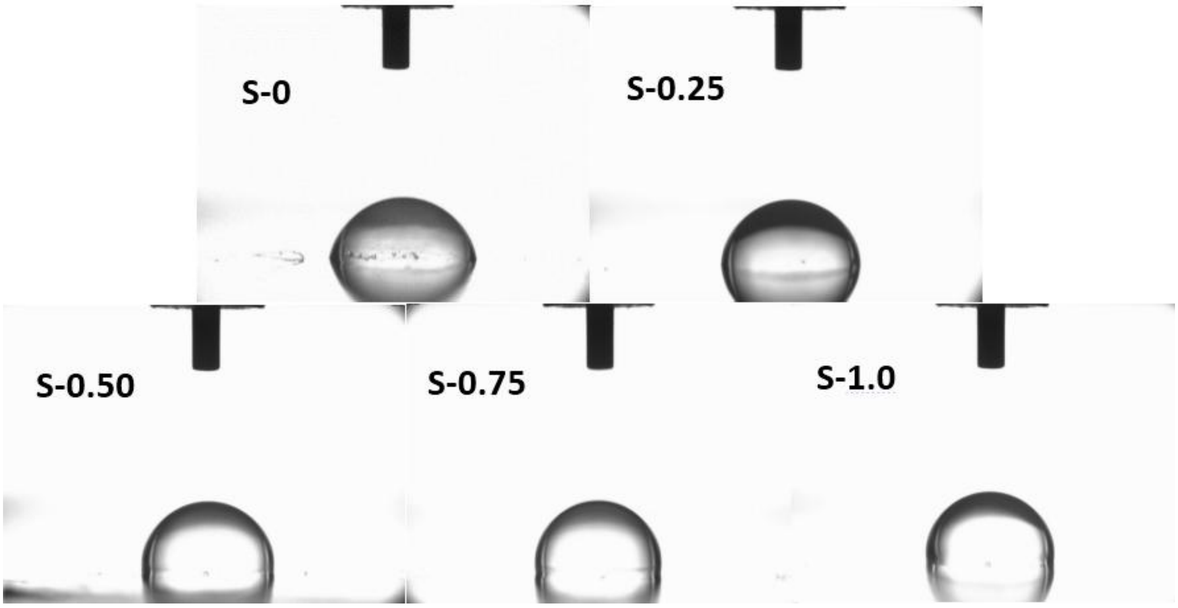


Figure 6. Pictures of static water contact angles

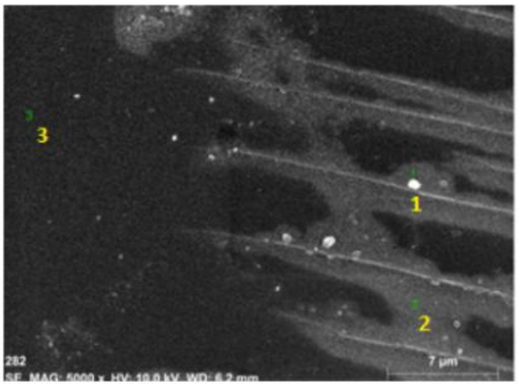
One of the important factors affecting the acceptability of a novel coating in engineering applications is the degradation of the coating by the moisture that will affect the physical and mechanical performances and be causing it to fail. For that reason, hydrophobicity has been a demanded factor in most applications. The degree of hydrophobicity increases with increasing fluorine ratio.

Contact angle measurement was applied to the coatings on aluminum substrates. Static contact angles of water on the air-side surface of the coated samples were measured at room temperature using a contact angle goniometer. Figure 6 shows the views of the static contact angles measured by a goniometer [11].

The higher the contact angle value exhibits the more hydrophobic character on the surfaces. The surface energy was also measured directly by the contact angle goniometer. While surface energy decreased, hydrophobic character increased due to the fluorine content. The high fluorination degree provides a high hydrophobicity for the coatings. Also, long fluorine chains in polymers can be more effective to increase the hydrophobicity [13].

As shown in Table 2, the long fluorine chain content increased the static contact angle until the ratio of 1 %. But the small content of fluorine chain increased the hydrophobicity much more than the larger contents. The contact angle of S-0.25 gives an increase of 34%. The contact angle value from S-0.25 to S-1 shows an increase of 5 %. This value can show the decrease of the fluorine ratio on the surface at the larger content due to the agglomeration of fluorine chains. Besides, the contact angle value of S-1 gives little decrease because of the agglomeration. These agglomerations of the fluorine chains can be observed in SEM micrograph in figure 7.

These results showed the important positive effect of PFOA in terms of hydrophobicity in epoxy acrylate systems. On the other hand, the total surface energy of the samples was measured. Contrary to the contact angle values, as expected, total surface energy values decrease with high fluorine content. Low surface energy is a very important parameter in terms of spreading something or any material on the substrate surface because the substrate surface tends to wet out the materials having high surface energy.



Atomic percent (%)

Spectrum	C	N	O	F
1	53.60	0.00	42.78	3.62
2	69.28	5.18	24.37	1.17
3	73.97	2.01	24.01	0.00
Mean value:	65.62	2.40	30.39	1.60
Sigma:	10.67	2.61	10.73	1.85
Sigma mean:	6.16	1.51	6.20	1.07

Figure 7. SEM micrograph and EDS analysis of S-1

Long fluorine chains in epoxy acrylate system seemed as the white point in SEM shown as figure 7. EDS measurements also confirm this situation. Also, some points seem larger in the micrograph. This situation may be derived from the partial agglomeration of the long fluorine chains.

Fracture surfaces of both samples were given in figure 8. Fracture surfaces of both samples in figure 8 exhibit brittle behavior.

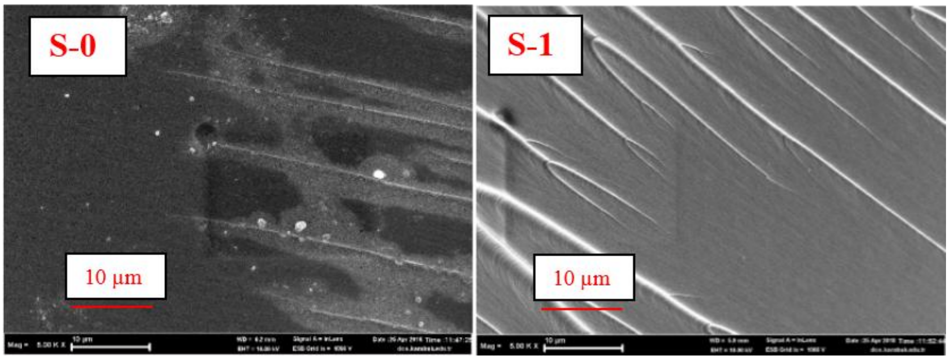


Figure 8. The fracture surfaces of S-1 and S-0

4. Conclusion

In this study, a series of epoxy acrylate containing long fluorine chains coatings were prepared in the range of 0 –1 wt %. By the increment of the long fluorine chains, hydrophobicity and abrasion resistance increased significantly. The low content of long fluorine chain increases the Taber abrasion resistance and the hydrophobicity significantly. Cross-cut adhesion, gloss 60^{o} and Sheen impact values of the coating samples exhibited satisfactory results at the larger fluorine chain contents such as S-0.5, S-0.75 and S-1 despite the decrease. Similarly, Shore-D hardness values slightly decreased due to the increasing content of long fluorine chains but these values exhibit acceptable results, too. On the other hand, pencil hardness increased slightly with the increase of the fluorine content and this test is a measurement of the scratch resistance of the coatings. In summary, The S-0.25 sample appears to be the most plausible, considering the overall results and the cost of fluroacrylate. In addition to excellent cross-cut adhesion properties and scratch and MEK based solvent resistance, very good Sheen impact resistance, gloss °60, Shore-D hardness and hydrophobicity values were achieved by using the smallest content of PFOA.

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