



Preparation and Characterization of Polyaspartic and a High Solids Acrylic Copolymer Polyol Based Polyurethanes

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Abstract: In this work, a high solids acrylic copolymer polyol (poly(MMA/BA/HEMA/AA)) was synthesized from the polymerization of methyl methacrylate (MMA), butyl acrylate (BA), hydroxyethyl methacrylate (HEMA) and acrylic acid (AA) and was added to the polyaspartic resin. The polyaspartic-polyol mixtures reacted with polyisocyanates to create hybrid polyurethane-polyaspartic hybrid coatings. Different amounts of synthesized acrylic copolymer (5, 10, and 20% of total resin mixture) were mixed into polyaspartic resin and subsequently reacted with polyisocyanates in a 1:1 molar ratio. The characterization of the polymer was performed with Gel Permeation Chromatography (GPC), Fourier-Transform Infrared-Attenuated Total Reflection (FTIR-ATR) and Differential Scanning Calorimetry (DSC). The determination of physical and mechanical properties of the hybrid coatings was accomplished by hardness, glossiness, abrasion, stress-strain, corrosion, and impact tests. The results indicated that by adding high solids acrylic copolymer (HSAC), the drawbacks of polyaspartic resin (short pot life, hardness and brittleness, and poor adhesiveness) have been largely eliminated without reducing its intrinsic properties. The pot life increased from 16 minutes to 27 minutes and shore D hardness decreased from 60-65 to 52-55 as the polyol content increased in the mixtures. The acrylic polyols and aspartic mixtures may be used in the preparation of paints and varnishes applied on concrete, metal, and wood surfaces.

Keywords: Acrylic copolymer, Coating, High solids acrylic polyols, Paint, Polyaspartic.

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1. INTRODUCTION

Polyurea coatings have been very popular for their superior properties such as, flexibility, high cure speed, higher mechanical and chemical resistance, and fast drying compared to the epoxies and polyurethanes (1-6). The chemistry of the polyurea is based on the reaction of primary amines with polyisocyanates. There is no need to use catalysts and it is performed without any heat applied. The curing time is too short (under minutes) that needs special machines like

spray guns and needed to be expertise in applications (7-8). Instead of using primary amines, a new technology, polyaspartic ester polyurea, was developed as shown in Scheme 1.

In polyaspartic polyurea system, a secondary amine is reacted with an aliphatic isocyanate in which sterically hindered hydrogens on nitrogen atoms slowly react with isocyanates that increases the pot life of the system (9-10).

Polyaspartic resins were initially used as diluents for polyurethane acrylic systems. They decrease the viscosity and increase the hardness and the curing speed of the polyacrylics to prepare fast cure polyurethane coatings (11). After all, these resins have been favored as more preferable environmentally friendly resins with superior properties such as, low VOC (volatile organic components), more hardness, fast cure, and have been used in many areas such as oil and natural gas piping lines, airports, mineral processing facilities, food facilities and factories, shipyards, marine enterprises, waste centers, walkways and balconies, water and wastewater treatment facilities, industrial production areas and power plants (12-16).

Polyaspartics exhibit superior physical, mechanical and chemical (color fastness, resistance to chemicals, solvents, acids and bases, excellent hardness and mechanical strength) properties compared to two component resins such as epoxies and polyacrylates (17-18). Being expensive as compared to epoxy and polyurethanes, they also suffer from the sensitiveness to the air moisture that makes the reaction with isocyanates faster and prevents adhesion to the substrates acting as a barrier. The shorter pot life of the polyaspartics is also a drawback due to that it prevents the resin from spreading and preventing it from penetrating the floor (20). In order to minimize the moisture effect and to increase the pot life and adhesiveness of the polyaspartic polyurea coatings, several attempts have been conducted by using nano-silica and hydroxyl functional soybean oil (21-22).

High solids acrylic polymers having hydroxyl functional groups react also with aliphatic isocyanates to prepare crosslinking polyurethane networks having superior mechanical properties (excellent clarity, good thermal resistance, high glossiness, and excellent gloss retention, resistance to discoloration by time, well flexibility, not brittle, tunable glass transition temperature,

good adhesiveness, etc.) that makes them withstand chemicals and alkalis, more durable to exterior factors. They may be utilized in a variety of industries, including wood coatings, automotive goods, ships, and storage tanks (23-26). In the last decade, due to the environmental awareness, the polyurethanes have been prepared from bio-based chemicals (27-28).

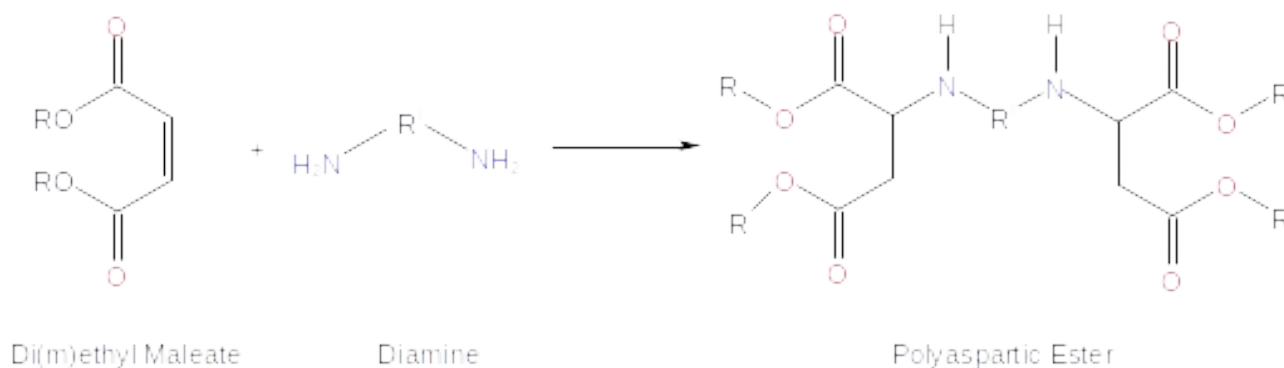
In this study, a poly(MMA/BA/HEMA/AA) acrylic copolymer with low cost, high yellowing resistance, and high solid value was synthesized and mixed in different proportions with polyaspartic ester (PAE) resins to eliminate the disadvantages of polyaspartic ester (PAE) resins (expensiveness, poor adhesiveness, and short pot life). FTIR, DSC, and GPC were used to characterize the resins.

In addition to determining physical characteristics including color, viscosity, gloss, hardness, drying time, pot life, yellowing resistance, and gloss loss following UV exposure, mechanical characteristics were also assessed using impact, tensile, abrasion, and salt spray tests. A suitable paint formulation was designed to PAE and PAE with acrylic copolymers, and physical and mechanical properties of the paints were also examined and compared.

2. EXPERIMENTAL SECTION

2.1. Materials

Butyl acetate, methyl methacrylate (MMA, 98%, ARKEM), butyl acrylate (BA, >99%, Ataman Chemical), 2-hydroxyethyl methacrylate (2-HEMA, >99%, Prochema Chemical LTD.), acrylic acid (AA, 98%, ARKEM), tert-butylperoxybenzoate (TBPB, Merck) were purchased and used without any further purification. Aliphatic isocyanate (Tolonate HDT-LV2) used for curing studies was purchased from Vencorex. The polyaspartic ester was kindly obtained from İZEL KİMYA SANAYİ VE TİCARET A.Ş. with the code of IZASP 14. All other materials were used without any further purification.



Scheme 1: Polyaspartic ester synthesis.

2.2. Characterizations

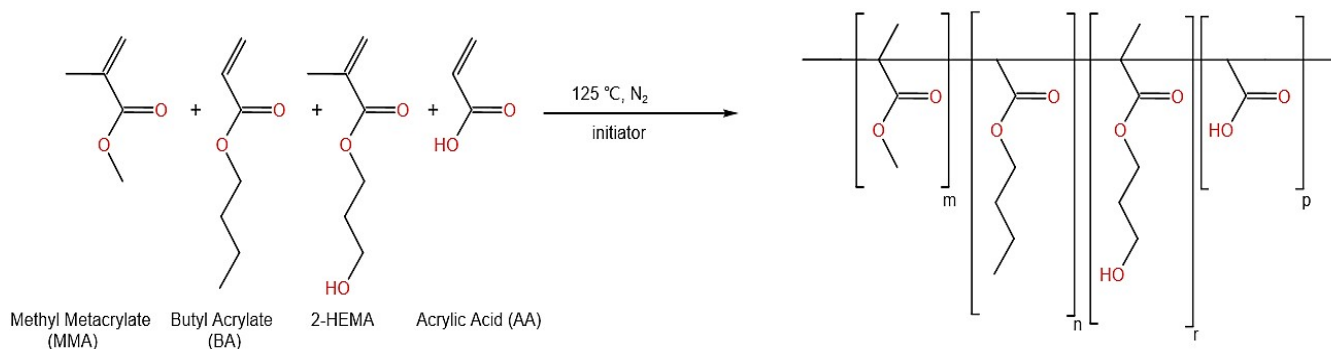
FTIR spectra were measured with JASCO FT/IR-

4200 with ATR (JASCO Corp., Tokyo, Japan). Spectra were obtained at mid-IR region (ca. 4000–700 cm^{-1}) at a resolution of 4 cm^{-1} with 16 scans (Spectra Manager II software, JASCO Corp.). Molecular weights and polydispersity indexes of the polymers were measured by gel permeation chromatography (GPC) employing an Agilent 1100 instrument equipped with a differential refractometer by using tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL/min at 30 °C. Molecular weights were determined by using polystyrene standards. Brookfield viscosity was measured by Brookfield viscometer (RVDV-I Prime, 25 °C, spindle SC4-21, 50 rpm). Cross-cut adhesion test kit CC2000 from TQC Sheen B.V. (Capelleaan den IJssel, Netherlands) was used to test the adhesion of dry coatings on their substrate. The brightness of the films was determined using a Novo-Gloss Trio glossmeter. The color controls of the materials were made with LICO 620. TQC Sheen Pendulum Hardness Tester /SP0500 I141 was used to determine the hardness. In the mechanical tests, impact test with TQC Sheen, tensile test with Devotrans (DVT GP/R D NN 10 kN), abrasion test with Taber Rotary Abraser (1700) and corrosion test with Programmable Salt Spray Cabinet (880/S) were used. DSC was performed on a TA-DSC 250 instrument. Approximately 50 mg of sample was placed in a pan and heated to 250 °C at a rate of 10 °C min^{-1} in nitrogen atmosphere.

2.3. Synthesis of Acrylic Copolymer

Free radical polymerization was accomplished according to an adapted procedure (Scheme 2) to create acrylic copolymer (poly(MMA/BA/HEMA/AA)) in nitrogen atmosphere

(29). All monomers and the initiator (MMA; 1 mol,



Scheme 2: Synthesis of high solids acrylic copolymer (poly(MMA/BA/HEMA/AA)).

3. RESULTS AND DISCUSSION

3.1. Characterizations of Resins and Cross-linked Polymeric Networks

As mentioned in section 2.3 and 2.4, the synthesis of acrylic copolymer, the chemical

BA; 2,5 mol, 2-HEMA; 0,9 mol, AA; 0,1 mol, TBPB; 0,1 mol) were put into an additional funnel and added for about 3-4 hours to a reactor with agitation containing butyl acetate pre-heated to 125 °C. After monitoring gas chromatography to ensure that all monomers had reacted, the agitation was halted. The final polymer solution was analyzed and the results are as follows: The solid content: 72.6%, acid value: 7.3 mg KOH/g, viscosity: 19.000 cP and the molecular weight (Mw): 2.4934 e^4 g/mol.

2.4. Preparation of Polyaspartic Resins and Acrylic Copolymer Mixtures

Polyaspartic ester resin (PAE) has the following properties: solid content; 96.7 %, viscosity; 1800 cP, amine value; 191 mg KOH/g and the equivalent weight; 290 g/mol. Polyaspartic resin and HSAC were mixed in different percentages as shown in Table 1 and the mixtures were cured with aliphatic isocyanate at a 1:1 ratio.

2.5. Preparation and characterization of paint formulations

A simple paint recipe was applied for mixtures of polyaspartic and polyacrylics resins. From these, white paints were made using the same ratio of resins, pigments, and other components. For mixing all ingredients in the paint, a high-speed mixer was used, and fineness of grinding was followed by using a grindometer. Paints were applied to the glass and metal surfaces by using a film applicator with 90 micrometer thickness. Adhesion, drying time, and gloss properties of the paints were determined by using metal surfaces. Glass panels were used for determination of hard drying times by drying time recorder.

analyses of the mixtures of polyaspartics and polyacrylic before and after curing and the final prepared coatings has been carried out by ATR-FTIR, GPC, GC and DSC measurements.

In Figure 1, the synthesis of high solids acrylic

copolymer was followed by checking the functional group analysis by ATR-FTIR. At the beginning while all the monomers were mixed, there were peaks around 1637 cm^{-1} that show us the presence of the acrylic double bonds. After the reaction, the disappearance of this peak proved that all acrylic monomers were reacted. Acrylic copolymer has typical absorption bands corresponding to acrylate and methacrylate units. The peak around 3350 cm^{-1} were assigned to the -OH symmetric stretching vibrations from hydroxyl group. 2950.55 cm^{-1} (C-H bond stretching vibrations), 1727.56 cm^{-1} (C=O absorption peak of the carbonyl ester group), 1238.08 cm^{-1} (C-O stretching modes), 1157.08 cm^{-1} (C-O-C stretching vibrations) (30-31).

The synthesis of HSAC were also followed by using GPC for molecular weight measurements. The GPC showed us that all monomers were reacted

and a polymer were existed as shown in Figure 2. The molecular weight: $M_w: 2.31 \times 10^4\text{ g/mol}$, $M_n: 5.74 \times 10^3\text{ g/mol}$, PDI: 4.03.

The monomer residue analysis was also conducted by using headspace-GC. Abundance to time graph showed that the signals for acrylic monomers at the time interval between 2-4 minutes was so low after the polymerization. There were almost no identified monomers (below 0.1%) in the final acrylic solution showing that all the monomers were reacted with each other to give a polymer as shown in Figure 3.

After the mixing of the acrylic to polyaspartic resins and then with the isocyanate, the presence of ester and amine groups is observed in the main absorption bands in the FTIR spectrum of the PAEs as shown in Figure 4.

Table 1: The amount of ingredients in weight percentage (wt%) of the PAE-HSAC mixtures.

Sample	Polyaspartic (PAE) (%)	Acrylic Copolymer (HSAC) (%)
Control-F ₁	100	0
F ₂	95	5
F ₃	90	10
F ₄	80	20

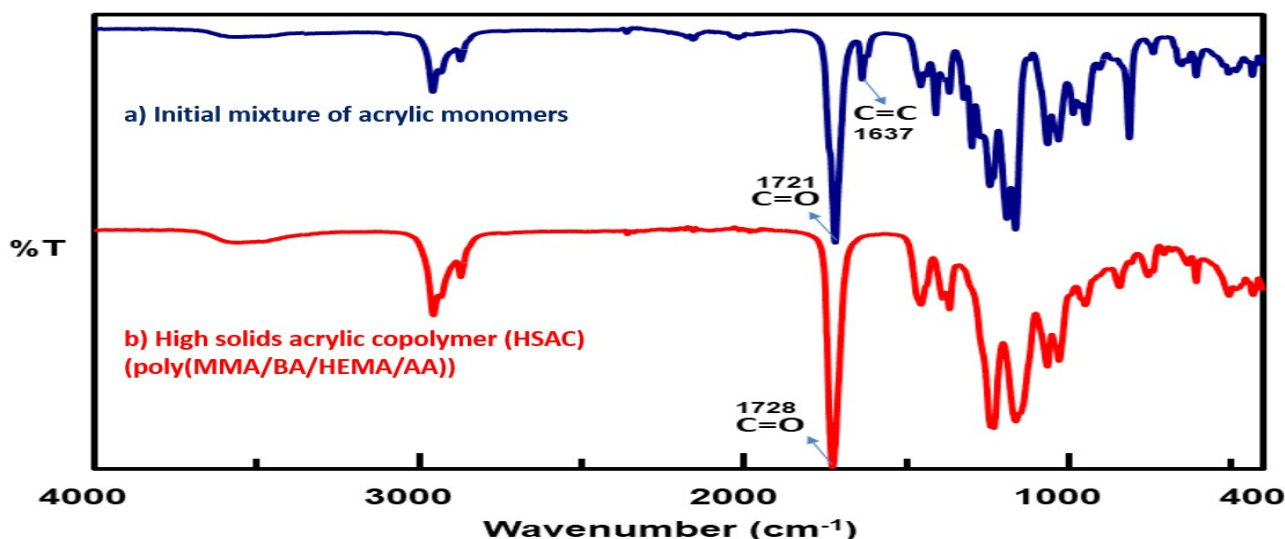


Figure 1: ATR-FTIR spectra of a) Initial mixture of acrylic monomers and b) HSAC (poly(MMA/BA/HEMA/AA)).

The presence of the peak at around 2264 cm^{-1} was related to the -OCN groups. The

disappearance of the -OH and -NH groups at around 3350 cm^{-1} proved the existence of the curing process. All isocyanates can be reacted with -OH and -NH groups or sometimes some

groups could not react because of the insufficient mixing or there were not enough reactive functional groups reacting with isocyanates (21). As in the case of PAE-20, there were not peaks at around 3300 cm^{-1} and at around 2264 cm^{-1} , that showed us the all functional groups were completely reacted with each other as shown in Figure 5.

After the curing, the -OH and -NH groups reacted with -OCN groups and turned out the cross-linking polymeric networks containing the final polyurea and polyurethane bonds as shown in

Scheme 3.

After the coatings were prepared, the glass transition temperatures (T_g) of the coatings were determined by using differential scanning calorimeter (DSC). Measurements were made for the T_g value which is of great importance in obtaining information about the properties of the polymers that whether it will be flexible or hard. The graphs are given in Figure 6 for PAE, poly(MMA/BA/HEMA/AA), PAE-5, PAE-10 and PAE-20.

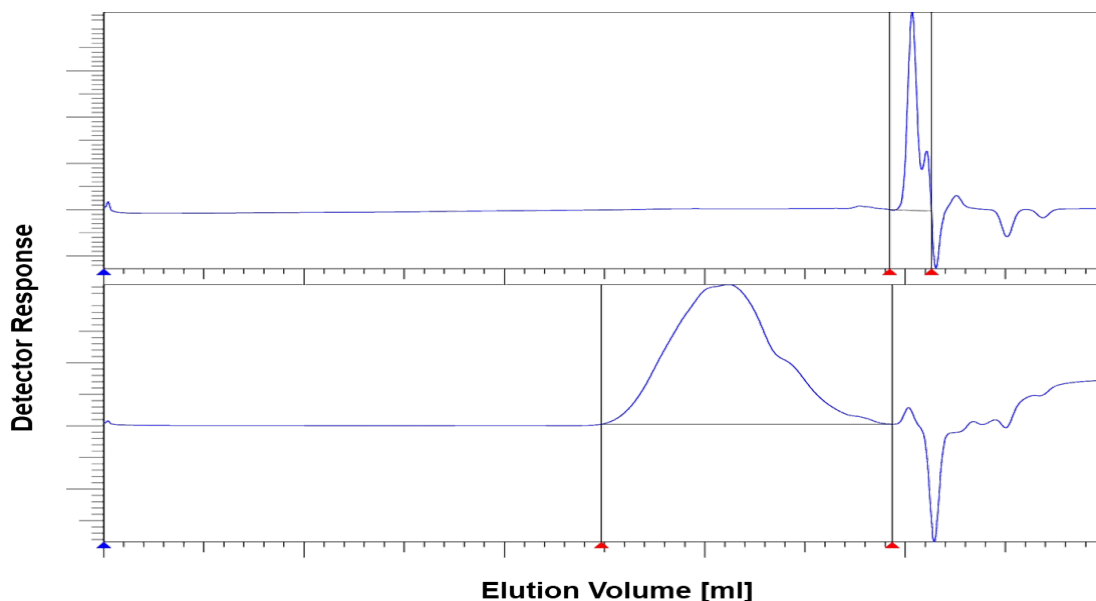


Figure 2: GPC spectra of initial mixture of acrylic monomers and HSAC (poly(MMA/BA/HEMA/AA)).

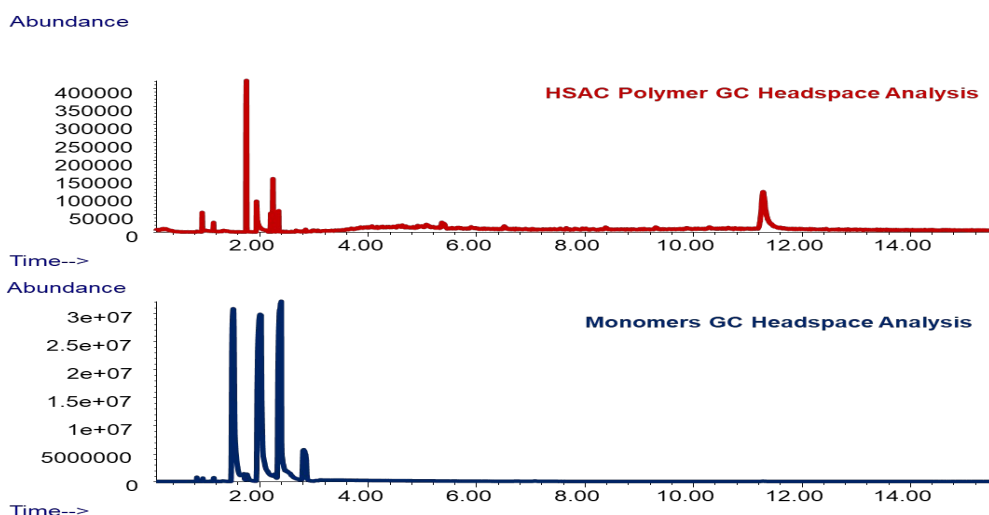


Figure 3: Headspace-GC analyses of initial mixture of acrylic monomers and HSAC (poly(MMA/BA/HEMA/AA)).

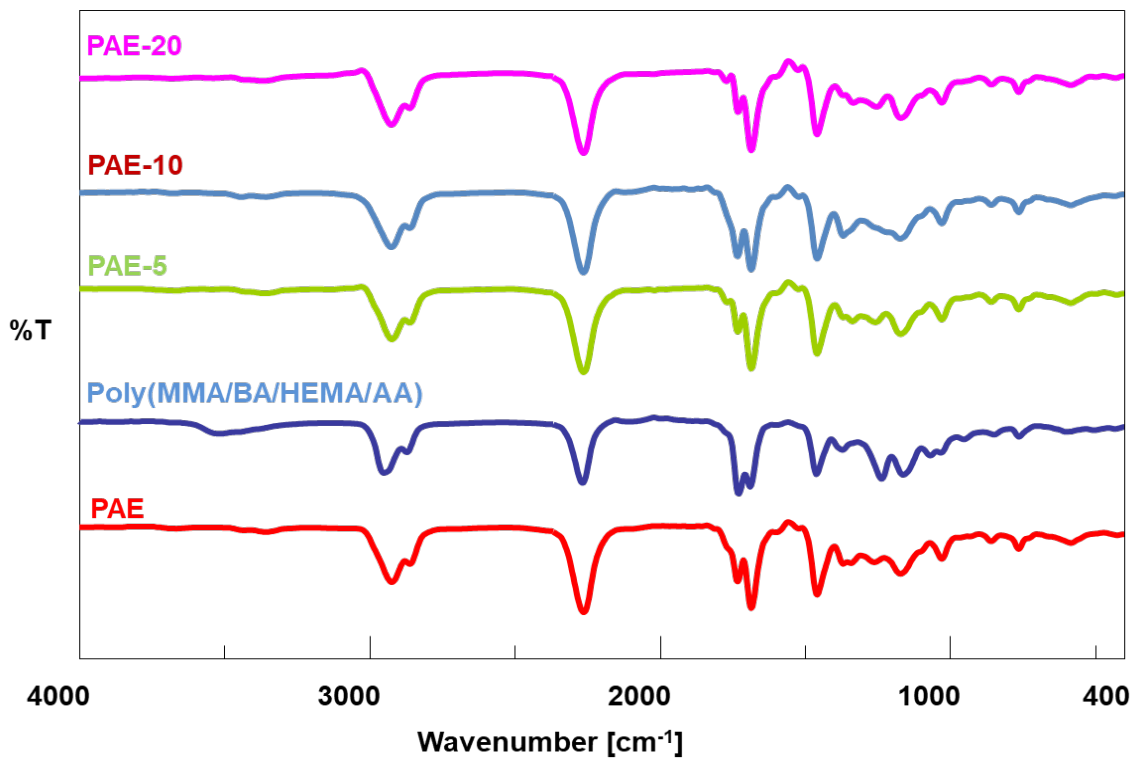


Figure 4: FTIR spectra of materials before curing.

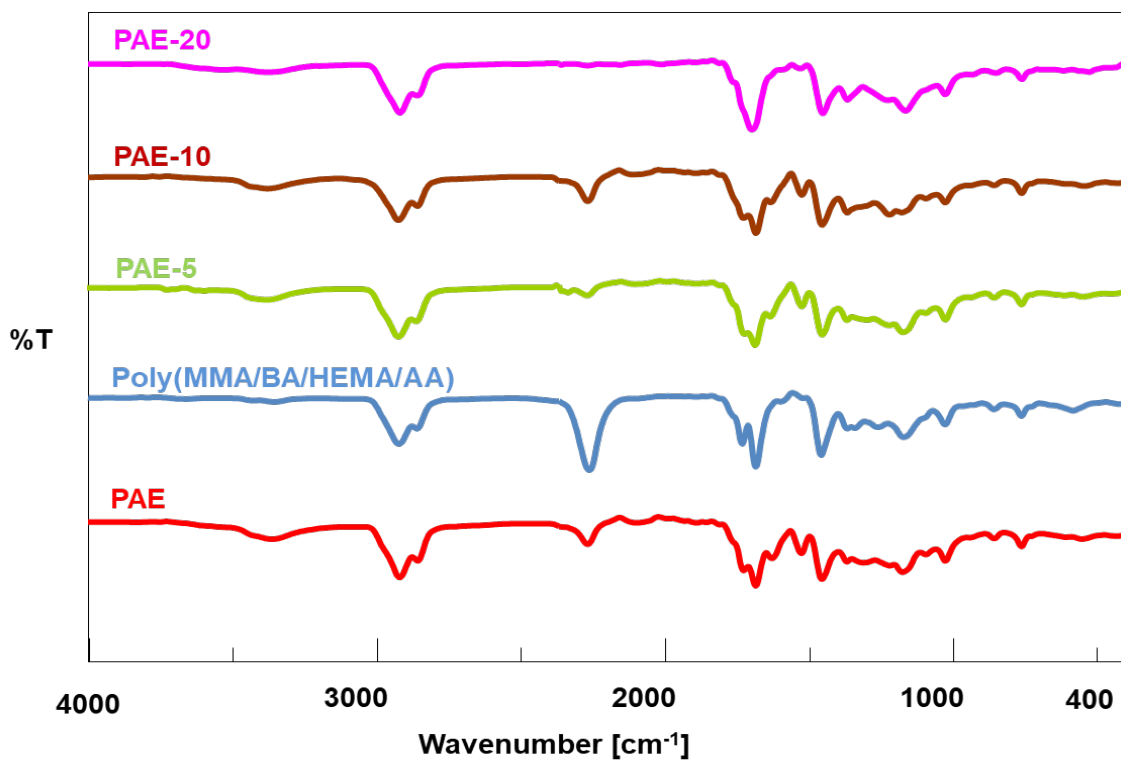
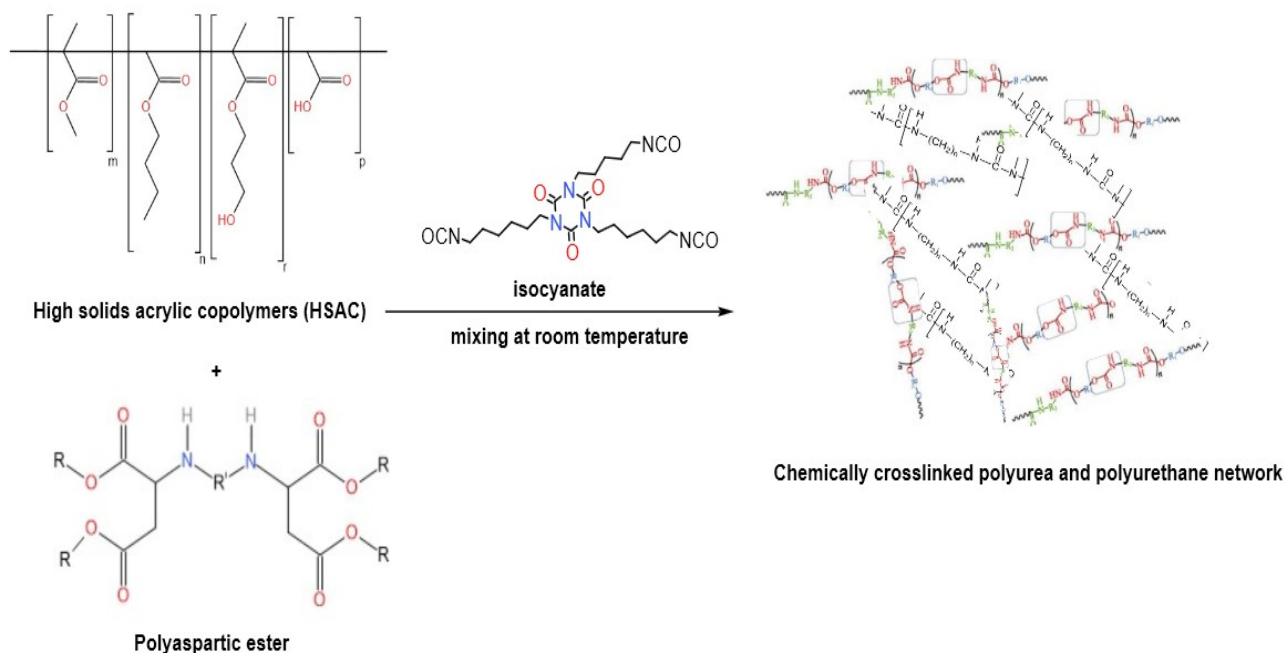


Figure 5: FTIR spectra of materials after curing.



Scheme 3: Preparation of cross-linking networks by the reaction of PAE and polyacrylic polyol (HSAC) with isocyanate.

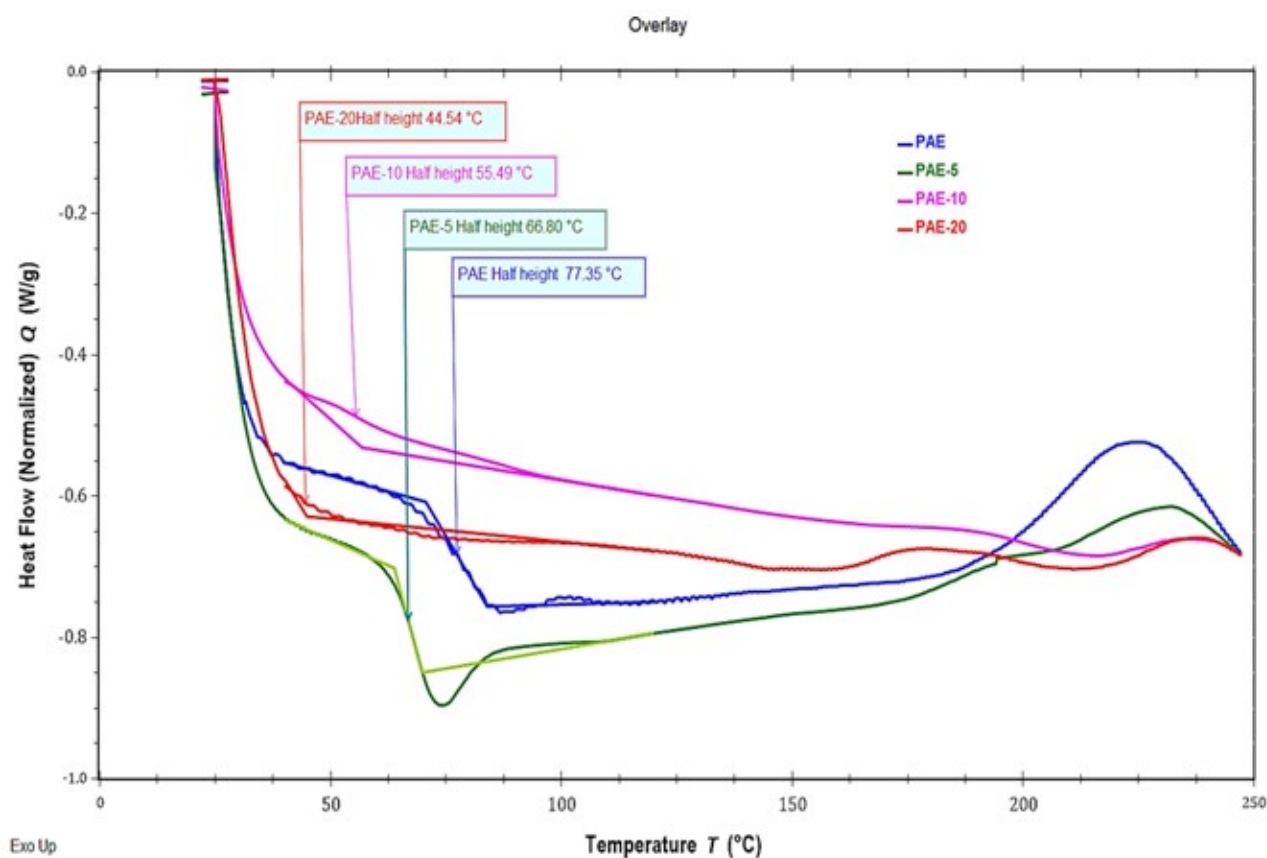


Figure 6: DSC graphs for a) PAE, b) PAE-5, c) PAE-10, and d) PAE-20.

The Tg of the neat PAE was measured as 77.35 °C. As the poly(MMA/BA/HEMA/AA) content of the samples increased, their Tg gradually decreased as 66.80, 55.49 and 44.54 °C for the 5, 10 and 20%, respectively. Insufficient amounts of polymerizable groups and more flexible monomers in the backbone or sidechain of polymers were likely to be responsible for the low Tg values, which also led to a poor crosslinking density (32-33). HSAC chemical structure contains flexible butyl acrylate groups that makes it very flexible. Long alkyl chain length groups in acrylic polyols leads to increase the movements of the molecular structure that lowers the Tg. Increasing the acrylic content consumed the isocyanates more fully and all isocyanates reacted as the disappearance of the peak related to isocyanate around 2264 cm⁻¹ as shown in the FTIR spectrum of PAE-20. Decrease in Tg resulted more flexibility to the polymeric network and makes enhancements in their adhesion to the substrates.

3.2. Mechanical and Physical Properties of the Mixtures of PAE and HSAC and the coatings

The physical and mechanical properties (color, viscosity, glossiness, hardness, drying time, and pot life) of the resins and coatings were given in the Table 2.

According to the results given, Hazen color

value of PAE resin, which is relatively high (171), decreased to 150, 145 and 130, respectively, with the increase of acrylic copolymer ratio in the mixture. These results show that the color status, which is very important for polyaspartic ester resin, can be improved by mixing with acrylic copolymers.

Viscosity values measured as Brookfield at 25 °C, on the other hand, were increased as predicted with the increase in the acrylic copolymer ratio, which has a very high viscosity value. It was determined that there was no loss in the gloss and Persoz hardness values, which are the important features of the polyaspartic ester resin, after mixing and showing that these properties were preserved. Decrease in drying times while increasing the pot life is desirable property for the workability with the resins. The increase in pot life can be because of the isocyanate groups cannot find the hydroxyl groups easily in the polymeric backbone due to the other functional groups that can hinder sterically the hydroxyl groups for the reaction.

The decrease in drying times can be due to more functional hydroxyl groups react with isocyanate groups that increase the number of the reactive crosslink points with increasing the crosslink density. More crosslinking leads to drying faster.

Table 2. Mechanical and physical properties of the resins and coatings.

Tests	PAE	HSAC	PAE-5	PAE-10	PAE-20
Color (Hazen)	171	11	150	145	130
Viscosity (cP, Brookfield, 25°C)	1800	19000	2200	2500	3400
Gloss (20 degree)	87	80	87	87	87
Persoz Hardness (150 micron, 7 days)	300-310	200-210	300-310	300-310	300-310
Shore Hardness (7 days)	65-70	40-45	65-70	60-65	50-55
Drying (hour)	12	12	7.5	6.0	5.5
Pot life (min)	16	71	17	21	27

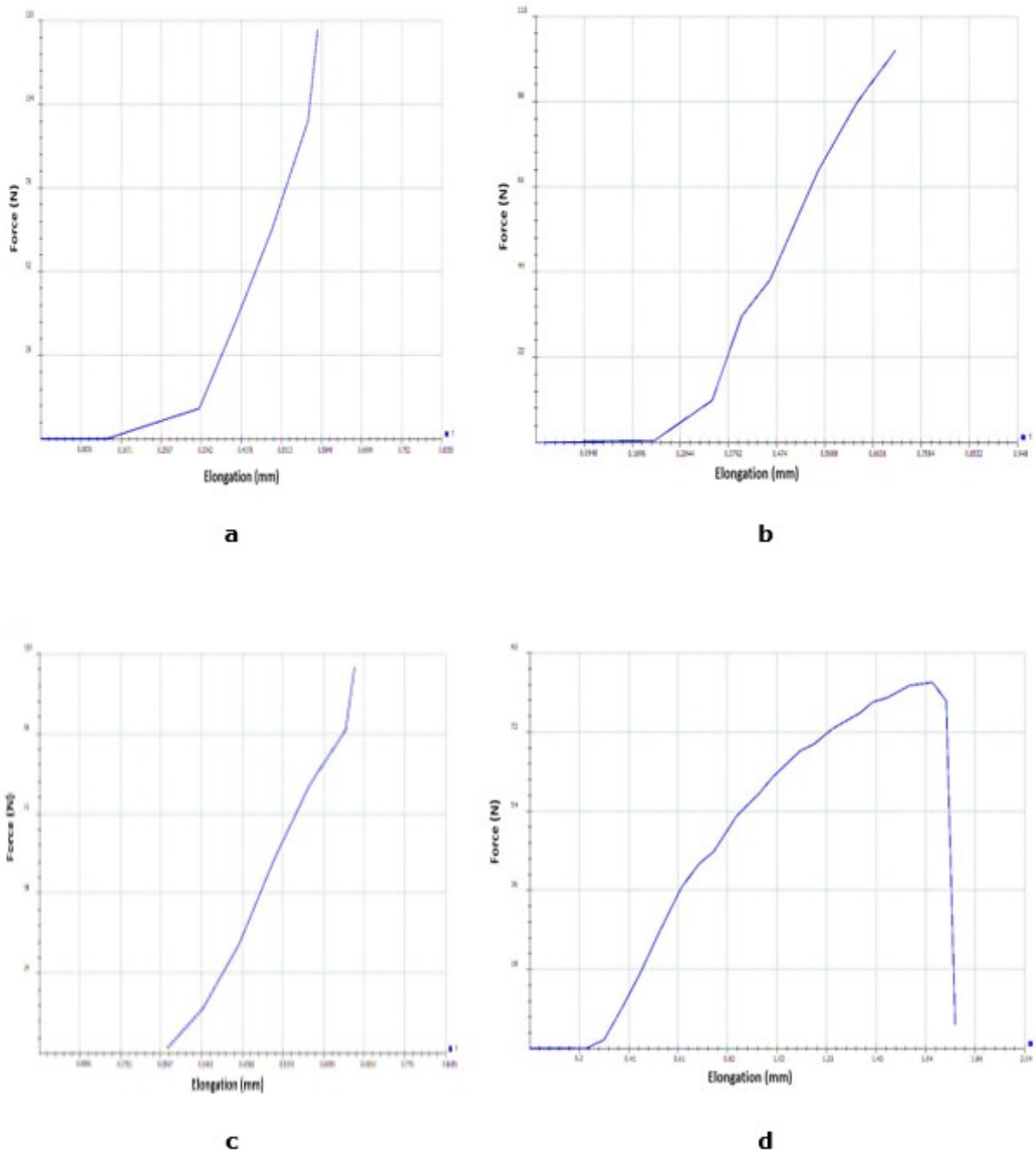


Figure 7: Force (N)-Elongation (mm) graphs of a) PAE, b) PAE-5, c) PAE-10, d) PAE-20.

Tensile testing is a destructive process that provides information about the material's properties such as tensile strength and ductility. It measures the force required to break or rupture the material and how far the sample has stretched to that break or break off point. For this purpose, control was achieved under operating conditions adjusted for 100 mm/min test speed and 100 N target force, and elongation and elastic modulus values were examined. The Force (N)-Elongation (mm) graphs of PAE resin and

mixtures and the results are given in Figure 7 and Table 3.

According to the values given in Table 3, the elongation values were approximately 24.5%, 56.1% and 189.5% for the acrylic copolymer ratios added; elasticity modules increased by 2.2, 4.1 and 21.5%. This could be due to flexible acrylic polymer backbone and the flexible functional groups (2-HEMA and butyl acrylate) that made the crosslink networks more flexible. According to tensile test results, the incorporation

of more acrylic resins into polyaspartics decreased the tensile strength due to the less strong polyurethane linkages compared to strong

polyurea linkages.

Table 3. Elongation and elasticity modules of PAE, PAE-5, PAE-10, and PAE-20.

Product	Elongation at break (mm)	Elasticity Modulus (N/mm ²)	Tensile Strength (N/mm)
PAE	0.57	183.70	7.067
PAE-5	0.71	187.24	5.863
PAE-10	0.89	191.26	5.621
PAE-20	1.65	223.15	4.627

In the test applied according to the ASTM D4060 standard and mass loss, the original weight of the sample was measured. The test sample was then placed in the abrasion tester. A load of 500 g was placed on the abrasive wheel and allowed to rotate for 1000 cycle. When the number of cycles was completed, the final weight was measured and the amount of material removed from the surface was determined. The results of the abrasion test performed with this method were given in Figure 8 for PAE, PAE-5, PAE-10 and PAE-20.

The graph given in Figure 8. C was calculated according to the Taber Wear Index given in Equation 1.

$$\text{Taber Wear Index} = (I \times 1000) / C \quad (\text{Eq. 1})$$

In Equation 1, I=A-B, A=weight (mass) of specimen before abrasion, B=weight (mass) of specimen after abrasion, n=number of test cycles.

Accordingly, for PAE and PAE-10, with the increase in the number of cycles, the Taber Wear Index decreased, that is, there was less wear. With the increase in the acrylic polymer ratio in the mixture, the abrasion started to increase in the mixture added 10% and it had a high abrasion rate for 20%. For PAE and PAE-5, the decreasing index values with the increase in the number of revolutions can be interpreted as lower hardness in the inner layers after surface wear and therefore lower wear.

3.3. Paint Formulation and Test Results

The paint formulation given in Table 4 was used for the mixture made with polyaspartic ester resin and acrylic copolymer. Some physical properties of the prepared paints and some mechanical properties of the films were investigated.

The test results for the paint mixtures prepared according to the guide formulation given in Table 4 are summarized in Table 5.

The cross-cut test was performed according to ASTM D3359 standard for aluminum, galvanized, and sheet surfaces. The visuals of the test result are given in Figure 9.

The gloss measurements of the samples were made to examine the aesthetic properties for paint mixtures (34).

The gloss measurements of the paint mixtures to which PAE and acrylic copolymer were added at the specified rates at 20 degrees were measured as 85 gloss, and it was determined that there was no decrease in the gloss value as a result of the addition. In addition, when the effect of UV rays on the film was examined, it was determined that there was no decrease in yellowing resistance after a period of 10 days.

Corrosion often causes failures that shorten the life of connections. When exposed to certain conditions such as humidity and salinity, durability and mechanical strength are affected and failures may occur more frequently. The salt spray test is an accelerated test used to determine the ability of surface coatings to resist atmospheric corrosion (35-36).

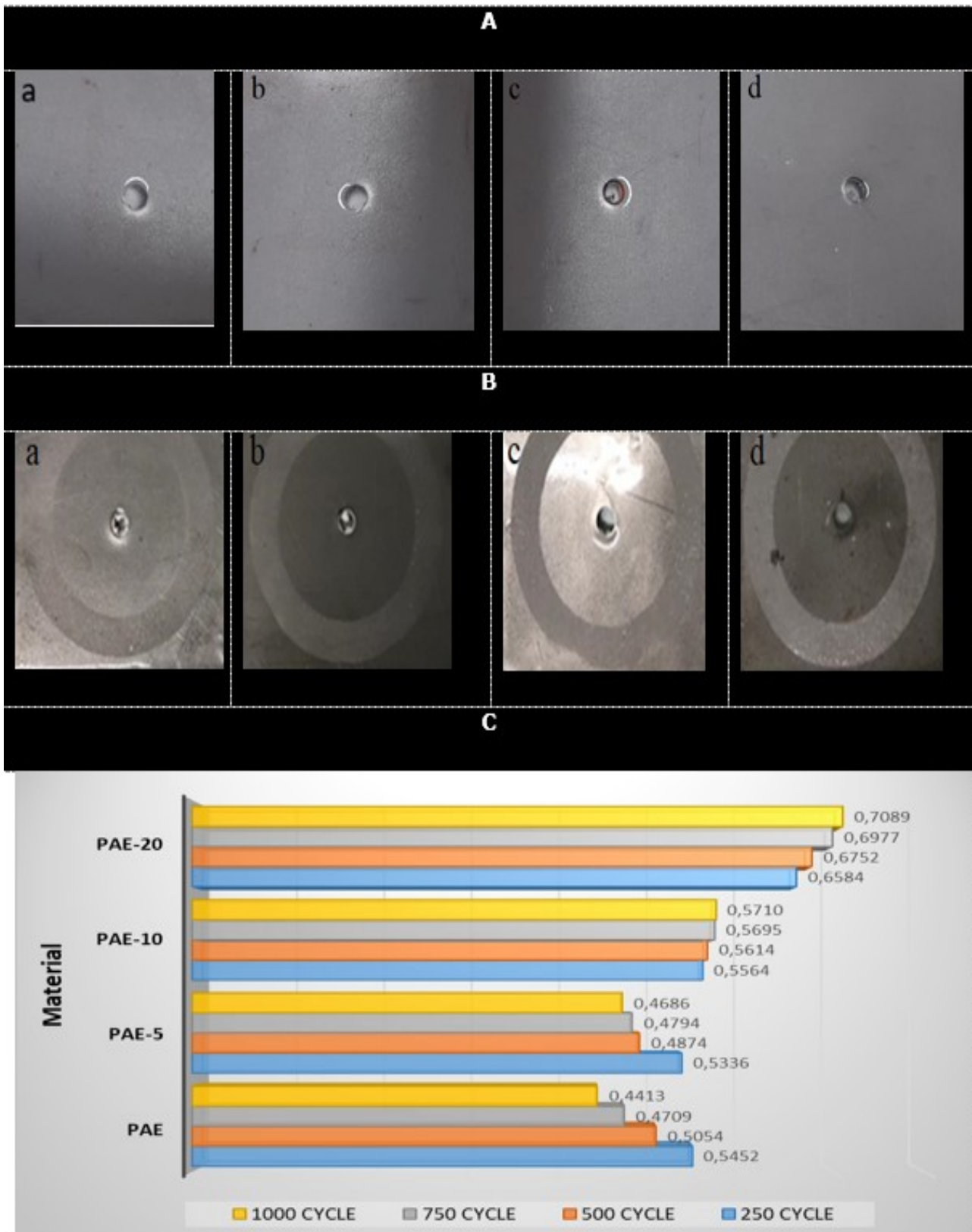


Figure 8: Abrasion test images of A) Before ND, B) After the 1000 cycle a) PAE, b) PAE-5, c) PAE-10, d) PAE-20, and C) Graphical images according to Taber Wear Index.

Table 4. Guide paint formulations.

	PAE	PAE-5	PAE-10	PAE-20
Contents	g	g	g	g
PAE	51.00	48.45	45.90	40.80
poly(MMA/BA/HEMA/AA)	-	2.55	5.10	10.20
Wetting and dispersing additive	0.50	0.50	0.50	0.50
Titan (for cloaking)	25.00	25.00	25.00	25.00
Barite (for filler)	12.50	12.50	12.50	12.50
Dehumidifier	1.60	1.60	1.60	1.60
Defoamer	1.00	1.00	1.00	1.00
Wetting substrates	0.60	0.60	0.60	0.60
UV absorber	0.60	0.60	0.60	0.60
UV absorber	0.60	0.60	0.60	0.60
Butyl Acetate	2.90	2.90	2.90	2.90
Xylene	3.70	3.70	3.70	3.70
Total	100	100	100	100
For 100 g of paint				
Aliphatic isocyanate	35.00	35.00	35.00	35.00
Butyl Acetate	15.00	15.00	15.00	15.00

Table 5. The properties of the paint prepared from PAE, PAE-5, PAE-10 and PAE-20.

Tests	PAE	PAE-5	PAE-10	PAE-20
Viscosity (Brookfield, 25°C)	350 cP	410 cP	460 cP	750 cP
Gloss (20 degree)	85	85	85	85
PersoZ Hardness (150 micron, 7 days)	290-300	285-290	270-280	265-275
Shore Hardness (7 days)	65-70	65-70	60-65	52-55
Drying (hour)	7	6	5	4.5
Pot life (hour)	7.5	5.5	4.5	3.5
Gloss after UV (20 degree)*	85	85	85	85
Abrasion Test (mg loss/1000 cycle)*	0.1771	0.2325	0.2487	0.3489
Impact Strength (500 g/30, 50, 70 cm)*	4,4,2	4,4,2	4,4,4	4,4,5
Cross-cut Adhesion Test (aluminum/galvanized/sheet)*	1,1,4	0,0,3	0,0,3	0,0,0
Salt Spray Test (350 hours)*	4	5	5	5

*1 was rated as the worst and 5 as the best.

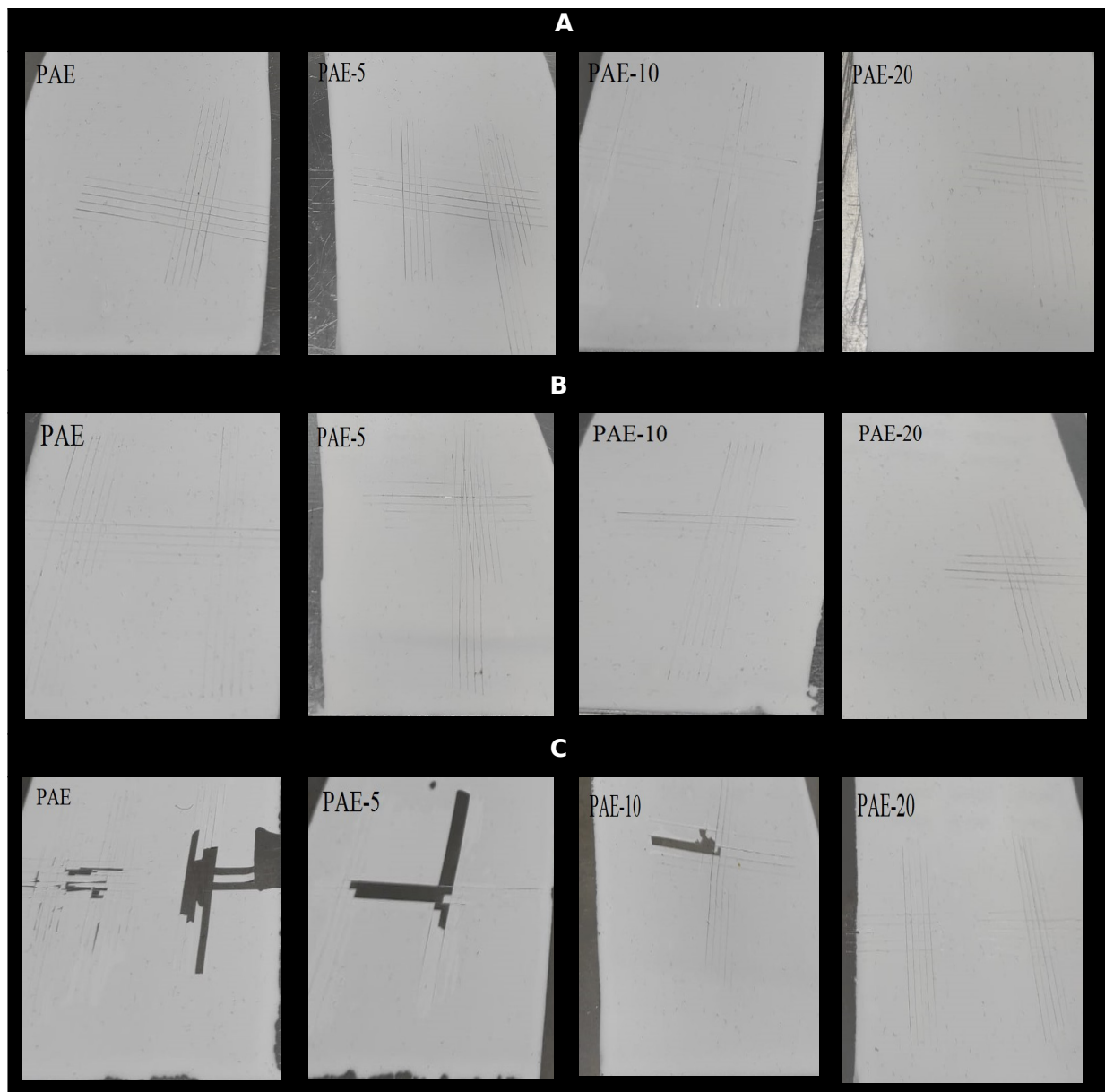


Figure 9. Cross-cut images for A) aluminum, B) galvanized and C) sheet surfaces.

In this study, the panels of paint mixtures prepared at the same film thickness were kept in a salt spray cabinet containing 20% NaCl solution for 250 hours. The images obtained at the end of the period are given in Figure 10. It was observed that the corrosion resistance increased with the increase of the acrylic copolymer ratio in the mixture, this improvement may have been achieved due to increased adhesion to the ground and reduced the amount of areas reached by the salt solution.

In impact testing, which is used to evaluate the toughness, fracture resistance, or impact

resistance of the material during an impact, a generally known weight is released from a known height so that it collides with the sample with a sudden force. The layers coated with the paints prepared in this study were subjected to an impact test with a weight of 500 g at 30, 50 and 70 cm heights. Experiment result images are given in Figure 11. There was no difference in impact strengths for 30 and 50 cm heights. When the height of 70 cm was increased, the impact resistance increased especially in mixtures prepared from resins with 10% and 20% acrylic copolymer added.

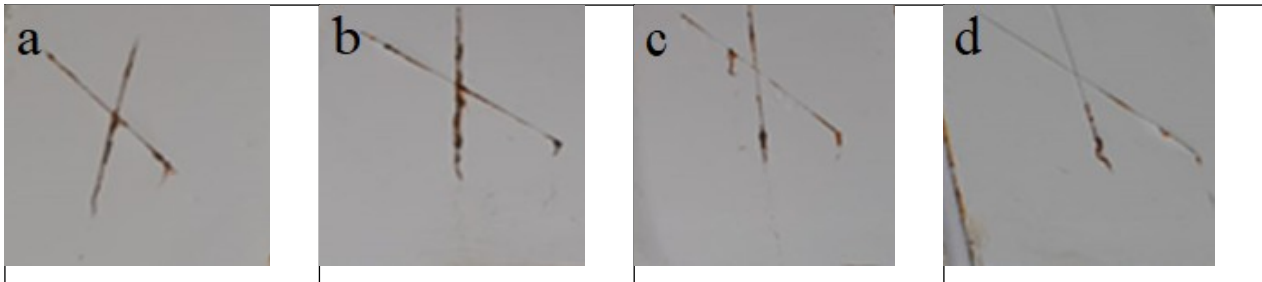


Figure 10. Paint salt spray test results of a) PAE, b) PAE-5, c) PAE-10, d) PAE-20 after 250 h.

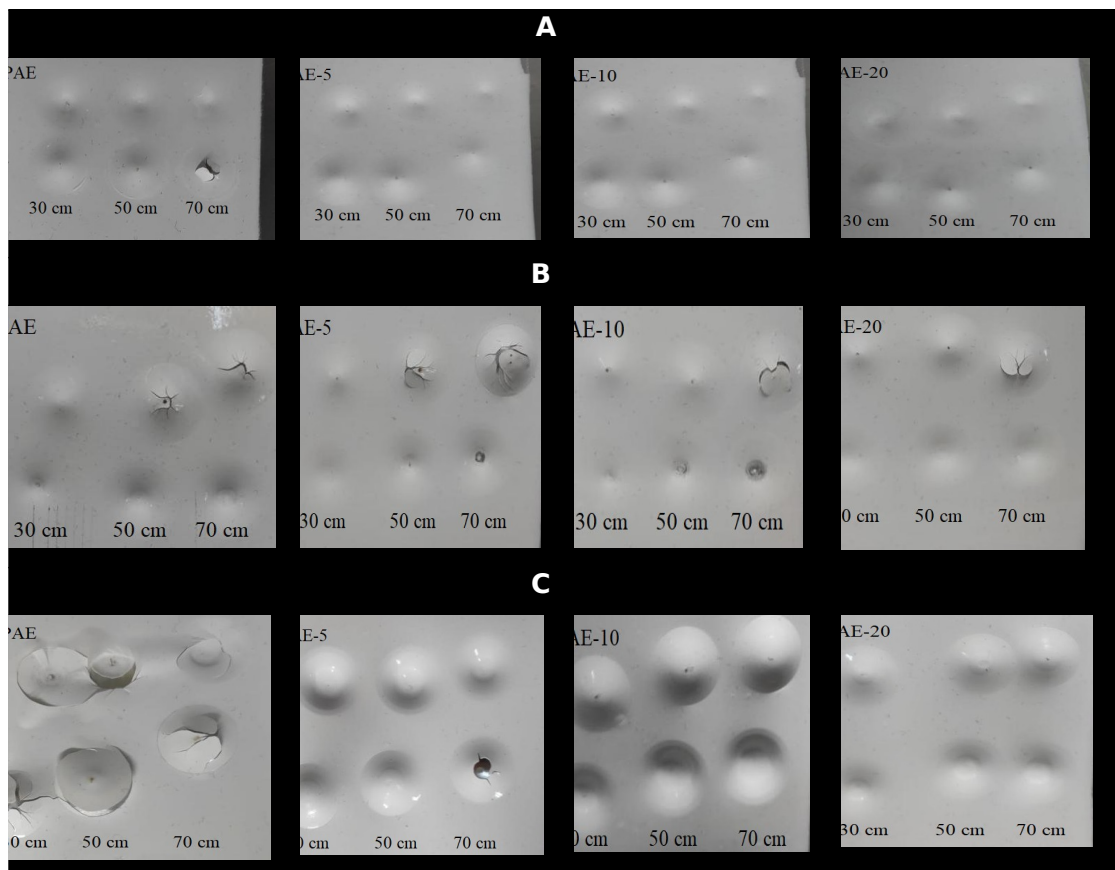


Figure 11. Paint impact test results of A) aluminum, B) galvanized and C) sheet surfaces.

4. CONCLUSION

In this study, besides the prominent and very important properties of polyaspartic ester resin, which is a new generation aliphatic coating system, studies were carried out to improve the properties such as, pot life, flexibility, color, adhesion etc... that can be considered as negative. The properties to be investigated were made by adding an acrylic copolymer with high OH value at 5, 10 and 20% ratios to PAE. The adhesion property was examined by the cross-cut test and increased according to the standard test method. This result was obtained especially for

properties. The acrylic polyols and aspartic mixtures may be used in the preparation of paints and varnishes applied on concrete, metal, and wood surfaces.

mixtures containing 10 and 20% copolymers. The flexibility of PAE was examined by the tensile-tensile test, and the increase in flexibility with the increase of the acrylic copolymer ratio added to the mixture was evaluated by taking into account the elasticity modules. The improvement of these properties has been achieved in PAE's superior yellowing resistance property and again without decreasing its superior pre- and post-UV gloss properties. These results, which are positive and do not lose the existing properties, also reduced the cost by adding acrylic copolymer to PAE. All results increased the application potential of a new system, polyaspartic ester resin, with new

5. CONFLICT OF INTEREST

There is no conflict of interest.

6. ACKNOWLEDGMENTS

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