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# Investigation of the effect of cyclic borate ester groups in acrylic copolymers on paint and varnish coatings

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#### **ARTICLE INFO**

# ABSTRACT

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Keywords: Acrylic coatings Borate ester Boron acrylate copolymers Paint and varnish In this study, cyclic borate ester-bearing methacrylic monomers were synthesized and then employed to synthesize acrylic copolymers with varying boron acrylate monomer contents (5, 10, and 20%). The monomers, methyl methacrylate, butyl acrylate, acrylic acid, and boron acrylate, were used to synthesize all of the polymers via free radical polymerization method in a solvent media. The polymers were characterized using Fourier Transform Infrared Spectrophotometer (FTIR), Differential Scanning Calorimetry (DSC), Gel Permeation Chromatography (GPC), Proton and Boron Nuclear Magnetic Resonance spectroscopy (<sup>1</sup>H and <sup>11</sup>B NMR). Metal surfaces, such as sheet metal, galvanized steel, and aluminum were covered with varnish and paint compositions that had a fixed thickness. The physical characteristics of the coatings such as contact angle value, glossiness, hardness, drying time, pot life, yellowing resistance, and gloss loss following UV were all measured. According to the findings, with the addition of borate ester groups to polymers their hardness was increased whereas the drying time of the coatings was decreased. When compared to the binders used in commercially available paints, the polymer that contains 10% boron acrylate monomer can be utilized to produce paints and varnishes with equal or superior physical properties.

#### 1. Introduction

Turkiye has the greatest boron deposits in the world, hence boron and its derivatives are very important to our nation. In recent years, it has become more important to find new uses for boron and its derivatives in various applications to create goods with a high added value. Earth's crust has two stable boron isotopes, <sup>10</sup>B and <sup>11</sup>B, with isotope abundances of 19.10-20.31% and 79.69-80.90%, respectively. Boric acid and other byproducts are created when boron combines with water at a high temperature. Depending on temperature and condensation, reactions with mineral acids can be either extremely slow or explosive. The most popular boron derivative is boric acid [1-4]. A wide range of sectors and applications, such as agriculture, metallurgy, energy storage, automobile (airbags, hydraulic brakes, etc.), water treatment applications, pigments and dryers, nuclear and space applications, and pharmaceutical and chemical sectors, all employ boron minerals and boron-based goods. They are generally used as fire retardant chemicals in resin additive materials [5-8]. On the other hand, there are studies in which boric acid and its derivatives are used as monomers in the development of many polymers, especially acrylic polymers [9-12]. Different acrylic copolymers containing boron monomers were used as binders in paints for their antifouling

and self-polishing properties [13-16]. The polymers were prepared via emulsion polymerization of boroncontaining monomers for composite, flame retardant and adhesive applications [17-20]. Road marking paint made from acrylic copolymers is crucial since it can be used in cold regions and it dries quickly -within minutes-which is an important aspect to prevent traffic delays when applied. They are highly favored since they are compatible with different surfaces and are simple to apply with brushes and hand sprayers. Researchers employ several acrylic monomer types to enhance physical, mechanical, and thermal qualities including hardness and weather resistance [21-24].

To the best of our knowledge, there is no study about boron-containing acrylic copolymer-based road marking paints in the literature. In this work, it was found that, the incorporation of boron monomers into the acrylic copolymer backbones enhanced all the above-mentioned significant features compared to the acrylic copolymers that do not contain boron monomers.

#### 2. Materials and Methods

#### 2.1. Materials

Ortho-phosphoric acid (>85.0%, Sigma Aldrich), boric



acid (BA, 99%, Sigma Aldrich), neopentyl glycol (NPG, >99%. BASF). 2-hvdroxvl ethvl methacrvlate (HEMA. >99%, Prochema Chemical LTD.), 4-methoxy phenol (MeHQ, 99%, Sigma Aldrich), toluen (>99%, Sigma Aldrich), methyl methacrylate (MMA, 98%, ARKEM), butyl acrylate (Bac, >99% Ataman Chemicals), acrylic acid (AA, 98%, ARKEM), tert-Butyl peroxybenzoate (AKPA, Ataman Chemicals), N-dodecyl mercaptane (NDM, 98%, Ataman Chemicals) were purchased and used without any further purifications.

#### 2.2. Methods

#### 2.2.1. Synthesis of boron methacrylate monomer (BOM) (2-(5,5-Dimethyl-1,3,2-dioxaborinan-2yloxy)ethyl methacrylate)(1)

The boron methacrylate monomer (BOM) was synthesized according to the modified procedure described in the literature and the synthetic route of whole reaction process is depicted in Figure 1. The monomer was obtained by two subsequent esterification reactions. Initially, 60 g of boric acid, 101.4 g of neopentyl glycol, 200 ml toluene, and 0.11 g of aqueous ortho-phosphoric acid was added to a 1000 ml four-necked round bottom flask equipped with a Dean-Stark trap and a condenser. After 3 hours of mixing at reflux temperature, two equivalents of water was removed. Then, the heater was closed and, 117.6 g of HEMA and 0.67 g of MEHQ were added at room temperature. After stirring for about five minutes, the reaction was heated to reflux temperature to remove one equivalent of water by azeotropic distillation with Dean-Stark. The solvent was then removed by vacuum distillation. The product was transparent, colorless liquid (yield: 95%).

# 2.2.2. Synthesis of boronate ester-containing acrylic co-polymers (2-5)

Free radical polymerization was accomplished according to an adapted procedure (Figure 2) to acrvlic copolymers (poly(MMA/BA/BOM/ create AA)) in nitrogen atmosphere. All the monomers and the initiator were fully charged in a 3-4 hours of time interval to a three-necked round bottomed flask filled with pre-heated toluene at reflux temperature under the nitrogen atmosphere. The reaction was monitored by ATR-FTIR and the measurement of the solid content at every half hour. After the reaction was completed, the mixture was cooled down to the room temperature.

The amounts of the monomers, solvent and initiator were shown in Table 1. The blank polymer that did not contain any boron monomer was synthesized as reference to understand the effect of the boron monomer on the paint and varnish coatings. The solid amount was adjusted to 60% for all polymerizations meaning that each resin composition contains 40% solvent and 60% polymer. Acrylic copolymers containing 5%, 10% and 20% borate esters were abbreviated as AC-5%-Boron Acrylate, AC-10%-Boron Acrylate, and AC-20%-Boron Acrylate, respectively.

#### 2.2.3. Characterization of monomer and polymers

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<sup>-1</sup>) at a resolution of 4 cm<sup>-1</sup> with 16 scans (Spectra Manager II software, JASCO Corp.). <sup>1</sup>H NMR and <sup>11</sup>B NMR analyses were performed with an Agilent VNMRS spectrometer at 500 MHz. Tetramethylsilane (TMS)





Table 1. The compositions of borate ester containing acrylic co-polymers (2-5).							
Raw materials	Blank (2)	AC-5%	AC-10%	AC-20%			
	. ,	Boron Acrylate (3)	Boron Acrylate (4)	Boron Acrylate (5)			
MMA (g)	50	50	50	50			
BAc (g)	40	40	40	40			
AA (g)	1.2	1.2	1.2	1.2			
Tert-Butyl peroxybenzoate (g)	1.2	1.2	1.2	1.2			
Boron Acrylate (g)	0	4.92	10.38	23.35			
Solid amount (g)	92.4	98.32	103.78	116.75			
Solvent (g)	61.6	65.54	69.2	77.84			
Total amount (g)	154	163.86	172.98	194.59			
Solid %	60.00	60.00	60.00	60.00			
Boron Acrylate %	0.00	5.00	10.00	20.00			

Table 1. The com	positions of borate	ester containing	acrvlic co-r	olymers (	2-5)
	poolitionio or portato	ootor oontaining			<u> </u>

was used as internal standard in <sup>1</sup>H NMR spectra ( $\delta$ =0). Deuterated chloroform (CDCl3) was used as solvent  $(\delta_{11}=7.26 \text{ ppm})$ .<sup>11</sup>B NMR spectra were referenced to external BF, etherate ( $\delta$ =0). 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<sup>-1</sup> 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). Crosscut adhesion test kit CC2000 from TQC Sheen B.V. (Capelleaan den IJssel, Netherlands) was used to test the adhesion of drv coatings on their substrate. The brightness of the films was determined using a Novo-Gloss Trio glossmeter.

# 2.2.4. Preparation of paint and varnish formulations

A simple paint recipe was applied for the polymeric resins, separately. Varnishes (no pigment) and white paints (with pigment) were prepared in each case by using the same amount of resins, pigments and other ingredients in the formula. For mixing all ingredients in the paint, a high-speed mixer was used, and fineness of grinding was monitored by using a grindometer.

Paints were applied to the glass and metal surfaces by using a film applicator with 90 micrometer thickness. Adhesion, touch, drying time, and gloss properties of the paints were determined by using metal surfaces. Glass panels were used for the determination of hard drying times by drying time recorder. The paint formulations were shown in Table 2.

#### 2.2.5. Characterization of painted and varnished surfaces

#### 2.2.5.1. Drying time measurements

Touch drying times were checked in regular intervals by applying a force with fingertip to a painted or varnished surface on a metal panel. Hard drying time was determined by drying time recorder. A paint or varnish was applied to a glass panel and the glass panel was putted on the machine. The scratching ending on glass panels shows the complete dry time.

#### 2.2.5.2. Adhesion test

After keeping the paint applied on the surface of a metal panel for about one day cross cut adhesion method was applied. In the adhesion test the panel sliced with 1 mm gap between 4 vertical and 4 horizontal lines. Cellophane tape was applied to whether the paint was

Table 2. The compositions of paints that are given as a percentage.							
Contents (%)	Blank	AC-5%	AC-10%	AC-20%			
A anylia conclumera	25.0			DOI OIT ACT yiate			
Acrylic copolymers	25.0	25.0	25.0	25.0			
Wetting and dispersing additive	0.5	0.5	0.5	0.5			
Titanium dioxide (TiO <sub>2</sub> )(for cloaking)	10.0	10.0	10.0	10.0			
Barite (for filler)	10.0	10.0	10.0	10.0			
Calcite	28.0	28.0	28.0	28.0			
Defoamer	1.0	1.0	1.0	1.0			
Wetting substrates	0.6	0.6	0.6	0.6			
UV absorber	0.6	0.6	0.6	0.6			
Solvent	23.7	23.7	23.7	23.7			
Total	100.0	100.0	100.0	100.0			

Table 2. The compositions of points that are given as a percentage

removed from the surface or not to get the adhesion degree.

#### 2.2.5.3. Contact angle measurements

The contact angle measurements of UV-cured coatings were performed using standard goniometer (250, Ramehart instrument company, USA) by applying sessile drop method.

# 2.2.5.4. Gloss test of the coatings

Using an applicator, paints with and without boron acrylate groups were applied to the zebra card to create a 90 micron thick layer. In accordance with ISO2813 and ASTM D523 standards, 20/60/85° gloss measurements were performed using a glossmeter after the films were dried.

#### 2.2.5.5. Surface hardness

Using an applicator, a 150  $\mu$ m thick layer of paints with and without boron acrylate groups were applied to the glass plates. The König or Persoz technique, as described in ISO 1522, was used to measure the hardness of the surfaces using the Pendulum Hardness Tester.

#### 2.2.5.6. Conical bend test

Using paints and resins with and without boron acrylate groups, 90 micron-thick films were created on sheet metal, galvanized steel, and aluminum metal plates. TS EN ISO 6860 and ASTM D522 standards have been used to assess the flexibility or cracking resistance of coatings, paints, and varnishes. A magnifying lens was used to identify fractures and rips.

# 2.2.5.7. Impact test

On sheet metal, galvanized metal, and aluminum metal plates, 90  $\mu$ m thick coatings were created using paints and resins with and without boron acrylate. In line with TS EN ISO 6272-1 requirements, various plates were set up in the impact test apparatus, and 1 kg weights were put on the metal surfaces with 5N force from a height of 50 cm. A magnifying lens was used to interpret the fractures that appear.

# 2.2.5.8. Taber abrasion test

Paints and resins were applied with a brush to 8x8 cm square sheet plates for the Taber abrasion test. According to ASTM D4060 standards, the applied plates were put through a wear test at 1000 rpm and 72 rpm using the mass loss technique.

# 3. Results and Discussion

# 3.1. Characterization of Boronate Ester Acrylic Monomer (BOM) and Polymers

Structural analysis of the acrylic monomer and polymers

were achieved by using ATR-FTIR and <sup>1</sup>H NMR. In the ATR-FTIR spectrum of the BOM monomer, as shown in Figure 3, the stretching bands of hydrogens on CH<sub>2</sub> and CH<sub>3</sub> groups showed characteristic peaks at 2958 and 2923 cm<sup>-1</sup>, respectively. Strong absorption around 1724 cm<sup>-1</sup> corresponded to the vibration of the C=O double bond of ester groups. In addition, the presence of the acrylate group was confirmed by the absorption bands observed at 1635 and 813 cm<sup>-1</sup>. The characteristic peak at 1419 cm<sup>-1</sup> indicated the B-O bond of cyclic borate ester. In the ATR-FTIR spectrum of the acrylic copolymers, as shown in Figure 3, the polymerization of acrylate groups was confirmed by the absence of the absorption bands of the acrylic double bonds observed at 1635 and 813 cm<sup>-1</sup> in the monomers before polymerization.



**Figure 3.** ATR-FTIR spectrum of A) BOM monomer and B) blank and 5%, 10% and 20% boron containing copolymers.

The structures of the BOM monomer and copolymers were further confirmed by <sup>1</sup>H NMR spectroscopy. Figure 4 shows the <sup>1</sup>H-NMR spectra of boron acrylate monomer and boron containing acrylic copolymer in CDCI<sub>3</sub>. The peak at 2-2.2 ppm (c) indicated CH<sub>3</sub> protons in the boron acrylate monomer. The peaks at 5.5-6.3 ppm (a+b) prove the presence of the acrylic double bonds (-C=C-). Protons attached to carbons at the ester groups (-OCH<sub>2</sub>-CH<sub>2</sub>-) were detected at



Figure 4. <sup>1</sup>H-NMR spectra of boron acrylate monomer (BOM) and boron containing acrylic copolymer in CDCl<sub>a</sub>.

3.90-4.30 ppm (d, e and f). The apparent peak at 0.99 ppm was due to the  $CH_3$  protons in the cyclic ring of the borate ester. The peak seen at 3.6 ppm was due to the  $CH_2$  protons of the borate ester. In the spectra of the acrylic copolymers, the absence of the peaks related to acrylic double bonds at 5.5-6.3 ppm confirmed the polymerization of acrylic monomers.

The molecular weight characteristics of the polymers were presented in Table 3. In case of the addition of boron methacrylate monomer into the polymers in different ratios, the weight average molecular weight (Mw) of the polymers was increased. This may be due to the high molecular weight of the boron containing monomer (more massive than the other monomers) addition made the polymer chains more massive leading the contribution in Mw.

**Table 3.** Molecular weight characteristics of blank and boron containing acrylic copolymers.

Polymer	Mn (g/mol)	Mw (g/mol)	Polydisper- sity Index (PDI)
Blank	1609	2706	1.68
AC-5% Boron Acrylate	1309	2456	1.88
AC-10% Boron Acrylate	1310	2516	1.92
AC-20%-Boron Acrylate	1343	2861	2.13

The DSC graph given in Figure 5 indicated that increasing the proportion of boron-containing

monomers in the polymers decreased the glass transition temperature of the polymers. This might be caused by the enhanced flexibility of the polymers due to the pendant long chain of monomers.

# 3.2. Mechanical and Physical Properties of the Resins and Paints

Physical and mechanical characteristics of the coatings are listed in Table 4, including color, glossiness, hardness, drying time, pot life, adhesiveness, bending, and corrosion behavior.

# 3.3. Adhesiveness of the Resins into Different Substrates

For aluminum, galvanized, and sheet metal surfaces, a cross cut test was performed in accordance with the ASTM D3359 standard. Following the cut, it was removed from the surfaces using adhesive tape. Figure 5 depicted the test results for the adherence of blank resin and resins with boron acrylate ratios in varnish coatings.

#### 3.4. Softening Test For the Resins

Thermoplastic resins are polymers that soften when heated and harden when cooled. This study investigated how various boron acrylate ratios influenced the produced film's softening point. Glass surfaces were coated with 200 micron thick resins, then flakes of identical weight and diameter were placed on

		AC-5%	AC-10%	AC-20%
Test	Blank	Boron	Boron	Boron
		Acrylate	Acrylate	Acrylate
Gloss (20 degree)	72.2	74.3	75.2	71.6
Persoz Hardness (150 micron, 7 days)	51-94	60-120	78-142	53-114
Drying (min)	20	15	10	85
Impact Strength (1000 g/50 cm)*	3/3/3	3/2/3	1/1/1	1/1/2
Cross-cut Adhesion Test (aluminum/galvanized/sheet)*	0/0/2	0/0/2	0/0/1	0/0/2
Conical Bending (aluminum/galvanized/sheet)*	0/0/1	0/0/1	0/0/0	0/0/0
Salt Solution Resistance* (10 days immersed in salt solution)	0	0	0	0

Table 4. Physical and mechanical properties of the blank and boron containing polymer coatings.

\*0 is the best and 5 is the worst.



Figure 5. a) DSC graphs for blank and boron containing acrylic copolymers, cross-cut images for b) galvanized, c) aluminum and d) sheet surfaces.



Figure 6. Softening behavior of blank and boron containing resins.

it and allowed to dry for a day. The glass plates were dried, then placed upright in an oven and heated for 15 minutes at 60°C before being incubated for 30 minutes at 80°C. Figure 6 depicted the test results. According to the softening test, the flake placed on the Blank resin slides down 3 cm at 60°C and 15 cm at 80°C as a result of the resin softening. At 80°C, it was found that resins containing 5% and 10% boron acrylate moved down 3 cm and 2 cm, respectively. It was determined that boron acrylic resin containing 20% boron provided unsatisfactory results. Given the extended drying time of 20% boron acrylic resin, it was fair to predict that softening would be greater under the same conditions.

#### 3.5. Impact Test for Resins

In the impact test, which is used to evaluate the hardness, fracture resistance, or impact resistance of a material during an impact, a generally known weight is released to collide with the sample with a sudden force from a known height. Sheet metal plates coated with paints were subjected to the impact test from a height of 50 cm and weight of 1000 gr. Test results were given in Figure 7. It was observed that the impact strengths were very close in the paint prepared with Blank resin and resin containing 5% boron acrylate, and there was an improvement in paints prepared with resins containing 10% and 20% boron acrylate.

#### 3.6. König Bending Test for Resins

Bending strength is the resistance of the paint film





**Figure 7.** Impact test results for the paints obtained from blank and boron containing polymers.

to cracking, breaking, and peeling faults when bent with the metal panel on which it is applied. Bending strength was tested by bending the panel around cylinders, conical cylinders or bending directly by folding. The paints were applied to the plates at 90 microns and left to cure for one day using blank, 5%, 10%, and 20% boron acrylic resins. The sheet metal plates were submitted to the conical bend test after drying. They were bent around a steel mandrel in roughly 1 second with a steady force. The frequency of fractures generated in the paint film from the top of the cone was inspected and analyzed following the tests. The sheet metal plates were displayed as a result of the Conical Bend Test in Figure 8. Cracks were seen in the blank resin paint due to the force applied during the bending test. In the bending test, it was observed that there was no cracks or shedding in the paints prepared with resins containing 10% and 20% boron acrylate, but only small cracks were revealed in the 5% boron acrylate resin paint. Furthermore, the resistance against defects such as, cracking, breakage and separation from the surface increased as the boron acrylate ratio increased.

#### 3.7. Gloss Test

Using an applicator at a 60 micron thickness, the glosses of the blank resin and the resins containing boron acrylate in different ratios were measured using a glossmeter for the gloss test. The glossmeter data



Blank AC-5% AC-10% AC-20% Figure 8. Conical bending test results of the sheet plates covered with paints made from blank and boron containing polymers.

showed that the brightness of the resins containing boron acrylate were enhanced compared to the blank sample (Figure 9).

#### 3.8. Taber Abrasion for the Resins

The sample's original weight was calculated first in the test performed in accordance with the ASTM D4060 standard and mass loss. The test sample was then placed in the abrasion tester. The abrasive wheel was loaded with 500 g of load and spun 1000 times.



After the prescribed number of cycles, the final weight was measured, and the amount of surface material removed was determined. The wear test results for the following materials were shown in Figure 10 for acrylic copolymers containing 5, 10, and 20% boron. In Eq. 1, A is weight of the specimen before abrasion, B is weight of the specimen after abrasion, and C is the number of test cycles. The Taber Wear Index was calculated as in Eq. 1 and thecalculated values were used to create the graph in Figure 10c.

Taber Wear Index = 
$$((A - B) \times 1000)/C$$
 (1)

When the number of spins for blank and 10% boroncontaining acrylic copolymer increased, less wear occurred. The drop in the Taber Wear Index values pointed to this (Figure 10c). As the boron ratio in the mixture increased the wear began to decrease. The Taber abrasion test could not be performed for the



Figure 10. A) Pre-test, B) Abrasion test images after 1000 cycles a) Blank, b) 5%, c) 10%, and C) Graphical displays according to the Taber Wear Index.

resin containing 20% boron acrylate because it did not fully dry and remained soft. The rise in the index values for boron-containing acrylic copolymers that include 5%, 10%, and blank can be interpreted as an increase in hardness and subsequent increased wear in the internal layers after surface wear.

#### 3.9. Contact Angle, Surface Tension, and Surface **Energy Tests for the Resins**

The wettability of coatings containing boron acrylate resin was assessed using the water contact angle test. The perspectives of the coatings in relation to water contact were shown in Figure 11. It was measured that the contact angle of the glass surface was 41°, but it rose to 72° as the boron acrylate ratio increased to 20%.



In general, a paint layer will be able to wet the substrate effectively if it has lower surface tension than the substrate. Although the glass surface had a 43 mN/m surface tension, as illustrated in Figure 12, it was discovered that when the boron acrylate ratio increased, the adhesion to the surface improved and the surface tension decreased by 41 mN/m.



Figure 12. Surface tension test results.

Figure 13 demonstrated that when the boron acrylate ratio increased, the surface energy decreased and the surface hydrophobicity increased. It was discovered that the top coat paint or varnish adhered to the covered surface more strongly when surface energy dropped.



When the influence of UV radiation on the film was investigated, it was discovered that there was no deterioration in yellowing resistance over a 10-day period. The saline solution resistance of the coatings used on the glass panels was tested (Table 5). They were immersed in a 20% NaCl solution for 72 hours, and four glass test panels were also immersed for 72 hours. At the end of the experiment, the experimental panel was removed and dried using blotting paper. The presence of spills or surface trenches was examined with the help of a lens and it was observed that it was resistant to saline solution. It was observed that the drying time was prolonged and the surface hardness decreased when the boron acrylate ratio of the paint exceeded 10%. It was observed that as the boron acrylate ratio in the paints increased, the hardness and, accordingly, the abrasion increased. The paint made of thermoplastic resin containing boron acrylate was subjected to the softening test in an oven at 80°C and 120°C, and it was observed that the paints did not soften at 80°C and 120°C.

#### 4. Conclusions

In the light of the findings of the study conducted, it became clear that 10% boron acrylate resin performed better in the gloss test than other resins. As the amount of boron acrylate was raised, the properties that are crucial for road marking paints -high surface hardness, late wear, and weather resistance-also increased. Yet, when boron acrylate content rises, it becomes a perfect resin for primer applications as surface energy

Table	5.	Test	results	for	paints.
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Test	Blank	AC-5%-Boron Acrylate	AC-10%-Boron Acrylate	AC-20%-Boron Acrylate			
Persoz Hardness (150 micron, 7 days)	51-94	60-120	78-142	53-114			
Drying (min)	25	20	15	110			
Abrasion Test (mg loss/1000 cycle)*	0.485	0.574	0.614	-			
Conical Bending (aluminum/galvanized/sheet)*	2	1	1	1			
Salt Solution Resistance*	0	0	0	0			

falls and adhesion in topcoat applications rises. The resin containing 10% boron acrylate had the greatest hardness value in the hardness test. The quick drying time of road line paints is a desired quality. Therefore, the drying period was shortened by adding up to 10% more boron acrylate than blank resin. When compared to blank resin, resins with additional boron acrylate have a better effect on softening. Comparing 10% boron acrylate resin to other resins, the results of the adhesion and impact tests show that it performs better. In comparison to other resins, 10% boron acrylate resin exhibited reduced wear in the abrasion tests. It was found after all the test data were analyzed that the copolymers containing 10% boron acrylate had improved qualities when employed in varnish and paint formulations.

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#### References

- [1] Özkan, Ş. G., Çebi, H., Delice, S., & Doğan, M. (1997). Bor minerallerinin özellikleri ve madenciliği [Properties and mining of boron minerals], 2. Endüstriyel Hammadddeler Sempozyumu [2. Industrial Raw Materials Symposium], İzmir, 224-228. https://doi.org/10.1021/acs.iecr.8b06337.
- [2] Kar, Y., Şen, N., & Demirbaş, A. (2006). Boron minerals in Turkey, their application areas and importance for the country's economy. *Minerals & Energy-Raw Materials Report*, 20(3-4), 2-10. https://doi. org/10.1080/14041040500504293.
- [3] Zhu, Y., Cai, J., Hosmane, N. S., & Zhang, Y. (2022). Introduction: Basic concept of boron and its physical and chemical properties. In *Fundamentals and Applications* of Boron Chemistry (pp. 1-57). Elsevier. https://doi. org/10.1016/B978-0-12-822127-3.00003-X.
- [4] Elçiçek, H. (2012). Sulu ortamda karbondioksit basıncı altında üleksit cevherinin çözünme kinetiği ve optimizasyonu [Dissolution kinetics and optimization of ulexite ore in aqueous medium under carbondioxide pressure] [M. Sc. thesis, Ataturk University]. Council of Higher Education Thesis Center (Thesis Number 312914).
- [5] Karadagli, E., & Cicek, B. (2020). Boron mining and enrichment waste: A promising raw material for porcelain tile production. *International Journal of Applied Ceramic Technology*, 17(2), 563-572. https://doi.org/10.1111/ ijac.13438
- [6] Murthy, T. S., Sonber, J. K., Sairam, K., Majumdar, S., & Kain, V. (2020). Boron-based ceramics and composites for nuclear and space applications: synthesis and consolidation. In *Handbook of advanced ceramics and composites: Defense, security, aerospace and energy applications*, 703-738. Springer International Publishing. https://doi.org/10.1007/978-3-030-16347-1\_22.
- [7] Gol, F., Kacar, E., Saritas, Z. G., Cibuk, S., Ture, C., Arslan, M., & Sen, F. (2023). The use of boron based materials on efficiency of environmentally friendly porous ceramics. *Environmental Research*, 216, 114454. https://

doi.org/10.1016/j.envres.2022.114454.

- [8] Dogan, M., Dogan, S. D., Savas, L. A., Ozcelik, G., & Tayfun, U. (2021). Flame retardant effect of boron compounds in polymeric materials. *Composites Part B: Engineering*, 222, 109088. https://doi.org/10.1016/j. compositesb.2021.109088.
- [9] Chauhan, N. P. S., Hosmane, N. S., & Mozafari, M. (2019). Boron-based polymers: Opportunities and challenges. *Materials Today Chemistry*, 14, 100184. https://doi.org/10.1016/j.mtchem.2019.08.003.
- [10] Akarsu Dulgar, C., Çakır Çanak, T., & Serhatlı, İ. E. (2019). Effect of boron acrylate monomer content and multi-acrylate functional boron methacrylate on adhesive performance for water-borne acrylic polymers. *Polymer Bulletin*, 76, 2499-2517. https://doi. org/10.1007/s00289-018-2490-z.
- [11] He, C., & Pan, X. (2020). MIDA boronate stabilized polymers as a versatile platform for organoboron and functionalized polymers. *Macromolecules*, 53(10), 3700-3708. https://doi.org/10.1021/acs.macromol.0c00665
- [12] Dong, J., He, C., Xu, C., Yun, J., & Pan, X. (2022). Vinyl boronate polymers with dynamic exchange properties. *Polymer Chemistry*, *13*(46), 6408-6414. https://doi. org/10.1039/D2PY01274J.
- [13] Song, F., Wang, J., Zhang, L., Chen, R., Liu, Q., Liu, J., & Duan, J. (2022). Synergistically improved antifouling efficiency of a bioinspired self-renewing interface via a borneol/boron acrylate polymer. *Journal of Colloid* and Interface Science, 612, 459-466. https://doi. org/10.1016/j.jcis.2021.12.187.
- [14] Li, Y., Chen, R., Feng, Y., Sun, X., Tang, L., Takahashi, K., & Wang, J. (2019). Synthesis of amphiphilic acrylate boron fluorinated polymers with antifouling behavior. *Industrial & Engineering Chemistry Research*, 58(19), 8016-8025. https://doi.org/10.1021/acs.iecr.8b06337.
- [15] Li, Y., Liao, J., Zhang, H., Tang, X., Zhong, S., Yu, Y., & Li, Q. (2021). Super-structural 2D ultrathin carbon nitride/acrylate boron silane polymer with multi-function for enhancing antifouling performance. *Journal of Coatings Technology and Research*, 18, 1051-1064. https://doi.org/10.1007/s11998-020-00459-5.
- [16] Zhang, Z., Li, Y., Chen, R., Liu, Q., Liu, J., Yu, J., ... & Wang, J. (2021). Photocatalytic antifouling coating based on carbon nitride with dynamic acrylate boron fluorinated polymers. *New Journal of Chemistry*, 45(2), 780-787. https://doi.org/10.1039/D0NJ05132B.
- [17] Temelkaya Bilgin, E., Akarsu Dülgar, C., Çakır Çanak, T., & Serhatlı, İ. E. (2021). Effect of boron methacrylate monomer on the thermal and pressure-sensitive adhesive properties of 2-EHA-based copolymer latexes synthesized via mini-emulsion polymerization procedure. *Polymer Bulletin*, *78*, 133-145. https://doi. org/10.1007/s00289-020-03101-x.
- [18] Aliyeva, N., Canak, T. C., & Serhatlı, İ. E. (2021). Synthesis and characterization of boron-acrylate/Santa Barbara Amorphous-15 polymer composite. *Journal of Applied Polymer Science*, *138*(20), 50445. https://doi. org/10.1002/app.50445.
- [19] Rawat, R. S., Talwar, M., Diwan, R. K., & Tyagi, A.

K. (2021). A study on flame-retardancy property of UV curable epoxy coating for wooden surfaces using boron diluent and phosphorus based initiator. *Journal of Polymer Materials*, *38.* https://doi.org/10.32381/JPM.2021.38.3-4.9

- [20] Temelkaya Bilgin, E. (2019). Synthesis and characterization of water-based acrylic polymers for pressure-sensitive adhesive applications via miniemulsion polymerization. [Doctoral Thesis, İstanbul Technical University]. Council of Higher Education Thesis Center (Thesis Number 560917).
- [21] Mirabedini, S. M., Zareanshahraki, F., & Mannari, V. (2020). Enhancing thermoplastic road-marking paints performance using sustainable rosin ester. *Progress in Organic Coatings*, 139, 105454. https://doi. org/10.1016/j.porgcoat.2019.105454.
- [22] Lim, W. B., Kim, J. W., Lee, J. H., Bae, J. H., Min, J. G., & Huh, P. (2023). Synthesis of a room-temperature curable acrylic-urethane polymer binder for road markings with high transmittance. Materials, 16(3), 1322. https://doi.org/10.3390/ma16031322.
- [23] Pereira, A. P., Ribeiro, J. L., Oliveira, A. C. F., Vasconcelos, C. K. B., Viana, M. M., & Lins, V. D. F. C. (2021). Ligninmodified road marking paint: weathering aging studies. *REM - International Engineering Journal*, 74, 225-233. https://doi.org/10.1590/0370-44672020740113
- [24] Hadizadeh, E., Pazokifard, S., Mirabedini, S. M., & Ashrafian, H. (2020). Optimizing practical properties of MMA-based cold plastic road marking paints using mixture experimental design. *Progress in Organic Coatings*, 147, 105784. https://doi.org/10.1016/j. porgcoat.2020.105784.