

Preparation and Characterization of UV-Curable, Boron-Containing, Transparent Hybrid Coatings

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ABSTRACT: A series of ultraviolet (UV)-curable, boron-containing hybrid coatings were prepared by an anhydrous sol-gel technique from a mixture of an acrylated bisphenol A based epoxy resin, methacryloxymethyl triethoxysilane, and boric acid. The use of boric acid allowed the hydrolysis and condensation of hybrid silicon alkoxides without the further addition of water or a catalyst. The chemical structure of the boron-containing hybrid coatings was characterized with Fourier transform infrared, real-time infrared, and ²⁹Si cross-polarization/magic-angle spinning NMR techniques. UV-curable coatings were applied to polycarbonate and Plexiglas substrates. The physical and mechanical properties of the UV-cured coatings (e.g., pendulum hardness, pencil hardness, con-

tact angle, gel content, methyl ethyl ketone rubbing test, tensile test, abrasion resistance, chemical resistance, neutron absorption, and limiting oxygen index) were examined. The hybrid coatings showed a significant enhancement in their radiation-shielding properties. The thermal behavior of the coatings was also evaluated. It was observed that the thermal stability of the coatings mainly depended on their boron and silicate contents. The results of all analyses of the free films and coatings were examined. © 2010 Wiley Periodicals, © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2112–2121, 2011

Key words: coatings; crosslinking; flame retardance; irradiation; neutron reflectivity

INTRODUCTION

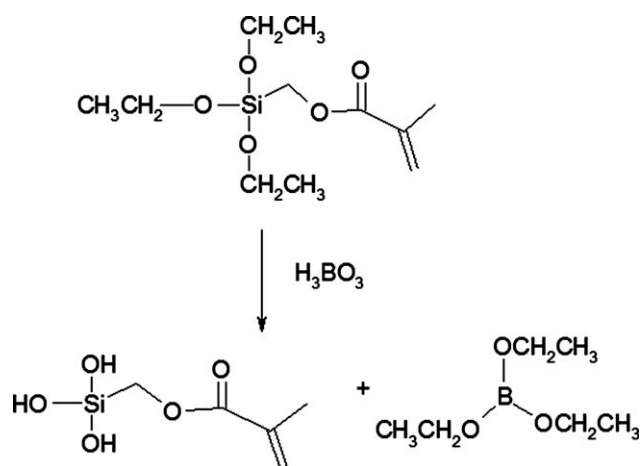
Most organic-inorganic hybrid materials reported in the literature are thermally cured. Alternatively, hybrid materials can be prepared by radiation curing.¹ Ultraviolet (UV)-curing technology has been widely employed because it has some advantages, such as a high speed, lower energy consumption, room-temperature operation, lower processing costs, high chemical stability, and environmental friendliness through the avoidance of solvents.² In UV-curing industries, epoxy and epoxy acrylate derivatives have been widely used as surface coatings, structural adhesives, and advanced composite matrices. Epoxy resins and polymers have excellent chemical and solvent resistance, good thermal and adhesion properties, and versatility in crosslinking.^{3,4}

Organic-inorganic hybrid materials offer the opportunity to combine the desirable properties of organic polymers (elasticity, ductility, toughness, and process-

ability) and inorganics (hardness and chemical and thermal resistance). Hydrolysis and condensation reactions of the inorganic part and photopolymerization of the organic moieties lead to a glasslike material at room temperature.^{5–7} The hybrid inorganic-organic materials produced by the conventional sol-gel process generally have high OH absorption from residual silanols or adsorbed free water, and this can adversely affect the application of such materials as optical devices. For the reduction of the residual OH concentration, an anhydrous sol-gel process that is based on the hydrolysis and condensation of alkoxides with weak acids has been developed.^{8,9} At low temperatures, boron exists predominantly as boric acid and allows the hydrolysis and condensation of hybrid silicon alkoxides without the further addition of water or a catalyst. The incorporation of boron oxide lowers the refractive index of silica; it is, therefore, interesting for planar optical waveguides. Boron-containing materials may be used for radiation protection. Because neutrons are uncharged particles that can travel through matter without ionizing that matter, it is difficult to detect them directly.¹⁰ Therefore, a prerequisite for neutron scintillators is the presence of neutron-absorbing elements to convert neutrons to detectable charged particles. It is well known that boron is a neutron-absorbing atom, and if the boron-containing coating material is thick enough, most of the charged neutron particles will be absorbed. Boron-

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Scheme 1 Preparation route for boric acid ester and hydrolyzed MEMO (MEMO-B).

containing materials afford the possibility of preventing the transport of neutrons. Because of this property, they could make shielding cheaper and possibly simplify the problem of construction.^{11,12} Boron-containing materials have been used as flame-retardant additives. The flame-retardant action of these compounds on polymeric materials is chemical and physical, and they can promote char formation in the burning process. The mechanism involving the formation of the char is clearly related to the thermal action of boric acid with alcohol moieties. Boron exerts its flame-retardant action on polymeric materials at a temperature well below that of the normal pyrolysis of these materials.¹³

In this study, we aimed to prepare and characterize UV-curable, boron-containing, epoxy acrylate based organic-inorganic hybrid coatings. Boric acid was used to hydrolyze methacryloxymethyl triethoxysilane (MEMO) and form boric acid ester and silanol groups. Borate ester could directly condense with hydrolyzed MEMO and diphenylsilanediol (DPSD) to form borosiloxane ($-\text{B}-\text{O}-\text{Si}-$) and siloxane linkages.^{14,15} Organic networks were prepared by the free-radical photopolymerization of acrylate-based resins with hydrolyzed MEMO. The prepared hybrid coatings were characterized through the analysis of various properties such as hardness, abrasion and chemical resistance, gloss, and neutron acquisition. The thermal and morphological behavior of the hybrid coatings was also evaluated.

EXPERIMENTAL

Materials

Bisphenol A based epoxy acrylate (621A-80) and tripropylene glycol diacrylate (TPGDA) were provided by EMA Group (Turkey). Boric acid and vinyltrimethoxysilane (VTMS) were purchased from Merck. MEMO was kindly supplied by Wacker. Diiodomethane (99%) and DPSD (98%) were obtained from Alfa Aesar. The photoinitiator (Irgacure 184) was provided by Ciba Specialty Chemicals. BYK331 was generously provided by BYK Chemie. Polycarbonate and Plexiglas panels (70 mm × 100 mm × 1 mm) were used in all coatings and were purchased from local suppliers. All chemicals and other panels were obtained from Labor Teknik, Istanbul-TURKEY.

Characterization

Fourier transform infrared (FTIR) spectra were recorded with a Shimadzu 8300 FTIR spectrophotometer (Ant teknik, Istanbul-TURKEY). To evaluate the coating properties of the crosslinked films, we applied the coating formulations to polycarbonate and Plexiglas panels with an applicator and cured them in a bench-type UV processor (EMA) with 120 W/cm, medium-pressure mercury UV lamps.

The wettability characteristics of the coatings were determined on a Kruss (Redoks Limited, Ankara-TURKEY) Easy Drop DSA-2 tensiometer. A sessile drop method was used to measure the contact angle of distilled water (3–5 μL), which was applied to the surface by means of syringes.

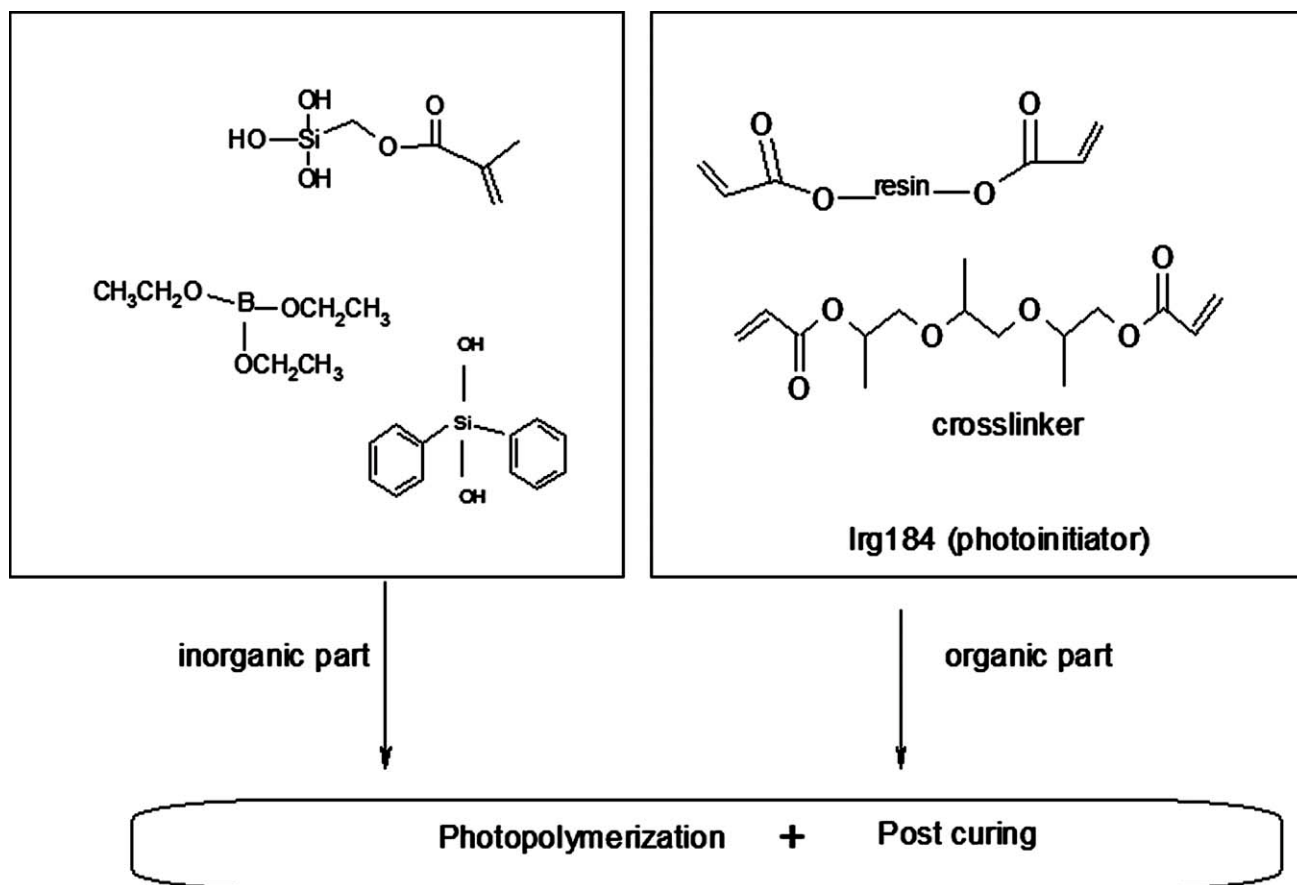
The gel contents of the UV-cured hybrid films were determined by the Soxhlet-extraction method for 6 h with acetone. The insoluble gel fraction was dried in a vacuum oven at 35°C to a constant weight, and then the gel content was calculated.

The solid-state ^{29}Si cross-polarization/magic-angle spinning NMR spectra were recorded with a Varian Unity Inova spectrometer (Bogazici univ, Istanbul-TURKEY) operated at 500 MHz.

The coating properties were measured in accordance with the corresponding standard test methods as indicated. The pendulum hardness (DIN 53157), tape adhesion (ASTM D 3359), methyl ethyl ketone (MEK) rubbing test (ASTM D 5402), and pencil hardness (ASTM D 3363) were used to check the cure of the coatings.

TABLE I
Compositions of the UV-Curable Hybrid Formulations

Sample	MEMO-B (g)	621A-80 (g)	TPGDA (g)	VTMS (g)	DPSD (g)	BYK331 (g)	Irgacure 184 (g)	Boron (%)
F1	—	1.7	0.2	0.30	0.5	0.05	0.081	—
F2	0.2	1.7	0.2	0.30	0.5	0.05	0.087	0.2
F3	0.4	1.7	0.2	0.30	0.5	0.05	0.093	0.4
F4	0.8	1.7	0.2	0.30	0.5	0.05	0.105	0.6
F5	1.0	1.7	0.2	0.30	0.5	0.05	0.111	0.7
F6	2.0	1.7	0.2	0.30	0.5	0.05	0.141	1.1



Scheme 2 Preparation of the boron-containing hybrid coating.

The mechanical properties of the UV-cured free films were determined by standard tensile stress-strain tests for measuring the modulus, ultimate tensile strength, and elongation at break. Standard tensile stress-strain experiments were performed at room temperature on a Z1010/TN2S material-testing machine (Kutlu Ltd. Istanbul-TURKEY) at a crosshead speed of 5 mm/min.

The abrasion resistance of the coatings was determined by the subsection of the coated substrates to a standardized Taber abrasion test (ASTM D 4060). CS10 wheels were used with a 250-g load on each wheel, and the substrates were abraded cumulatively for 200 cycles.

Thermogravimetric analyses (TGAs) of the UV-cured free films were performed with a PerkinElmer

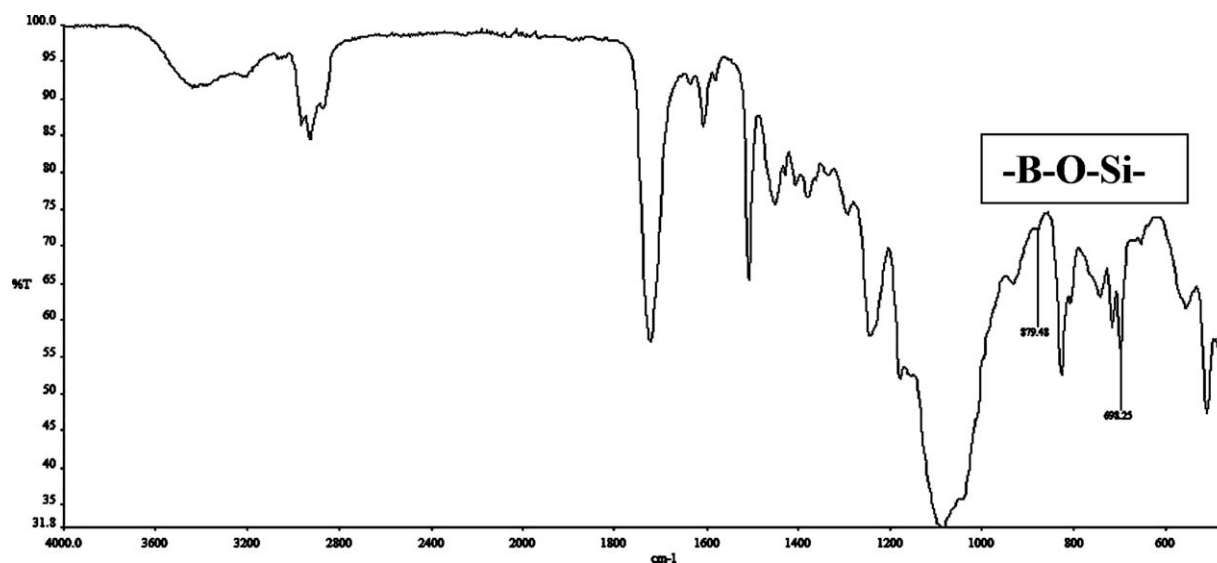


Figure 1 FTIR spectrum of a boron-containing hybrid coating (F4).

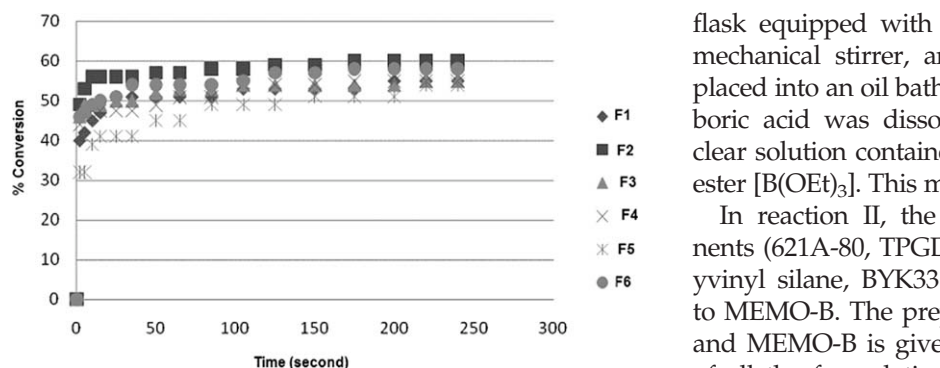


Figure 2 Effect of the irradiation time on the double-bond conversion of the coatings.

(Tetra Teknolojik Sistemler Ltd Sti. Istanbul-TURKEY) Pyris 1 thermogravimetric analyzer. Samples were run from 30 to 700°C at a heating rate of 10°C/min under nitrogen and air atmospheres.

The limiting oxygen index (LOI) values of the hybrid coating materials were measured with a Fire Testing Technology instrument (Doga Ltd. Ankara-TURKEY.) on a test specimen bar (120 × 60 × 3 mm³) according to ASTM D 2863 08.

Pretreatment of the substrates

The polycarbonate and Plexiglas panels were cleaned with 2-propanol after the removal of the protective foil. To improve the adhesion between the coating and the substrates, the polycarbonate and Plexiglas panels were treated with oxygen plasma created by an Ugur Elektronik UD-600 (Ugur Elektronik, Istanbul-TURKEY) corona generator under atmospheric pressure before the coating.

Preparation of the boron-containing hybrid coatings via the anhydrous sol-gel method

The anhydrous sol-gel process consisted of a hydrolysis reaction (I) and a condensation reaction (II). In reaction I, boric acid (3.05 g) and MEMO (14.5 g) were charged into a flame-dried, three-necked, 50-mL, round-bottom

flask equipped with a reflux condenser, an overhead mechanical stirrer, and a dropping funnel and were placed into an oil bath. The mixture was stirred until the boric acid was dissolved (75°C, 2 h).¹³ The obtained clear solution contained hydrolyzed MEMO and borate ester [B(OEt)₃]. This mixture is abbreviated as MEMO-B.

In reaction II, the UV-curable formulation components (621A-80, TPGDA, diphenylsilanediol, trimethoxyvinyl silane, BYK331, and Irgacure 184) were added to MEMO-B. The preparation route for boric acid ester and MEMO-B is given in Scheme 1. The compositions of all the formulations are given in Table I. Each formulation was prepared in a beaker with adequate stirring. To remove air bubbles that formed during mixing, the beaker content was heated to 80°C and then kept *in vacuo* for 20 min. After homogenization, the prepared formulations were applied to corona-treated polycarbonate and Plexiglas panels with a wire-gauged bar applicator. The applied wet coatings were hardened after six passes (180 s) by a UV processor equipped with a medium-pressure mercury lamp (EMA) situated 15 cm above the moving belt. The light dose was calculated to be 720 mJ/cm². After UV curing was achieved, the panels were annealed at 70°C for 1 h, at 80°C for 1 h, and then at 60°C for 1 day.

Hybrid free films were prepared via the pouring of the UV-curable, viscous formulations onto a surface-modified glass mold (10 mm × 50 mm × 1 mm). To prevent the inhibiting effect of oxygen, the resin in the mold was covered by a transparent Teflon film before irradiation with a high-pressure UV lamp; a quartz glass plate was placed over it. After 180 s of irradiation under the UV lamp, hybrid free films were annealed at 70°C for 1 h, at 80°C for 1 h, and then at 60°C for 1 day.

Analysis of the double-bond conversion

The degree of double-bond conversion of UV-curable formulations was obtained via real-time infrared (RTIR) spectroscopy data. The RTIR technique measures the conversion of double bonds in acrylate-containing resins by following, upon UV exposure, the

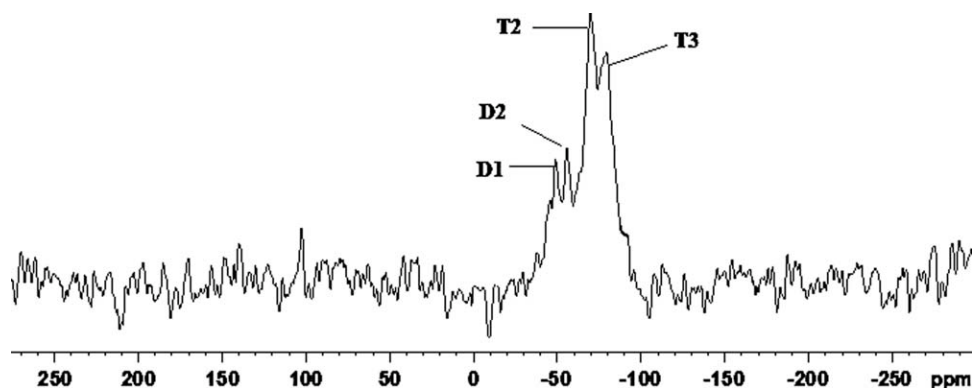


Figure 3 ²⁹Si-NMR spectrum of coating F4.

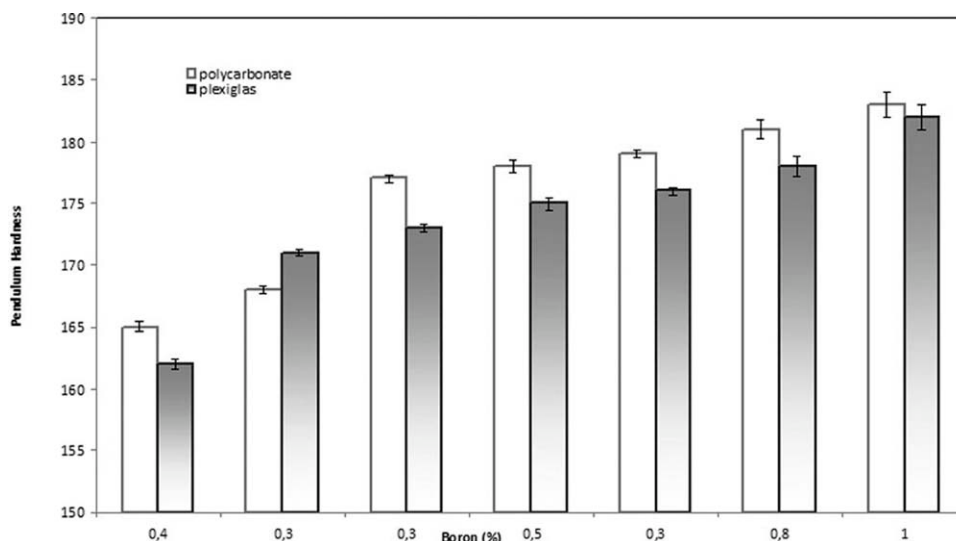


Figure 4 Effect of the boron content on the pendulum hardness of the hybrid coatings.

decrease in the bands at 1635 and 810 cm^{-1} associated with $\text{C}=\text{C}$ double-bond stretching. In one set of experiments, the UV-curable formulations were coated onto KBr disks in the usual way. The infrared (IR) spectrum of the unirradiated film was recorded, and then the wet film was subjected to UV exposure. The IR spectra of the films after UV curing were taken, and the percentage conversion was calculated from the ratio of the corresponding IR absorbances before and after UV exposure (A_0 and A_t , respectively) with the following equation:

$$\text{Conversion (\%)} = 100 [1 - (A_t/A_0)]$$

RESULTS AND DISCUSSION

The objective of this study was to investigate the effects of boron and silica on the physical and mechanical properties of UV-curable hybrid coatings. For this purpose, UV-curable, boron-containing, organic-inorganic hybrid coatings were prepared by an anhydrous sol-

gel technique. A commercially available acrylated bisphenol A based epoxy resin was used as a major organic component for the coatings, whereas the inorganic part of the hybrid system consisted of diphenylsilanediol, boric acid ester, and hydrolyzed MEMO. Scheme 1 depicts the preparation route of boric acid ester and hydrolyzed MEMO, and Scheme 2 shows the preparation route of UV-curable, boron-containing, organic-inorganic, hybrid coatings. The feed compositions of all hybrid formulations are collected in Table I.

The FTIR spectrum of hybrid coating F4 is shown in Figure 1. The bands at 879 and 696 cm^{-1} are the fingerprints of the borosiloxane bridges formed in a hybrid matrix. It also shows the characteristic $\text{Si}-\text{C}$ and $\text{Si}-\text{O}-\text{CH}_3$ stretching bands at 805 and 1083 cm^{-1} , respectively.¹⁵⁻¹⁷ The absorption bands in the $2800-3000\text{-cm}^{-1}$ region are typical of aliphatic $\text{C}-\text{H}$ stretching vibrations. It also shows the characteristic carbonyl stretching band at 1725 cm^{-1} .

The degree of double-bond conversion of the UV-curable formulations was obtained via RTIR spectroscopy. Figure 2 shows the conversion curves as a function of the irradiation time. More than 50% of the

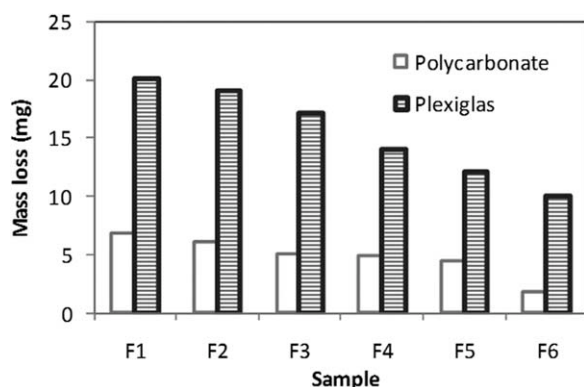


Figure 5 Mass loss after 200 cycles.

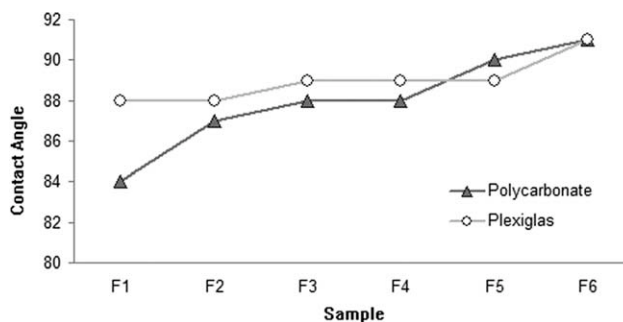


Figure 6 Contact angles of the hybrid coating materials with water.

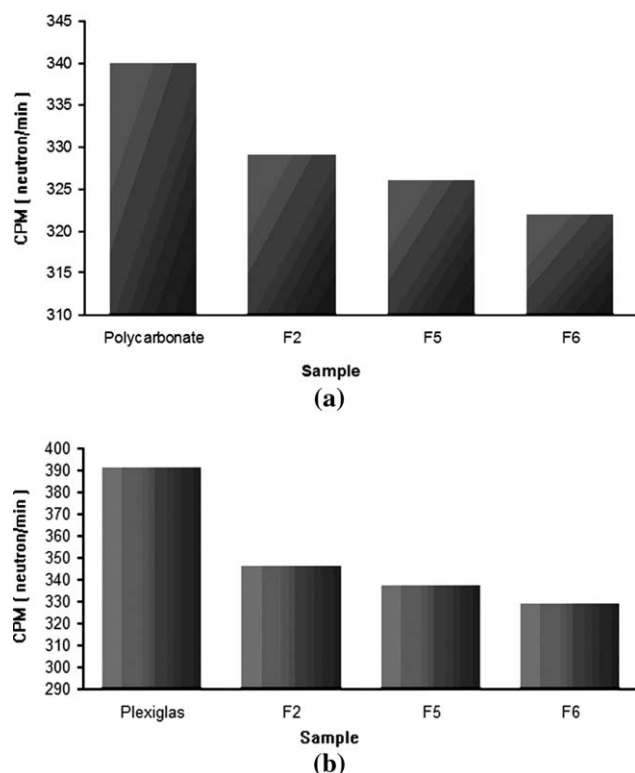


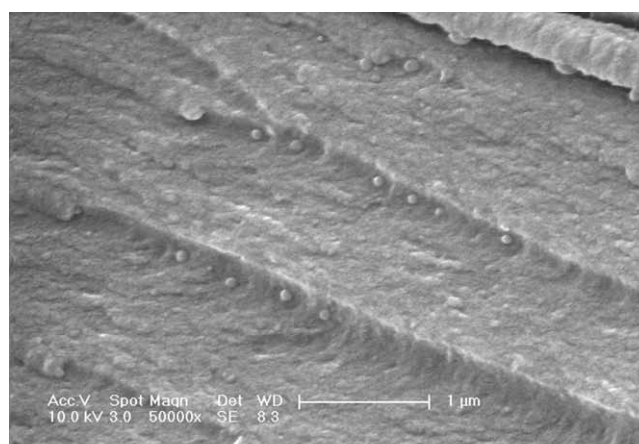
Figure 7 Neutron absorption of boron-containing hybrid materials: (a) polycarbonate and Plexiglas. CPM = Count Per Minute (neutron/min)

acrylate double bonds underwent the polymerization reaction within 30 s. After a fast start, the crosslinking reaction slowed, and the conversion of acrylate groups was fixed around 55–63%. The leveling of the conversion at longer irradiation times was attributed to the mobility restrictions occurring upon gelation and ultimately the vitrification of UV-exposed samples.¹⁸

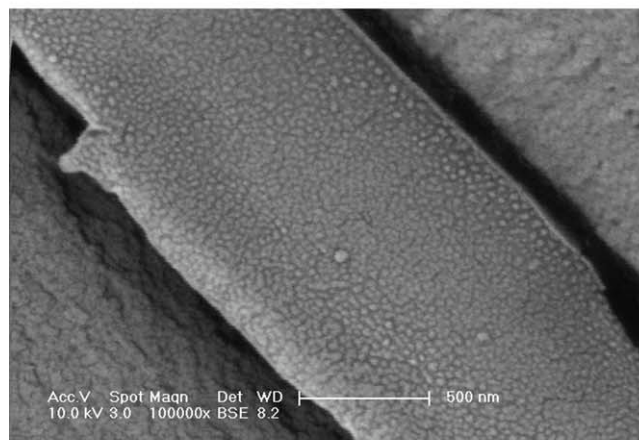
To assess the extent of the condensation reaction of the inorganic network, we employed ²⁹Si cross-polarization/magic-angle spinning NMR spectroscopy. As can be seen in Figure 3, four different kinds of signals were observed for the F4 hybrid coating material. The chemical shifts at −51 [R₂Si(OSi)(OH)], −55 [R₂Si(OSi)₂], −70 [RSi(OSi)₂(OH) or (RSi(OSi)₂(OCH₂CH₃))], and −81 ppm [R Si(OSi)₃] for the D1, D2, T2, and T3 signals, respectively, give an indication of partial condensation of diphenylsilanediol, MEMO, and VTMS. The observed chemical shift values agree closely with the data in the literature.^{18,19}

UV-curable, boron-containing hybrid coatings were applied to pretreated polycarbonate and Plexiglas substrates. Six samples of different coating compositions were prepared and characterized. Each result reported in this article is an average of five separate measurements. The solvent resistance of coatings was examined with the MEK rubbing test. The solvent resistance was excellent (500 MEK double rubs were exceeded), whereas the pencil hardness was greater than 5H; this was also indicative of a highly cross-

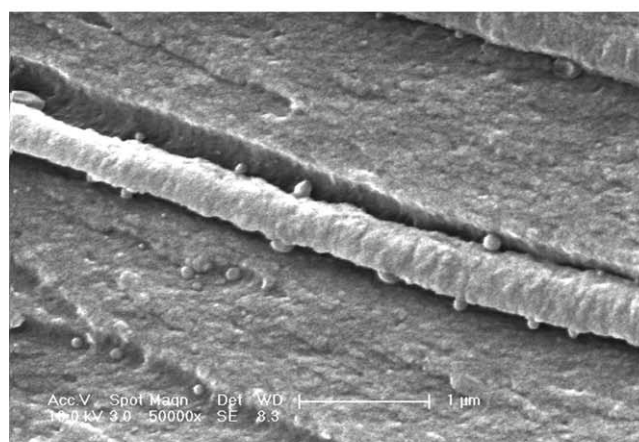
linked film. The gel content of the polymeric films was between 97 and 99%. The cross-cut adhesion experiment showed that 100% adhesion was reached for all coatings. The main reason for the good adhesion was probably the corona discharge pretreatment of the polycarbonate and Plexiglas panels before the coatings were applied. The chemical resistance of all hybrid coatings was also investigated via the



(a)



(b)



(c)

Figure 8 SEM micrographs of hybrid coating F4.

TABLE II
Tensile Properties of the Coating Materials

Sample	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (N/mm ²)
F1	23 ± 1.7	7 ± 0.3	334 ± 8.4
F2	18 ± 1.4	6 ± 0.1	320 ± 7.7
F3	17 ± 1.1	5 ± 0.2	335 ± 7.6
F4	12 ± 1.3	4 ± 0.2	339 ± 6.9
F5	11 ± 1.4	4 ± 0.1	327 ± 6.9
F6	10 ± 1.4	3 ± 0.1	302 ± 7.0

immersion of samples in various reagents (10% NaOH, 10% HCl, 10% H₂SO₄, and xylene) for 24 h. The general physical appearance of the samples was perfect, and no cracks were observed. This was probably due to the crosslink density of the hybrid coatings.

Boron-containing materials have many excellent surface properties, including corrosion resistance, very high hardness, refractory properties, and a strong tendency to bond with most substrates.²⁰ The hardness of a coating is the most important factor affecting the abrasion and scratch resistance. Hard coatings provide better scratch resistance, whereas abrasion resistance is also affected by surface friction. In Figure 4, the pendulum hardness of transparent hybrid coatings as a function of the boron content is shown. The incorporation of boron greatly improved the hardness.

Abrasion resistance is often characterized by the Taber abraser method, which measures the mass decrease caused by the mechanical degradation of protective layers treated by abrading grinders. Figure 5 shows the mass loss after 200 cycles with two 250-g loads and CS10 grinders. The formulation with a high boron content demonstrated better protective performance in comparison with the other formulations.

The contact angle is the angle at which a liquid interface meets a solid surface. If the solid surface is hydrophobic, the contact angle will be larger than 90°. ²¹ To investigate the surface properties of the hybrid materials, we used water as the probe liquid for contact-angle measurements. Each contact angle in Figure 6 represents an average of five to seven readings. There was a slight enhancement in the contact angle as the inorganic content of the coating increased orderly. This was expected because we assumed that pendent borosiloxanes made the surface more hydrophobic.

Neutron poisons are most effective for absorbing thermal neutrons; the most common of these are boron, cadmium, and lithium. Boron is a thermal neutron scavenger; this means that it can absorb neutrons that may have otherwise been available for causing further nuclear reactions.²² A polyethylene composite of 5 wt % boron is widely used in neutron-shielding

applications because of its excellent nuclear and physical characteristics. The borated polyethylene material has been used around research and test reactors to shield personnel and equipment for neutron radiography and other specialized experiments.

To assess the neutron-shielding capacity of the boron-containing hybrid coatings, thermal neutron lights were applied for 1 min to the polycarbonate and Plexiglas panels, which were coated with different compositions, and the number of neutrons that passed within this period was determined. During this measurement, test plates were placed on a Howitzer neutron source (Nuclear Chicago Corp. Model NH 3, obtained from Chicago-USA), and the number of neutrons that passed from the plates was measured with the IdentiFINDER apparatus (Target). Figure 7(a) (polycarbonate) (Labor Teknik, Istanbul-TURKEY) and Figure 7(b) (Plexiglas) show that the boron-containing coatings had the ability to absorb neutrons. A slight improvement in the neutron-absorption ability was observed with the boron content of the coatings increasing. Factors such as the geometry of the detector, the distance from the plates to the light source, the thickness of the plates, and the thickness of the coatings affected the measured neutron number.

In most cases, the surface morphology of materials is of great importance for many technical applications. The compatibility of the organic polymer and the inorganic part greatly affects the thermal, mechanical, and optical properties. The morphology of the fractured surfaces was observed by scanning electron microscopy (SEM). Figure 8(a–c) presents SEM images of the F4 hybrid coating material. The SEM micrographs show that spherical borosilicate particles were distributed within the hybrid system. The approximate particle size was less than 100 nm. The SEM micrographs show that the borosilicate nanoparticles were dispersed homogeneously in the hybrid coatings. Therefore, the borosilicate nanoparticles had an important effect on the properties of the coatings. The introduction of boron to the coatings via B–O–Si–C bonds

TABLE III
TGA Data for the Coatings in Nitrogen and Air Atmospheres at a Heating Rate of 10°C/min

Sample	Boron (%)	Nitrogen			Air		
		T _{5%} (°C)	T _d (°C)	Char yield (%)	T _{5%} (°C)	T _d (°C)	Char yield (%)
F1	—	186	396	18.0	293	397	6.0
F2	0.2	206	400	26.1	307	415	11.3
F3	0.4	204	406	28.1	307	418	15.2
F4	0.6	218	406	30.0	308	418	17.0
F5	0.7	188	406	31.1	309	420	18.8
F6	1.1	188	404	32.0	310	421	23.4

T_{5%} = temperature at a 5% weight loss; T_d = decomposition temperature.

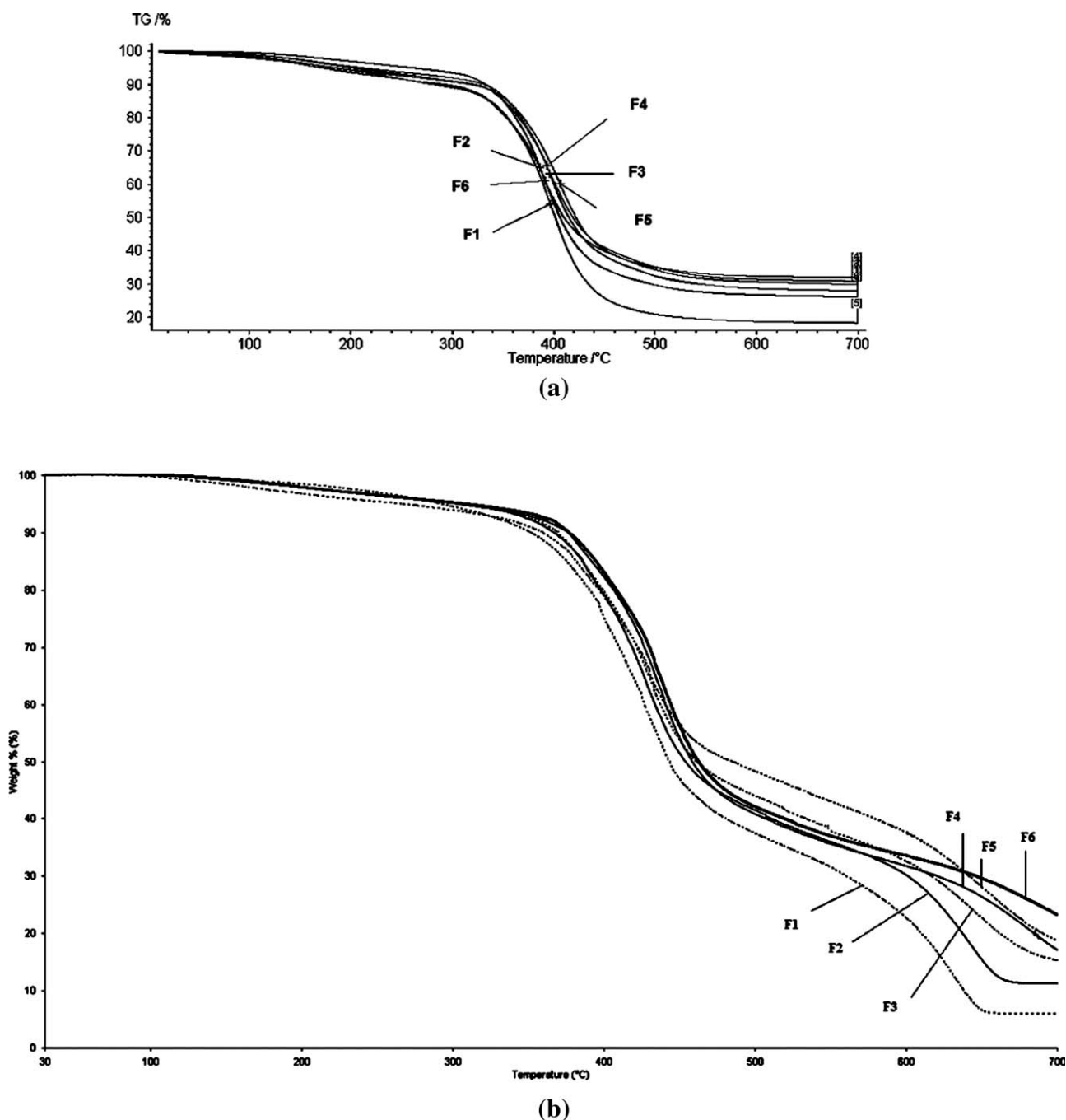


Figure 9 Weight loss versus the temperature as a function of the modification percentage in (a) a nitrogen atmosphere and (b) an air atmosphere.

resulted in a highly crosslinked matrix with improved abrasion resistance, thermal stability, and hardness. Also, it was foreseen that the high surface area of the nanoparticles would improve the radiation-shielding capacity of the coatings.

Evaluated stress-strain data for the hybrid coatings (Young's modulus, ultimate tensile strength, and elongation at break) are listed in Table II. The mechanical features of the hybrid materials basically depended on the organic and inorganic network density. There was a systematic decrease in the

modulus, elongation at break, and tensile strength with increases in the boron and silicate contents of the coatings. The decrease in the tensile strength might have been due to the agglomeration of the inorganic part. On the basis of these results, the boron-containing hybrid coatings could be classified as hard and brittle materials. This was due to the higher crosslinking density of the borosiloxane hybrid coatings.

To determine the thermal stability of the hybrid coatings, TGA was carried out under nitrogen and

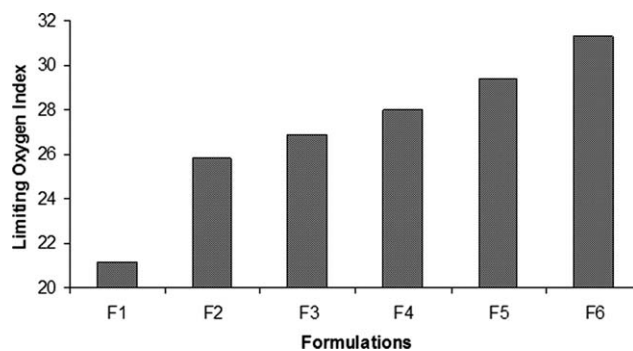


Figure 10 LOI values of the hybrid coatings.

air. The boron-free and boron-containing hybrid coatings were investigated with TGA. Table III collects the TGA data for the weight loss with the temperature. Figure 9(a,b) shows TGA thermograms of the hybrid coatings under nitrogen and air, respectively. Under both atmospheres, the temperature at a 5% weight loss for all coatings slightly changed. For all the boron-containing hybrid coatings, the main degradation step was observed at 400–406°C under nitrogen and at 415–421°C under air. The main degradation step under air appeared at higher temperatures and corresponded to the thermooxidative degradation of char moieties. The char yields at 700°C were also collected. In this case, the experimental char yields under nitrogen for the boron-containing coatings were not significantly different. Under air, however, significant differences were observed. Although the char yields for the boron-free coating was practically nonexistent, the char yields for the boron-containing hybrid coatings increased with the boron content (see Fig. 9). Boron, therefore, plays a role in char formation, and the char yield has been correlated to flame retardancy.²³ The experimental results suggest that the addition of a proper fraction of boron precursors can improve the oxidative stability of coatings.

The flame retardancy of the hybrid materials was examined with LOI values; Figure 10 shows that the LOI values increased from 21.1 ± 1.0 to 31.6 ± 1.1 for the hybrid films. Consequently, boron- and silicate-containing hybrid materials showed fire resistance versus the F1 control formulation.

The optimum fraction of boron could be determined by a careful comparison of the results. When we compared F3 to the other samples, we saw that the main degradation temperature did not show a dramatic change (418–421°C). Also, the radiation-shielding effect of F3 was between the effects of F2 and F5. There was a slight difference between the neutron-absorption abilities of F2 and F5. The same interpretations were true for the tensile modulus and the pendulum hardness. Therefore, the amount of boron

used in F3 could be regarded as the amount of boron needed for the optimum properties.

CONCLUSIONS

UV-curable, boron-containing, organic–inorganic hybrid coatings were prepared by an anhydrous sol-gel technique. The FTIR study indicated that boron atoms were incorporated into the siloxane network via —B—O—Si— bridges. Boron atoms in the precursors were dispersed in the siloxane network via Si—O—B bonds. The properties of the boron-containing hybrid coating materials, such as hardness, chemical and abrasion resistance, and adhesion, were improved. All obtained hybrid coatings were crack-free and transparent. The solvent- and chemical-resistance experiments proved that all the hybrid materials are promising candidates for related applications. The morphology studies indicated that the micrometer-scaled inorganic particles dispersed homogeneously in the hybrid system. The thermal stability of the hybrid coating materials improved with the amount of boron increasing in the coating compositions. The results clearly showed that the hybrid coatings had a significant enhancement in radiation-shielding properties. Boron-containing, transparent hybrid coatings may be used in research and test reactors to shield personnel and equipment for neutron radiography and other specialized experiments.

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