Novel Coatings Based on Mixtures of Blown Soybean Oil and Acrylate Prepolymers

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Commercial blown soybean oil (BSBO) was shown by titration to contain a substantial level of (hydro)peroxy groups, presumably formed during the blowing process. Thus, BSBO can initiate free-radical polymerization. To explore the potential for film formation, BSBO was blended with (meth)acrylate monomers and/or prepolymers in different proportions. The monomers were trimethylopropane triacrylate esters (TMPTAE), 1,6-hexanediol dimethacrylate (HDDMA), and isobornyl acrylate (IBOA); the prepolymers were ethoxylated bisphenol A dimethacrylate (EBDMAE), and a hydrophobic aromatic urethane acrylate (HAUA). All blends required a catalyst (cobalt naphthenate) and temperatures of about 100°C to induce crosslinking and film formation. Blends with monomers gave formulations that could be applied with no added solvent, but film properties (pencil hardness, MEK double rub resistance, adhesion, and impact resistance) were not very good. Better film properties were obtained by blending prepolymers with BSBO and TMPTAE; these formulations required solvent for application, but VOC levels as low at 140 g/L were possible. FTIR spectra showed that free radical polymerization of the monomers and prepolymers occurred during film formation. Gel content studies indicated that part of the BSBO is incorporated into the crosslinked film, but a substantial fraction is not chemically bound to the network.

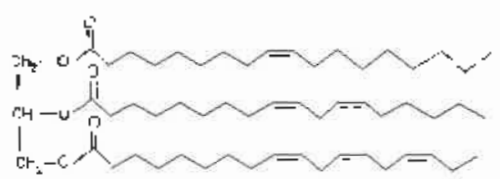
INTRODUCTION

Soybean oil (SBO) is an inexpensive, biorenewable commodity material. It is widely used in alkyd resins for coatings, and its derivatives are used to modify various resins.[1-4] Blown soybean oil (BSBO) is prepared directly and economically from SBO. It has been a commercial commodity for decades.[5,6] In view of the potentially abundant supply of BSBO and its low cost, it is surprising that few published studies have addressed the properties and applications of BSBO as a raw material for coatings. Commercial BSBO, which is an oligomer of SBO, might be an attractive starting material for preparation of coatings since its viscosity and molecular weight are higher than SBO. One consideration is that BSBO contains hydroperoxide and/or peroxide residues from the blowing process. These residues may be a drawback or an advantage; in this study we try to make use of them.

The possibility that these (hydro)peroxides could be utilized to generate free radicals and initiate polymerization of monomers to form coating films was explored. Our approach is to blend BSBO with di- and tri-(meth)acrylate monomers and prepolymers, to cast coating films, and to cure and evaluate the coatings. Dry film properties such as pencil hardness, MEK double rub resistance, adhesion, and impact resistance, have been evaluated using standard methods.[9,10] The results of this research show that low VOC, high-solids coatings can be made by this approach.

SOYBEAN OIL AND BLOWN SOYBEAN OIL

SBO is a triglyceride of unsaturated and saturated aliphatic acids. An idealized structure of SBO, showing only the most prevalent unsaturated acids, is given in the following:



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While the published literature contains considerable information about blown linseed oil, relatively little information about BSBO has been published. Like blown linseed oil, BSBO can be manufactured by heating SBO to 140-150°C and passing air through the hot oil until the viscosity increases to a target level.[11] At this temperature the process is slow, and it is probable that commercial processes accelerate it with higher temperatures or catalysts. The chemical mechanisms of the oligomerization reactions that lead to the viscosity build-up have not been described in the recent literature. For purposes of this paper, we presume that they involve autooxidation reactions analogous to those that occur when oils containing polyunsaturated fatty acids are crosslinked.

It is well known that the autooxidation of drying oils is accompanied by the uptake of significant quantities of oxygen and the evolution of volatile degradation products.[12-16] Wexler reviewed the polymerization of drying oils and presented a mechanism of drying oil autooxidation in the presence of primary driers such as oil-soluble cobalt salts.[14] Subsequent studies, for example by Muizebelt et al.[15] have provided additional information about this complex process, but the details are not fully known.

According to present knowledge, the first step in the thermal crosslinking reaction of BSBO is the decomposition of hydroperoxides present in natural oils.

$$ROOH \rightarrow RO\bullet + \bullet OH$$

The resulting free radicals can abstract hydrogen atoms from the methylene groups between double bonds of other fatty acid moieties to form new free resonance stabilized pentadienyl radicals which, in turn, can react with oxygen to form hydroperoxy radicals. As the concentration of radicals increases, the frequency of coupling reactions to form ROR and ROOR linkages between oil molecules increases, leading to the observed build up of molecular weight and viscosity.

A number of secondary reactions may also occur, including decomposition of (hydro)peroxides to form a complex mixture of saturated and unsaturated aldehydes, ketones, esters, and hydrocarbons. Several workers have used infrared spectroscopy to follow the changes in a drying oil film throughout the autooxidation process. They all came to similar conclusions. There is a disappearance of cis unsaturation and formation of trans.[16-18] A band appears in the hydroperoxide/hydroxyl region and a large shoulder on the ester band due to carbonyl/carboxyl groups. Falla studied the structure of dry films formed from both soybean oil and methyl linoleate by using infrared spectroscopy, gel permeation chromatography, and liquid chromatography-mass spectrometry.[18] He established the chemical composition of films formed by air-drying oil-based coatings and found the evidence of typical autooxidation reactions by comparing the infrared spectra of methyl linoleate before and after drying.

Based on the assumptions that BSBO undergoes similar reactions during its formation and that its subsequent reactions also involve similar reactions, we postulated that BSBO should be capable of initiating chain-growth polymerization of vinyl monomers, such as acrylates and methacrylates. Some of the possible initiating reactions are illustrated in the following, where M and M* represent the vinyl monomer and prepolymer:

$$ROOH \rightarrow RO\bullet + HO\bullet$$
$$RO\bullet + RH \rightarrow R\bullet + ROH$$
$$\bullet OH + RH \rightarrow R\bullet + H_2O$$
$$R\bullet + M \rightarrow RM\bullet$$
$$RO\bullet + M \rightarrow ROM\bullet$$
$$ROM\bullet + M^* \rightarrow ROMM^*\bullet$$

If M or M* is a di-, tri-, or poly (meth)acrylate, this process will lead to a crosslinked network.

Further reaction of these termination products with radical results in a progressive increase in molecular weight and form the intermolecular crosslinking products between BSBO and acrylate prepolymers.

The crosslinking process may be amplified by termination reactions of the free radical process, some of which join two oil moieties together:

$$R\bullet + \bullet R \rightarrow R\text{-}R$$
$$R\bullet + RO\bullet \rightarrow R\text{-}O\text{-}R$$
$$RO\bullet + RO\bullet \rightarrow R\text{-}O\text{-}O\text{-}R$$

Other chain free radicals join each other to yield intermolecular crosslinking:

$$RM\bullet + R\bullet \rightarrow RM\text{-}R$$
$$RM\bullet + RM\bullet \rightarrow RM\text{-}MR$$
$$RM\bullet + ROM\bullet \rightarrow RM\text{-}MOR$$
$$RM\bullet + ROMM^*\bullet \rightarrow RM\text{-}M^*MOR$$

EXPERIMENTAL SECTION

Materials

Commercial BSBO and alkali refined SBO were obtained from Cargill, Inc. with the CAS numbers 68152-81-8 and 8001-22-7, respectively. They were used without further purification. The characteristic values of BSBO such as peroxide content, molecular weight and molecular weight distribution, viscosity, glass transition temperatures (T_g), and VOC were determined (see *Table* 1).

Sartomer Company kindly supplied the prepolymers and monomers as follows: trimethylopropane triacrylate (TMPTAE, SR351), ethoxylated bisphenol A dimethacrylate (EBDMAE, SR348), ethoxylated bisphenol A diacrylate (EBDAE, SR349), hydrophobic aromatic urethane acrylate (HAUA, CN978), isobornyl acrylate (IBOA, SR506). They were used as received.

The drier, six percent cobalt Nap-All, was provided by OMG Americas Company. Monomers and solvents were obtained from Aldrich Chemical Co. including 1,6-hexanediol diacrylate (HDDA), 1,6-hexanediol dimethacrylate (HDDMA), methyl methacrylate (MMA), meth-

Table 1—Characterization of Commercial BSBO

M_n	M_w	M_w/M_n	Viscosity (mPa.s)	Peroxide content (mg/g BSBO)	Nonvolatile (%)	VOC (g/L)
2.9×10^3	1.1×10^4	3.9	5780	12.3	98.3	16.6

acrylic acid (MAA), and methyl ethyl ketone (MEK). All chemicals were used as received except for MMA and MAA, which were purified by treatment with active aluminum oxide before use. Steel test panels or phosphated steel panels were purchased from Q-Panel Company and cleaned with acetone before use.

Coatings Formulations

To prepare the coatings, commercial BSBO and other components such as (meth)acrylate monomers or prepolymers were blended in the proportions shown in *Tables* 2-7 and 0.02-0.4 wt% drier based on the amount of film forming compositions was added. Wet films approximately 75 μm (3 mils) in thickness were cast onto the test panels with draw down square. The films were then heated to cure at 100 or 110°C for one hour and equilibrated at ambient temperature for seven days before testing, unless otherwise stated. The coatings were evaluated as clear films.

Measurements

Molecular weight and molecular weight distribution were measured by a gel permeation chromatography (GPC) apparatus equipped with Hewlett Packard (HP) Series 1050 Quad Pump and HP 1047A Differential Refractometer. Tetrahydrofuran (THF) was used as solvent at a flow rate of 0.9 mL/min, and polystyrene standards were used for calibration.

The infrared spectra were recorded on a Nicolet Magna 510P FTIR spectrometer at 4 cm^{-1} resolution with 16 scans per spectrum. Film samples were peeled off the panels for DSC measurements. T_g of film samples were measured using a TA Inst 2100 Modulated DSC instrument, with the heating rate of 10°C/min, while a nitrogen gas purge was used. Samples were encapsulated in standard aluminum DSC pans and heated from –100 to 150°C. Data processing was carried out with the software furnished by an instrument manufacturer.

Viscosity was measured with a cone and plate type viscometer (Brookfield Model DV-II+) at 2.0-10 rpm at 25°C. VOC was determined according to ASTM D 3960-98. The peroxide content in commercial BSBO was determined by titration according to ASTM D 2340-96. This ASTM procedure is designed for titration of peroxides in styrene monomer. It was adapted for use with BSBO by using smaller BSBO samples to adjust for the higher peroxide content of BSBO.

Film thickness was measured by using an eddy current/magnetic film thickness gauge from Twin City International Inc., according to ASTM D 1186-93. MEK double rub resistance was measured following ASTM D 4752-98. Pencil hardness tests were performed with a Gardco pencil scratch hardness kit according to ASTM D 3363-92a. Impact test was measured with a heavy duty impact tester (Gardner Laboratory Inc.) with 1.8 Kg (4 lb) mass and 1.27 cm (0.5 in.) diameter round nose punch, according to ASTM D 2794-93. Adhesion was determined by the cross-hatch tape test, ASTM D 3359-97.

The extent of crosslinking was characterized by a solvent extraction method. It was performed at room temperature by immersing the weighed dry film in *p*-xylene for 24 hr. The swollen films were lifted, patted dry, and weighed at regular intervals until equilibrium was attained. Then the films were heated in an oven at 120°C to reach constant weight. The gel content (%) was calculated from the expression:

$$\text{Gel content (\%)} = (W_1/W_0) \times 100 \qquad (1)$$

where W_0 is the initial weight of the film before extraction with solvent, and W_1 is the weight of the dried film after extraction.[19,20]

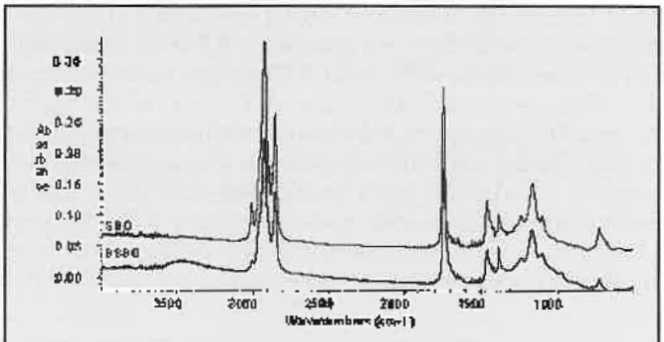

Figure 1—FTIR spectra of commercial BSBO and SBO

RESULTS AND DISCUSSION

The characteristics of the commercial BSBO are given in *Table* 1. The number average molecular weight (M_n) and weight average molecular weight (M_w) were 2.9×10^3 and 1.1×10^4, respectively. The polydispersity (M_w/M_n) was thereby 3.9. Compared to the molecular weight of pure commercial SBO around 880, the number average degree of polymerization of BSBO is about 3.3. The viscosity of this sample of BSBO is 5780 mPa.s at room temperature. As expected, its VOC is extremely low, only 16.6 g/L.

Titration showed that the average "peroxide content" of BSBO was 12.3 mg per gram of BSBO, corresponding to 36 g of "peroxide"/mol BSBO on a number average basis. The ASTM titration method probably does not discriminate among peroxides (ROOR), hydroperoxides (ROOH), and perhaps other oxidizing structures in BSBO. It assumes that all oxidants are peroxides with an equivalent weight of 17. Thus, this titration indicates that, on a number average basis, there are about two equivalents of (hydro)peroxide per mol of BSBO. There is some uncertainty about the results of this titration because the method was adapted from an ASTM method for titration of peroxide content in styrene monomer and was not validated for vegetable oils with higher (hydro)peroxide levels. Even allowing for possible error, it is expected that there is plenty of (hydro)peroxide present to initiate polymerization under proper reaction conditions, and that a substantial fraction of the BSBO should become bound to the polymer during polymerization.

The FTIR spectra of BSBO and SBO are shown in *Figure* 1. Comparing the spectra of BSBO with SBO, a new, broad absorption band at about 3500 cm^{-1} was detected in the

BSBO spectrum, consistent with the presence of substantial levels of hydroperoxy groups (–OOH) but also possibly attributable to –OH or –COOH groups in the material. The sharp peaks of BSBO at about 3010 cm^{-1} and 1710 cm^{-1} are smaller, suggesting substantial consumption of double bonds during the blowing process. These observations are all consistent with published literature about autooxidation of oils and unsaturated fatty acids. Various studies indicate that the products of blowing oils contain hydroperoxide, peroxide, and epoxide groups.[11,16,21,22]

Film Properties of Coatings Formulated from BSBO and HDDMA and HDDA

In order to get crosslinked film, diacrylates were chosen as co-reactants for BSBO because their C=C double bonds would be susceptible to initiation by the free radicals generated by decomposition of the (hydro)-peroxides in BSBO. HDDMA and HDDA were blended with BSBO, separately. *Table* 2 presents the film properties of coatings formulated from BSBO, HDDMA, and HDDA. The wet films were cast on phosphated steel panels and then heated at 145-120°C for one hour. Film BH-1, which contains no drier, had very poor film properties. In the presence of drier, however, both HDDMA and HDDA reacted with BSBO at 120°C for one hour, and gave excellent adhesion and impact resistance (films BH-3 and BH-4). This result illustrates the necessity for a catalyst, presumably to accelerate decomposition of (hydro)peroxides to form free radicals. However, the films are soft and would have little or no utility as industrial coatings. Adding MMA to increase T_g (film BH-5) did not increase hardness. Apparently, either monomers with high molecular weights or more highly functional acrylate oligomers are required.

Film Properties of Coatings Formulated from BSBO and TMPTAE

When mixtures containing trimethylolpropane triacrylate (TMPTAE) and BSBO containing drier but no solvent were cast on steel panels as wet films and then heated at 100°C for one hour, they formed hard, colorless, transparent, and glossy films. The film properties for coatings formulated from BSBO and TMPTAE are shown in *Table* 3 (films BT-1–BT-3). For reference, a film was cast from BSBO and drier, with no crosslinker. T_g and pencil hardness decreased sharply as BSBO content of the coatings increased. The film of 100% BSBO has the lowest T_g of –21°C after baking, while BT-1 with 50% BSBO has the T_g of 29°C.

Table 2—Film Properties of Coatings Formulated from BSBO, HDDMA, and HDDA

Sample	Composition (wt%)	Heating Temperature (°C, 1 hr)	Adhesion	Pencil Hardness	Impact Resistance (in.-lb), D/R
BH-1	BSBO 75 HDDMA 25	145	/	/	/
BH-2	BSBO 75 HDDMA 25 Drier 0.1	145	5B	4B	160/160
BH-3	BSBO 50 HDDMA 50 Drier 0.1	120	5B	3B	160/160
BH-4	BSBO 50 HDDA 50 Drier 0.4	120	5B	3B	160/160
BH-5	BSBO 20 HDDA 5 MMA 72.5 MAA 7.5 Drier 0.4	120	5B	4B	160/160

Table 3—Film Properties of Coatings Formulated from BSBO and TMPTAE

Sample No.	Compositions (wt%)	Thickness (mils)	Adhesion	Pencil Hardness	MEK Resistance, Double Rub	Impact Resistance (in.-lb), D/R	T_g (°C)
BT-1	BSBO 50 TMPTAE 50 Drier 0.02	0.87	5B	3H	>200	160/160	29
BT-2	BSBO 60 TMPTAE 40 Drier 0.02	0.87	5B	H	>200	160/160	24
BT-3	BSBO 70 TMPTAE 30 Drier 0.02	0.85	5B	F	190	160/160	6
BS-1	BSBO 100 Drier 0.02	/	3B	6B	/	/	21

Table 4—Gel Content of Films Formulated BSBO and TMPTAE

Sample No.	BSBO:TMPTAE (w/w)	Gel content (%)
BT-1	50:50	71.2
BT-2	60:40	68.9
BT-3	70:30	62.5

A comparison of the infrared spectra of TMPTAE and BSBO as shown in *Figure* 2 with the FTIR spectra of BT-type films as shown in *Figure* 3 demonstrates that the crosslinking reaction occurred between BSBO and TPMTAE. *Figure* 3 is the infrared spectra on a frequency-expanded scale between 2000 and 700 cm^{-1}. As for original BSBO/TMPTAE (50/50, w/w) before curing, there are obvious peaks at 1633, 1296, 1266, and 1062 cm^{-1} and can be attributed to C=C and C–O stretching, respectively. After curing, changes in these regions occurred for BT-1, BT-2, and BT-3. Two peaks of cured films at 1296 and 1266 cm^{-1} were merged into one broad band, and the peaks 1633 and 1062 cm^{-1} weakened, suggesting that these moieties had been partly consumed in a chemical reaction. On the other hand, after the reaction of the three cured films, the peaks of C=O stretching at 1728 cm^{-1} and C–O stretching at 1182 cm^{-1} shifted to about 1740 and 1172 cm^{-1}, respectively. The peaks at 987 and 970 cm^{-1} can be attributed to the conjugated and nonconjugated trans C=C stretching. After crosslinking, they became weak, confirming that acrylate double bonds were partly consumed.[15]

While coatings such as BT-1 had excellent pencil hardness and solvent rub resistance, subjective examination

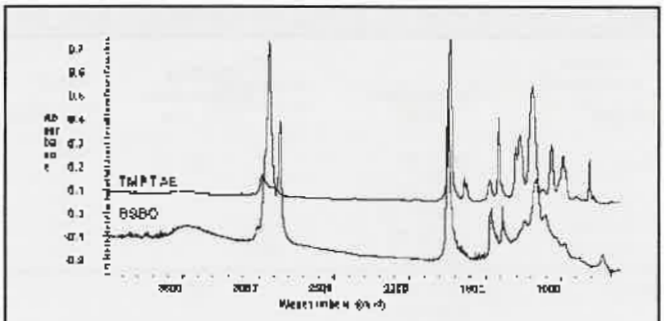

Figure 2—FTIR spectra of commercial BSBO and TMPTAE.

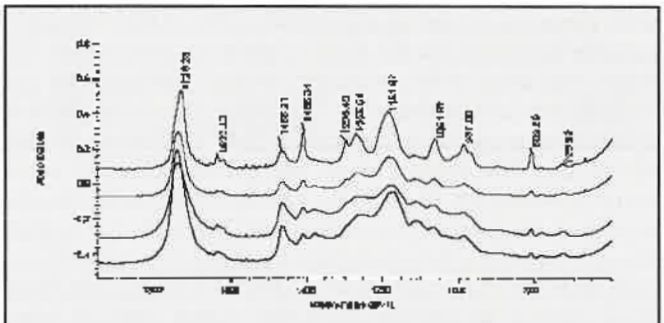

Figure 3—FTIR spectra of (a) original BSBO/TMPTAE (50/50) before heating compared with (b) BT-1, (c) BT-2, and (d) BT-3 after heating with a frequency-expanded scale between 2000 and 700 cm^{-1}.

Table 5—Viscosity and VOC of Coatings Based on BSBO and TMPTAE in Different Proportions

Sample No.	BSBO:TMPTAE (w/w)	Viscosity (mPa.s)	Dm (g/mL)	Nonvolatile (%)	VOC (g/L)
BT-1	50:50	1020	1.034	97.9	21.7
BT-2	60:40	1460	1.022	97.4	26.6
BT-3	70:30	2050	1.010	97.4	26.3
BSBO	100:0	5780	0.978	98.3	16.6

Table 6—Film Properties of Coatings Formulated from BSBO and Multi-Component Polyacrylates

Sample	Compositions (wt%)	Adhesion	Pencil Hardness	MEK Resistance, Double Rub	Impact Resistance (in.-lb), D/R
BM-1	BSO 50 TMPTAE 25 EBDMAE 12.5 HAUA 12.5 Drier 0.1 *p*-Xylene[a] 12.5	5B	3H	>200	160/160
BM-2	BSO 60 TMPTAE 25 EBDMAE 7.5 HAUA 7.5 Drier 0.1 *p*-Xylene[a] 12.5	5B	B	150	140/160
BM-3	BSO 70 TMPTAE 25 EBDMAE 2.5 HAUA 2.5 Drier 0.1 *p*-Xylene[a] 12.5	5B	2B	130	120/160

(a) *p*-Xylene was used as solvent to dilute the mixture and was based on the total amount of BSBO and other prepolymers.

Table 7—Film Properties of Coatings Formulated from BSBO and Multi-Component Polyacrylates Containing IBOA

Sample	Composition (wt%)	Heating Temperature (°C), 1 hr	Adhesion	Pencil Hardness	MEK Resistance, Double Rub	Impact Resistance (in.-lb), D/R
BM-4	BSO 40 TMPTAE 10 HAUA 30 IBOA 20 Drier 0.3	100	5B	2H	190	160/160
		110	5B	2H	>200	160/160
BM-5	BSO 20 TMPTAE 13 HAUA 40 IBOA 27 Drier 0.3	100	5B	3H	190	160/160
		110	5B	3H	190	160/160

with vigorous scraping suggested a lack of film integrity usually associated with films with these properties. To study the level of crosslinking of the coatings, the gel content was measured with the results shown in *Table* 4. When the proportions of BSBO/TMPTAE were 50/50, 60/40, and 70/30 by weight, the gel contents (%) were corresponding to 71.2, 68.9, and 62.5, respectively. As expected, the higher the content of TMPTAE, the higher the gel content. The unreacted material presumably results mainly from molecules of BSBO that did not have (hydro)peroxide groups from the outset, and/or from molecules that had (hydro)peroxide groups but did not react until after all the TMPTAE was used up. Formulations containing more TMPTAE were not tested since higher levels of TMPTAE caused brittleness and drastically reduced mechanical properties.

The greatest advantage of these coatings is that they did not contain any organic solvent. *Table* 5 presents the viscosity, density, nonvolatile content by mass (NVM), and VOC of BSBO and BT-type blends. The commercial BSBO has extremely low VOC, only 16.6 g/L, but its viscosity is high: 5780 mPa.s at room temperature. Since the viscosity of TMPTAE is low, it acts not only as a crosslinker and main ingredient of wet films, but also as a diluent for BSBO. As TMPTAE was added to BSBO, viscosity decreased, reaching about 2000 mPa.s at 30% TMPTAE and 1000 mPa.s at 50%. VOC remained low, always below 27 g/L. The NVM was 97-98%. Thus, a series of solventless coatings with high-solids content and low VOC has been obtained.

The possibility that formulations such as BT-1 could cure at ambient temperatures was investigated. However, little or no curing occurred in 30 days. The possibility that they would cure upon exposure to ultraviolet (UV) light was also studied. However, irradiation of wet films for one minute did not induce curing.

Effect of Multi-Component Systems on Film Properties

Further improvements in film properties were sought by introducing (meth)acrylate "prepolymers" such as hydrophobic aromatic urethane acrylates (HAUA) and ethoxylated bisphenol A dimethacrylate (EBDMAE) into the formulations. Coatings based on mixtures of these prepolymers and BSBO would be expected to have markedly different properties. These prepolymers were mixed with BSBO and TMPTAE in different proportions, cast on steel panels, and baked at 100°C for one hour. In order to reduce viscosity for application, it was necessary to add solvent; 12.5 wt% of *p*-xylene was used. As shown in *Table* 6, coatings with good film properties were obtained, the best being coating BM-1. In comparison with BT-type films in *Table* 4, the properties of these BM-type films containing HAUA and EBDMAE are similar to that of the former. BM-1 has the best performance.

The use of solvent is undesirable from the environmental standpoint so a monomer with low viscosity and low volatility, isobornyl acrylate (IBOA), was tested as a diluent to replace *p*-xylene. It was hoped that the high boiling point of IBOA, 119-121°C at 15 mm, would minimize evaporative losses. The wet films were applied on phosphated steel panels, and then heated at 100 or 110°C for one hour, respectively, to give coatings BM-4 and BM-5. *Table* 7 presents the formulations and cured film properties of these multi-components coatings. The VOC and gel content of BM-4 and BM-5 are given in *Table* 8. The VOC data indicate that a high proportion of IBOA evaporated from the film before it reacted under these conditions. The modest amounts of IBOA that became polymerized into the film may have had a modest positive effect on film properties, probably reflecting the increased T_g expected from adding IBOA.

Effect of Heating Time and Drier Concentration on Film Formation

At the same composition and heating temperature, the effect of heating time on the film formation was investigated. The film properties for the coatings given in *Table* 9 were based on the formulations as follows: BSBO (50 wt%), TMPTAE (25%), EBDMA (12.5%), HAUA (12.5%), and drier (0.018%). No solvent was used. The results of pencil hardness and MEK rubbing show that the film hardness and solvent-resistance strengthen as the heating time increases.

Similar experiments were effected with more drier (see *Table* 10). The film compositions were the same: BSBO (50

Table 8—VOC and Gel Content of Coatings BM-4 and BM-5

Sample	D_{nv} (g/mL)	Nonvolatile (%)	VOC (g/L)	Gel Content (%)
BM-4	1.00	85.8	142	65.9
BM-5	1.02	69.4	312	75.8

Table 9—Film Properties at Different Heating Times (0.018 wt% drier)

No.	Heating Time (min)	Thickness (mils)	Gel Content (%)	Pencil Hardness	MEK Resistance, Double Rub	Adhesion	Impact Resistance (in.-lb), D/R
A-1	10	/	/	5B	/	/	/
A-2	20	0.47	/	F	160	4B	140/120
A-3	30	0.50	50.7	HB	196	5B	160/160
A-4	45	0.51	/	H	200	5B	160/160
A-5	60	0.63	53.2	2H	>200	5B	160/160

Table 10—Film Properties at Different Heating Times (0.04 wt% drier)

No.	Heating Time (min)	Thickness (mils)	Gel Content (%)	Pencil Hardness	MEK Resistance, Double Rub	Adhesion	Impact Resistance (in.-lb), D/R
B-1	10	/	/	/	/	/	/
B-2	20	0.52	/	F	300	4B	160/160
B-3	30	0.60	48.6	H	360	4B	160/160
B-4	45	0.62	/	2H	370	5B	160/160
B-5	60	0.64	53.4	3H	370	5B	160/160

wt%), TMPTAE (25%), EBDMA (12.5%), HAUA (12.5%), and drier (0.04%). No solvent was used in the formulation. All wet films were tested on phosphated steel panels, and then heated at 100 °C with different times. Interestingly, higher drier levels in better cure, as reflected in the more rapid development of hardness and, especially, MEK rub resistance, although they had approximate gel contents around 50%. While, as noted previously, some minimum amount of drier is needed to effect curing of BSBO/polyacrylate coatings at practical rates. However, at ambient temperature, the wet films did not cure after 30 days, even when the concentration of drier was 0.04 to 0.4 wt%; high drier levels caused films to darken.

Film Properties for Coatings Formulated from BSBO and SBO

Attempted film formation using BSBO and SBO was carried out by directly casting them on steel test panels and allowing them to dry in oven at various temperatures for one hour. When drier was not used, the mixtures were still sticky after heating. Even when 0.4 wt% drier was used, good films were not obtained. SBO gave a tacky and soft film, and BSBO showed even less evidence of crosslinking. These results are not surprising. As is well known, SBO itself does not contain enough polyunsaturated fatty acids to enable it to cure to hard films. Apparently, the blowing process does not improve its capacity to harden.

The main shortcomings of the well-cured coatings are the presence of uncrosslinked materials in the film, as shown by gel fraction experiments. Practical utility of this type of coating probably depends on finding a way to increase the gel content of the cured films.

CONCLUSIONS

The work described has been carried out with the aim of demonstrating the use of BSBO both as a free-radical initiator and as a main ingredient to produce coatings. Novel, heat-cure coatings resins have been obtained by blending BSBO with single or multiple monomer/prepolymers. Their formulations and drying film properties, such as pencil hardness, MEK double rub resistance, adhesion, and impact resistance, have been investigated. Two-type blends, which are individually composed of BSBO and TMPTAE require no solvent to reduce application viscosity to about 1000 mPa.s. Blends that include prepolymers, such as HAUA and EBDMAE, are still low in VOC but require some solvent. With increasing proportion of BSBO in formulations, T_g and gel content of drying films decreased. Although the gel contents were only 62-75%, the film properties and FTIR spectra demonstrated that crosslinking reactions occurred after heating in the presence of cobalt driers. The effects of heating time and drier on film properties were studied. To get the coatings films with good performance, it is necessary for the wet films to be heated at 100°C for 0.5 to one hour in the presence of drier.

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