Hyperbranched Aliphatic Polyesters and Reactive Diluents in Thermally Cured Coil Coatings

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ABSTRACT Two hydroxy-functional hyperbranched aliphatic polyesters based on 2,2-dimethylolpropionic acid (bis-MPA) and a partially aromatic conventional polyester have been studied as thermoset resins for solvent-borne thermally cured polyester cross-linked with melamine coatings for precoated sheet metal, i.e., coil coatings. The hyperbranched polyesters differ with respect to the ratio of the end groups, being either hydroxyls or alkyl esters. The rheological properties of formulations with different polyester resin composition and reactive diluent, i.e., rape seed methyl ester, content have been evaluated with viscosity measurements. Films cured either under industrial cure conditions to obtain a peak metal temperature of 232−241 °C or at a lower temperature, i.e., 130 °C, on untreated or organic primer-coated hot-dipped-galvanized steel substrates have been prepared. The film properties have been evaluated with differential scanning calorimetry and conventional film characterization techniques, i.e., adhesion, impact, Erichsen cupping, pencil hardness, microhardness, and scratch and chemical resistance tests. Formulations possessing high drying ability with maintained suitable film application viscosity were obtained using a hyperbranched polyester resin and a reactive diluent. It is proposed that a solvent-free polyester/melamine formulation with sufficient film properties to withstand the rough forming procedures associated with coil coatings can be obtained by further modification of the resin and greater amounts of reactive diluent.

KEYWORDS: hyperbranched polyester resin • fatty acids • reactive diluents • coatings • thermal curing • film properties

INTRODUCTION

Coatings for precoated sheet metal, i.e., coil coatings, is a rapidly growing area in the field of organic coatings (1). The concept of precoated sheet metal comprises a continuous application process of organic coating systems onto sheet metal structures, which are then sold as coated metal coils. In the coil-coating process, bands of sheet metal are coated at a speed of 60−150 m/min and thermally cured in high-temperature convection ovens to reach a peak metal temperature (PMT) of approximately 240 °C within 30−40 s. This continuous and rapid process puts special demands on both the wet film formation and the curing chemistry to obtain a final product without defects like, i.e., sagging, frothing, and poor leveling (2, 3). The final coated metal sheet is cut, bent, and punched into various shapes by the customer. This harsh forming process requires good flexibility and adhesion of the coating. Several different systems, i.e., poly(vinyl chloride), poly(vinyl difluoride), polyurethane, and polyesters cross-linked by melamine, are used in coil coatings, where the polyester/melamine dominates the market internationally. Solvent-borne thermally cured resins with a solvent content of over 50 wt % are traditionally used to obtain suitable flow properties and application viscosities. The solvent evaporates during cure and is incinerated for energy recovery. Increased environmental, health, and safety awareness along with pressure from government legislations have led to an enhanced industrial interest to reduce or even omit the use of solvents in the coating industry (4−6). The use of solvent is further a cost that can be reduced if solvent is omitted. To eliminate the use of solvents in the coil-coating process, methods already used in the postpainting industries, i.e., water-borne (7), powder coating (2, 8−10), and UV-curable systems (2, 9, 10), have been proposed. However, many of these methods have drawbacks, e.g., exterior durability issues, cleanup difficulties upon the change of color, and cost concerns regarding restrained production speed and modification of the coil-coating production facilities (11). Another option to improve the present thermally cured solvent-borne systems is the use of reactive diluents (12−16) or modification of the resin to reduce the viscosity.

One area where viscosity reduction of thermoset resins has been described concerns the use of dendritic polymers that exhibit unique rheological behaviors (17, 18). Dendritic polymers (19) can be divided into three major categories: dendrimers, dendrigrafts, and hyperbranched polymers. The categories differ in polydispersity ranging from the monodisperse and perfect globular structure of dendrimers to the polydisperse hyperbranched polymers. Dendritic polymers obtain their unique rheological properties, e.g., low viscosity in relation to molecular weight compared to conventional polymers and their globular structure, which hampers chain entanglements (17, 18). The rheological properties, com-

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bined with a broad range of possible functional end groups in high amounts, enable good flow, efficient cross-linking, excellent chemical resistance, and good mechanical properties for many different film-forming systems. Recently, an increased interest has been seen in the use of dendritic structures as thermoset resins (20, 21), e.g., in radiation-cured (22−29), high-solid (30−32), and flame-retardant systems (33, 34).

Reactive diluents (35−38) act as solvents in liquid paint, lowering the viscosity, and then chemically react into the film during cure. To be able to work as a good diluent, the introduced compound must be compatible with the entire system and have low viscosity. A reactive diluent must further have low enough volatility to prevent evaporation and the right type and amount of reactive sites to be able to react into the film under the set cure conditions. The positive environmental impact would be 2-fold using a reactive diluent derived from a renewable resource because not only is the volatile organic compound (VOC) content reduced but also a renewable material is introduced into the final film. Previous studies (13−16) have shown that fatty acid methyl esters (FAMEs) derived from vegetable oils work well as reactive diluents in thermally cured polyester/melamine coil coatings. FAMEs are feasible as reactive diluents in coil coatings because they generally have low viscosity and good solubility properties and possess a functional group, the ester acyl moiety, that can react through transesterification (12, 13, 15, 39). Incorporation of the FAMEs via transesterification of the acyl moiety with the hydroxy groups of the polyester resin has been verified with extraction studies, spectroscopical analysis, and carbon-14 analysis of cured films (13−16). Oxidation and evaporation of FAMEs will to some extent compete with the transesterification reaction.

The present work aims to describe how introduction of hyperbranched polyester resins and reactive diluents can decrease the use of conventional solvents and how the final film properties are affected by the resin structure in a thermally cured solvent-borne polyester/melamine coil-coating system. Two aliphatic hyperbranched polyesters and a conventional polyester resin have been studied. The possibility of lowering the VOC content has been evaluated with rheological measurements of formulations with different composition and nonvolatile weight content. The impact on final clear-coat film properties has been studied with differential scanning calorimetry (DSC), and conventional film characterization, i.e., adhesion, impact resistance, pencil hardness, Erichsen cupping, microhardness, and chemical and scratch resistance evaluation.

EXPERIMENTAL SECTION

Materials. Two hyperbranched aliphatic polyesters, Boltorn H2003 (HP-1) and Boltorn H2004 (HP-2), based on 2,2-bis(methylol)propionic acid (bis-MPA) as the AB_2 monomer were supplied by Perstorp Specialty Chemicals AB, Perstorp, Sweden. HP-1 and HP-2 are based on a second-generation hydroxy-functional hyperbranched polyester in which 25% and 62.5%, respectively, of the 16 hydroxy-functional end groups have been modified with 8-carbon-long alkyl acids. The conventional polyester resin (CP-3) used was a hydroxy-functional polyester with a partially aromatic structure dissolved in a 3:1 (w/w) mixture of light aromatic solvent naphtha (CAS 64742-95-6) and butyl glycol (CAS 111-76-2) to a dry content of 70 wt %. The molecular weight, hydroxyl value, acid value, and number of hydroxyl end groups for HP-1, HP-2, and CP-3 as given by the suppliers are presented in Table 1. CP-3, hexamethoxymethylmelamine (HMMM; 99.7%, Ineos Melamines, Frankfurt, Germany), dodecylbenzenesulfonic acid (DDBSA; 70 wt % DDBSA in isopropanol), and light aromatic solvent naphtha (CAS 64742-95-6) were obtained from Akzo Nobel Nippon Paint AB, Gamleby, Sweden. HMMM is hexafunctional but is in the present work considered as trifunctional because of steric hindrance (3). Rape seed methyl ester (RME) was supplied by Norup Gård AB, Knislinge, Sweden. RME is a mixture of 58.3% methyl oleate, 20.9% methyl linoleate, 10.5% methyl linolenate, 4.3% methyl palmitate, and 6.0% other FAMEs, fatty acid derivatives, and oligomers. The fatty acid pattern of RME was determined by gas chromatography analysis performed by the SW Laboratory, Svalöf, Sweden. All chemicals were used as received. Neat and primed hot-dipped-galvanized (HDG) steel sheets were provided by SSAB Tunnplåt AB, Borlänge, Sweden, and used as substrates. The primed HDG steel substrates were pretreated with chromate-free Granodine 1455 T (supplied by Henkel, Mölndal, Sweden) and coated with a chromate-free polyester/melamine primer (supplied by Akzo Nobel Nippon Paint AB, Gamleby, Sweden).

Table 1. Molecular Weight, Hydroxyl Value, Acid Value, and Number of Hydroxyl End Groups for HP-1, HP-2, and CP-3 as Given by the Suppliers

	HP-1	HP-2	CP-3
molecular weight [g/mol]	2500	3200	4000
acid value [mg of KOH/g of resin]	7	7	8
hydroxyl value [mg of KOH/g of resin]	290	115	121
hydroxyl equivalent weight [g of resin/mol of OH]	190	490	460

Techniques. Thermal cure was performed in both a conventional convection T6 function line oven from Heraeus Instruments, Hanau, Germany (oven 1) and a convection oven built to simulate industrial coil-coating cure conditions manufactured by Tryckluftsteknik i Västervik AB, Västervik, Sweden (oven 2). In order to mimic the curing of a steel sheet entering and exiting a convection oven in a continuous process, the test panels were automately inserted, rotated inside the oven, and removed from oven 2.

Rheological measurements were performed on a TA Instruments ARES rheometer equipped with 25 mm parallel plates. The measurements were performed at 30 °C in the linear region with a frequency ramp from 0.1 to 10 Hz.

DSC studies were performed using a Mettler Toledo DSC820 equipped with a Mettler Toledo Sample Robot TSO801RO calibrated using standard procedures. Samples from coatings on neat HDG substrates were heated from −40 to +180 °C, cooled to −40 °C, and then once again heated to 180 °C at a rate of 10 °C/min. The midpoint glass transition temperature (T_g) was determined during the second heating.

A Braive Instruments impact tester was used to evaluate the impact resistance according to EN 13523-5. A standard weight (2 kg) was dropped onto the film from different heights. The impact value is given by the potential energy at which failure occurs, as inspected with 10 times magnification with an optical microscope.

Adhesion was determined according to ISO 2409. A lattice pattern was cut with a cross-hatch cutter and covered with adhesive tape. The cross-hatch pattern was visually checked at 10 times magnification after removal of the adhesive tape. For films cured in oven 2, the adhesion test was performed on prestrained samples with 4-mm-deep deformation dents pro-

Table 2. Formulation Details

sample name	polyester[a]	RME [wt %][b]	nonvolatile weight [wt %][c]
A	HP-1	0	100
B	HP-1 CP-3	0	81
C	HP-2	0	100
D	HP-2 CP-3	0	85
E	CP-3	0	73
F	HP-1 HP-2	0	100
G	HP-1	10	100
H	HP-1 CP-3	10	83
I	HP-2	10	100
J	HP-2 CP-3	10	87
K	CP-3	10	76
L	HP-1 HP-2	10	100

[a] Type of polyester in the polyester/HMMM hydroxyl/ether functional group ratio of 1.6:1 mixtures. In the case of two polyesters, the number of functional groups is equal between the two polyesters. [b] Weight percent added RME calculated on a wet polyester/HMMM mixture. [c] RME has been considered as a solid in the nonvolatile weight calculations.

duced with an impact tester, Braive Instruments (ISO 6272). Adhesion is reported as a value between 0 and 5, with the best adhesion at a value of 0.

Flexibility at a slow deformation rate was evaluated with the Erichsen dome test according to ISO 1520:1999. The greatest dent depth in millimeters without fracture, visually determined at 10 times magnification, is reported.

Chemical resistance was tested with methyl ethyl ketone rubbing of the films according to EN 13523-11. The number of double rubs before film rupture is reported.

The pencil hardness was tested according to ASTM 3363-00. The hardness of the hardest pencil used without rupture, visually determined, of the film is reported.

Scratch resistance was determined with an Erichsen Scratch Hardness Tester model 601 according to ISO 1518:1992 with a scratch rate of 1 mm/s. Load at failure is reported as scratch resistance.

A Fischerscope H100 equipped with a Vickers indenter was used to measure the microhardness according to ISO 6441. The sample was left to recover for 60 s at a 10% indentation depth and without any load.

Test Series. 1. ***Viscosity Measurements.*** Formulations, with a polyester/HMMM reactive hydroxyl/ether functional group ratio of 1.6:1 with and without 10 wt % RME, were prepared according to Table 2. The polyester part of the formulations was either a single resin or a 1:1 functional group mixture of two resins. Formulations F and L with hyperbranched resins were prepared to obtain an equal number of average hydroxy-functional groups per resin molecule as formulations E and K based on the conventional resin. The viscosity of the formulations was measured as the nonvolatile weight was decreased 5 wt % at a time by the addition of light aromatic solvent naphtha.

2. ***Fully Formulated Clear-Coat Sample Preparation and Cure.*** Formulations A–L were diluted with light aromatic solvent naphtha to a nonvolatile weight of 73 wt %. Formulations E and K diluted to a nonvolatile weight of 60 wt % were also prepared. A total of 3 wt % DDBSA, based on the wet formulation weight, was added before application. Films were manually applied using either a rod or a frame applicator to yield a dry film thickness of 23 ± 3 μm on neat or primed HDG steel substrates and cured in ovens 1 and 2, respectively. The films were cured in oven 1 at 130 °C for 10 min and in oven 2 at 360 °C for 43 s for HDG steel substrates and at 300 °C for 39 s for primed HDG steel substrates to obtain a PMT of 232–241 °C. The PMT was determined with temperature tape indicators mounted on the test panels. Differences in the heat reflectivity of the two substrates involve different cure temperatures and times.

RESULTS AND DISCUSSION

A solvent-borne paint formulation normally consists of solvents, a polymeric binder resin, pigments, and additives. The solvents in these coating formulations are used to aid the application and film formation process, where the solvents affect properties such as viscosity, flow behavior, and wetting of the surface. The use of organic solvents in coatings has in many cases been reduced by the introduction of new techniques and coating systems, e.g., powder and water-borne coatings. However, solvents are still extensively used in some areas such as precoated sheet metals, where the coating process is continuous, rapid, and associated with a high material throughput rate. Conventional coil coatings at present are thermally cured solvent-borne coatings with a VOC content of up to 50 wt %. The introduction of FAMEs as reactive diluents had previously been reported (14) to reduce this high solvent content in thermally cured polyester/melamine coil-coating systems. Further reduction is described, in the present work, by alteration of the resin structure, introducing a highly branched resin structure, i.e., hyperbranched polyesters.

Miscibility. The compatibility of resins with other components in the formulation is crucial to obtaining leveled, defect-free, and homogeneous cured coatings. Compatibility is inter alia depending on the molecular weight, polarity, and intermolecular interactions between the components. The use of cosolvents can increase the resin miscibility; however, there is a risk of phase separation during film formation and cure when the solvent evaporates. Previous studies (40) have shown that properties, such as the solubility and miscibility of hyperbranched polymers, are greatly affected by the end groups. Hyperbranched aliphatic polyesters based on bis-MPA have been extensively studied previously, and details about the molecular structures of these polymers can be found in the literature (26, 41–43). The hyperbranched polyesters used in the present study have been end-group-modified with alkyl chains to decrease the polarity and intra- and intermolecular secondary hydrogen bonds, induced by the hydroxy-functional end groups, of second-generation aliphatic bis-MPA hyperbranched polymers. HP-2 was modified to a greater extent than HP-1, giving a higher molecular weight and a lower amount of remaining hydroxyls. Compatibility with FAME was improved with the extent of modification of the hyperbranched polyester; i.e., HP-2 is more compatible with FAME than HP-1 is, although HP-1 and FAME, samples G and H, formed transparent formulations and cured coatings. However, HP-1 has poor compatibility with CP-3 and HP-2, as indicated by opaque wet mixtures of formulations B, F, H, and L, although clear single-phase films were attained after cure. Further, the somewhat polar HP-1 is compatible with the unpolar RME.

Rheological Properties. The rheological properties of formulations A–L have been evaluated with viscosity measurements at decreasing nonvolatile weight content

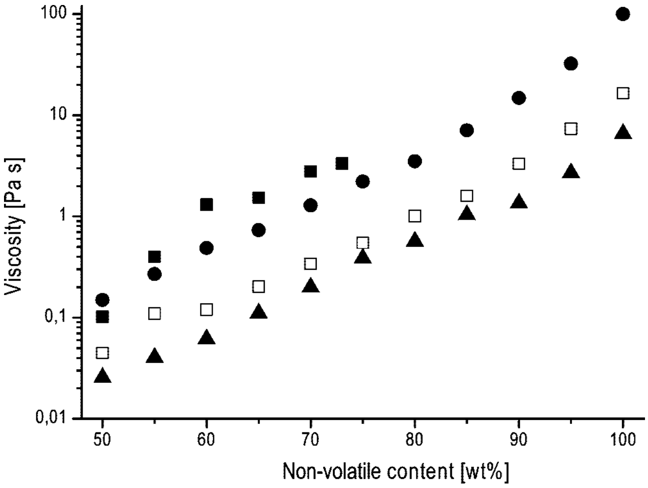


FIGURE 1. Viscosity versus nonvolatile content for samples A (●), C (▲), E (■), and F (□).

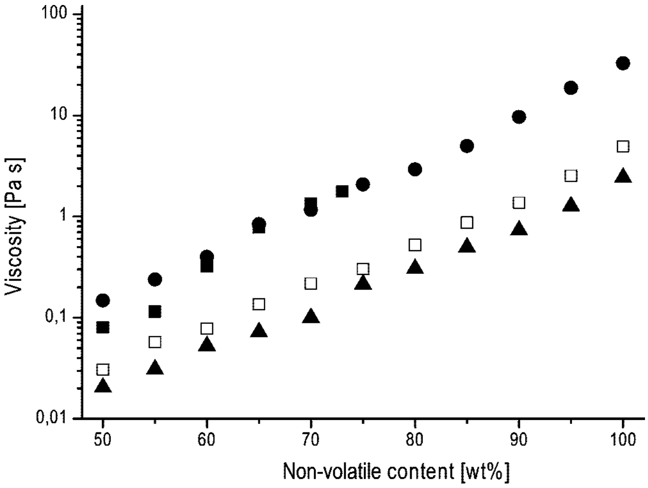


FIGURE 2. Viscosity versus nonvolatile content for samples G (●), I (▲), K (■), and L (□).

down to a nonvolatile weight of 50 wt %. The initial nonvolatile weight content of formulations B, D, E, H, J, and K is less than 100 wt % (Table 2) because CP-3 was obtained with a dry weight of 70 wt % from the supplier. The results (Figure 1) show that lower viscosity is obtained, at equal nonvolatile content, with a hyperbranched polyester resin compared to a conventional polyester resin. The decrease in the viscosity is greater for HP-2 than for HP-1 in spite of a higher molecular weight. The greater amount of hydroxy-functional end groups of HP-1 than of HP-2 causes more polar interactions and hydrogen bonding in mixtures based on HP-1. Formulation D (data not shown), consisting of both CP-3 and HP-2, exhibits an intermediate viscosity versus the nonvolatile content between the single polyester formulations C and E. However, the viscosity of formulation A, containing hyperbranched HP-1, is greater than that of formulations B (data not shown) and E at intermediate nonvolatile content, approximately 65 and 53 wt %, respectively. This difference is due to intermolecular hydrogen-bonding and polar interactions associated with the high number of hydroxyl end groups of HP-1.

The introduction of reactive diluents, i.e., 10 wt % RME, even further decreases the viscosity (Figure 2). The reduction in viscosity was, however, minor, with HP-1 as the binder resin, sample G, because of the high degree of hydroxyl end groups that present strong intermolecular secondary hydrogen bonds. These hydrogen bonds and the amphiphilic character of the resin further entail minor reductions in the viscosity upon the addition of reactive diluents, although RME with its acyl moiety is a hydrogen-bond acceptor that can associate with the polar portions of the resins.

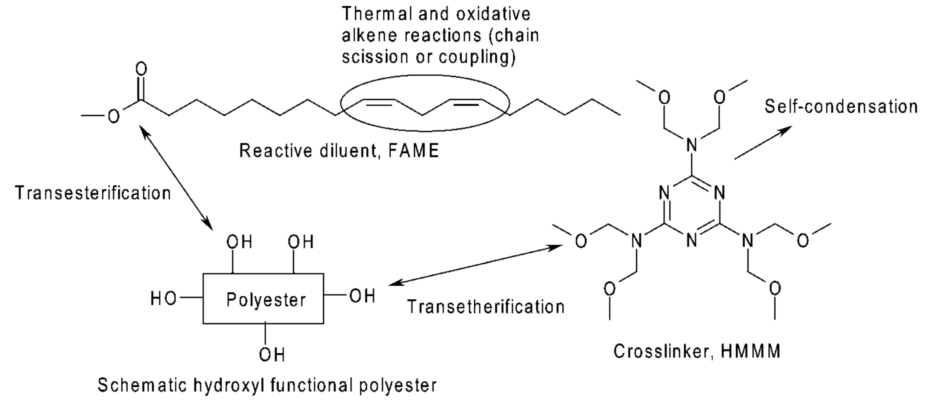
The results show that the nonvolatile content of the coil-coating paint can be increased by approximately 24 wt %, as calculated on a conventional application viscosity of 200 mPa · s, by introduction of a reactive diluent and modification of the polyester binder resin structure. It is suggested that the nonvolatile content can be decreased even more by greater reactive diluent content and further modification of the resin.

Curing. The coatings were cured under two different cure conditions: one resembling industrial cure conditions and one at lower cure temperatures. The network is cross-linked by transetherification of HMMM and the hydroxy-functional polyester. The reactive diluent is chemically incorporated by transesterification with the hydroxyl groups of the polyester and can also contribute to the cross-linking by alkene reactions. Reactions in the vicinity of the alkene groups in the fatty acid both include chain scissions as well as coupling reactions, either oxidative or thermally induced. Further details on the thermo/oxidative behavior of FAME alkenes are thoroughly described in the literature (39, 44–49). The main possible reactions in an acid-catalyzed polyester/melamine system with FAME as the reactive diluent are schematically described in Scheme 1. Previous studies have shown that conventional polyester binder resins cross-linked by melamine with FAMEs as reactive diluents form tack-free films under both evaluated cure conditions (14, 15). However, lower cure temperatures render softer coatings because of less evaporation of FAME (15). All formulations were diluted to a nonvolatile weight content of 73 wt %. However, the viscosity of sample E was too high to obtain films cured in oven 2 without froth and leveling defects on the HDG steel substrate. Therefore, films with a nonvolatile weight content of 60 wt % of formulation E and its equivalent with 10 wt % RME, formulation K, were prepared.

Physical and Mechanical Properties of Cured Films. The forming of products composed of precoated sheet metal requires coatings with good adhesion, flexibility, impact resistance, and hardness to prevent, e.g., flaking and film fractures. Warranty times of up to 15 years also imply a need for very high performance of the coating system. The metal sheets are pretreated and primed before being top coated to improve the film properties. Both untreated and organic primer-coated HDG steel sheets have been used as substrates in the present study.

The test results of adhesion, flexibility at slow and fast deformation rates, pencil hardness, universal hardness (HU), and chemical and scratch resistance for samples A–L cured in oven 2 on HDG steel substrates are presented in Table 3.

Scheme 1. Schematic Description of Possible Reactions in an Acid-Catalyzed Polyester/Melamine System with FAME as the Reactive Diluent



These kinds of film properties are affected by inter alia resin polarity, architecture, heterogeneity, and film thickness (2). Moreover, most of the performed test methods are mainly suitable for quality control because they are empirical and commonly test combinations of properties. The conventional polyester resin with partially aromatic content, sample E, has good adhesion to the substrate and is chemical and scratch resistant. However, the coating is harder and less flexible than eligible to withstand the forming process of precoated metal sheets. Flexibility at slow deformation rates and scratch resistance of the film is improved, while impact resistance is further impaired, upon the addition of the reactive diluent, sample K. This increased flexibility is expected because the long unpolar carbon chain of RME is known to plasticize thermally cured polyester/melamine systems (14, 15). The introduction of aliphatic hyperbranched polyester HP-1 to the formulation, sample B, entails decreased flexibility, hardness, and impact resistance of the coating compared to the aromatic structure containing sample E. These properties are even further impaired for films consisting entirely of HP-1 as polyester resin, sample A. This inferior formability of HP-1 resin formulations is due to the aliphatic structure and high amounts of hydroxy-functional end groups, an average of 12 hydroxyl groups per molecule, causing a brittle and too densely cross-linked network. On the other hand, HP-2, sample C, with an average of only six hydroxyl groups per molecule, gives a too loosely cross-linked network, i.e., tacky and soft films with very low chemical and scratch resistance. The introduction of CP-3 with greater functionality than HP-2, i.e., sample C, renders tack-free films with improved chemical and scratch resistance as the cross-link density is increased. Formulation F has an equal average number of hydroxyl groups, i.e., nine hydroxyl groups per molecule, as formulation E and is therefore plausible to exhibit similar film properties. However, the different network architectures with dangling alkyl chain ends and aliphatic structures associated with HP-1 and HP-2 result in lower hardness and scratch resistance. These alkyl chains on the hyperbranched polymers decrease the plasticizing effect of the reactive diluent, resulting in no significant change of the film properties upon the introduction of RME in formulations G−J and L. It is, furthermore, suggested that the dendritic backbone structure affects the overall network properties although it is not clear at present exactly what the network looks like.

Table 3. Film Properties for Samples A−L on Untreated HDG Substrate Cured under Simulated Coil-Coating Cure Conditions[a]

sample name	adhesion	impact resistance [J]	Erichsen flexibility [mm]	chemical resistance	pencil hardness	scratch resistance [N]	hardness [N/mm^2]
A	1	0	<1	>200	F	6	90.4
B	0	10	4	>200	HB	6	72.4
C	0	>18	5	18	<2B	1	0.8
D	0	16	5	>200	B	4	1.3
E[b]	0	8	3−4	>200	HB	8	113.6
F	0	4	3−4	>200	<2B	0	5.2
G	0	0	<1	>200	HB	7	94.0
H	0	6	5−6	>200	F	10	89.6
I	0	16	5	76	<2B	1	1.0
J	0	>18	6	>200	<2B	4	1.2
K	0	2	7	>200	H	12	126.8
K[b]	0	0	7	>200	2H	7	111.9
L	0	6	4	>200	<2B	1	5.4

[a] Cure was performed under simulated coil-coating cure conditions in oven 2 at 360 °C for 43 s to obtain a PMT of 232−241 °C. [b] Nonvolatile weight of 60 wt %.

Table 4. Film Properties for Samples A−L on Primed HDG Substrate Cured under Simulated Coil-Coating Cure Conditions[a]

sample name	adhesion	impact resistance [J]	Erichsen flexibility [mm]	chemical resistance	pencil hardness	scratch resistance [N]	hardness [N/mm^2]
A	1−2	0	<1	>200	2H	20	84.3
B	0	0	2	>200	H−2H	18	108.3
C	0	2	1	16	2B	16	1.5
D	0	4	2	49	HB	17	2.7
E	0	0	3	>200	3H	22	131.9
F	0	0	1	89	HB−F	17	8.7
G	0	0	<1	>200	2−3H	19	87.6
H	0	0	2	>200	2H−3H	21	107.5
I	0	0	2	19	2B	20	2.3
J	0	2	4	26	F	17	3.1
K	0	0	2−3	>200	2H	17	137.9
L	0	0	1	69	B−HB	19	8.4

[a] Cure was performed under simulated coil-coating cure conditions in oven 2 at 300 °C for 39 s to obtain a PMT of 232−241 °C.

The impact resistance and Erichsen flexibility of all coatings are more inferior on the organic primer-coated substrate compared to the neat HDG steel substrate; compare Tables 3 and 4. It should be noted that the flexibility and adhesion for all films on primed steel substrates were limited to the primer performance; i.e., the film rupture occurred at the steel/primer interface. Substitution to another primer system with improved film properties would presumably render greater formability of the evaluated top coats on organic primer-coated substrates. The scratch resistance is greater on primed than neat HDG steel substrates because both the primer and the top coat have to be ruptured.

A large amount of energy is consumed in order to heat the convection ovens in the precoated sheet metal industry. Decreasing the oven temperature can cut down the energy consumption and, in turn, production costs. However, a significant decrease in the cure temperature renders uncured films with poor adhesion; see the Supporting Information. Only samples A, B, and G have sufficient numbers of hydroxyl groups to obtain chemical-resistant films at this cure temperature. Less RME evaporates at this inferior temperature, as indicated by the lower HU value upon the addition of the reactive diluent. The presence of RME plasticizes the coating, whereas evaporation and alkene cross-linking give the opposite effect. It is proposed that greater amounts of RME evaporate and thermal alkene polymerization occurs at industrial cure conditions in oven 2 than in oven 1. DSC measurement further indicates a greater presence of either incorporated or nonreacted RME in the films cured in oven 1 because T_g is significantly reduced upon the addition of the reactive diluent for these films, exemplified in Table 5.

Even though the film properties of hyperbranched polyester films are not sufficient to fully withstand the coil-coating forming process, it is proposed that a coating with suitable film properties, i.e., good adhesion, flexibility, high impact strength, and chemical and scratch resistance, can be obtained by further resin modification and the use of an appropriate primer.

Table 5. DSC T_g for Samples E and K

sample name	cure[a]	T_g [°C]
E	1	21
K	1	−1
E[b]	2	25
K[b]	2	24

[a] (1) Cure was performed in a conventional convection oven (oven 1) at 130 °C for 10 min. (2) Cure was performed under simulated coil-coating cure conditions in oven 2 at 360 °C for 43 s to obtain a PMT of 232−241 °C. [b] Nonvolatile weight of 60 wt %.

CONCLUSIONS

The VOC content of thermoset solvent-borne thermally cured polyester/melamine coil-coating paint is reduced by introduction of an aliphatic hydroxy-functional hyperbranched polyester resin. The solvent content is further reduced by the addition of a reactive diluent, RME. The nonvolatile weight content has been shown to increase from 52 to 76 wt % in order to obtain a suitable application viscosity with hyperbranched resin and the addition of 10 wt % reactive diluent.

The forming process connected to precoated sheet metal demands hard, flexible, and scratch-resistant films with good adhesion. However, the different network architectures with many dangling alkyl-chain ends and the aliphatic structure of the hyperbranched polyester compared to the partially aromatic conventional polyester render softer and less flexible films than desired. The functionality of the hyperbranched polyester is also of importance because too many hydroxy-functional groups result in formulations with higher viscosity, due to hydrogen bonds, and brittle films. Too few hydroxyl groups give rise to undercured and tacky films. It is proposed that a solvent-free formulation with sufficient film properties to withstand the harsh forming process can be obtained by further modification of the resin and the addition of greater amounts of reactive diluent.

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Supporting Information Available: Film properties for samples A—L on untreated HDG substrates cured in a conventional convection oven. This material is available free of charge via the Internet at http://pubs.acs.org.

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