

# High-Solids Mar Resistant Clearcoats Prepared from an Isophthalate-Based Oligoester and a Melamine Resin. Study and Characterization of Mar Resistance with Scanning Probe Microscopy Method

CONSTANTINO S. D. DIAKOUMAKOS<sup>1</sup>, FRANK N. JONES<sup>2</sup>, HUIJUAN YE<sup>1</sup>, WEIDIAN C. SHEN<sup>1</sup>

<sup>1</sup> Coatings Research Institute, Eastern Michigan University, 430 W. Forest Avenue, Ypsilanti, Michigan 48197

<sup>2</sup> Physics & Astronomy Department, Eastern Michigan University, 303, Strong Hall, Ypsilanti, Michigan 48197

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**ABSTRACT** : A new series of high-solids [low-VOC (volatile organic compound) content] mar resistant clearcoats (CL-series) were prepared upon crosslinking of a new-synthesized hydroxyl-terminated isophthalate-based liquid oligoester (L-311) with an hexakis(methoxymethylol)melamine (HMMM) resin, via an acid-catalyzed etherification reaction. The chemical, physical, and mechanical properties of the CL-clearcoats were compared to those of a reference clearcoat (CRO). An attempt was made to investigate the effect that the amounts of catalyst and melamine resin had on the clearcoats' physical, chemical, and mechanical properties, and moreover, to correlate these properties to the films chemical structures. The new-formulated high-solids clearcoats (CL-series) presented enhanced processability and higher NVW values (lower VOC content) than the reference clearcoat CRO, and their properties (pencil hardness, knoop hardness, adhesion, impact resistance, solvent and gasoline resistance, mar resistance, and flexibility) were better or comparable to those of the CRO. More specifically, the mar resistance of the CL-clearcoats series was investigated by applying both the crockmeter test and a novel method that employed a modified scanning probe microscope. In addition, we identified and characterized the different responses of the CRO and certain CL-clearcoats to mar stress. The experimental data regarding the mar resistance of the new-formulated clearcoats fully justified our polymer design strategy, verifying our expectations for the possibility of preparing glossy, high-solids mar-resistant clearcoats that could present enhanced processability and solvent resistance, relatively high pencil hardness, and at the same time very good elastic recovery to mar stress. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1317–1333, 2002

**Key words:** oligoesters; polyester resins; melamine; high-solids clearcoats; low-VOC; mar resistance; scanning probe microscopy

## INTRODUCTION

Until the mid-1980s, the majority of typical polymers traditionally used by the manufacturers in

the preparation of coatings, paints, and finishes were generally supplied at approximately 50% solids by weight (NVW) (40–44% by volume). But over the last decade the popularity of these organic solvent solution coatings has been threatened by the growing proliferation of the VOC (Volatile Organic Compounds) regulations, imposed worldwide. Those traditional coatings formulations with VOC levels of approximately 5 pounds per gallon were well above the limits established for most typical finishing applications. It is believed that future environmental regula-

Correspondence to: C. D. Diakoumakos (c.diakoumakos@imel.demokritos.gr or constantinos.d@freemail.gr).

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\* Present address: Institute of Microelectronics, NCSR "Demokritos," Terma Patriarchou Gregoriou Str., 15343 Athens, Greece.

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tions will increasingly promote further the development of low-VOC coatings, and thus the development of new synthetic strategies and novel approaches on polymer design is nowadays the hottest issue in paints and coatings research field. And as the industry's appetite for these low-VOC coatings increases, a tremendous demand for new polymer vehicles suitable for low-solvent formulations will be a forcible driving force for paints and coatings chemists, formulators, and resin manufacturers.

Polyester resins are widely used in paints and coatings industry because of the excellent array of properties that are obtained when the resins are crosslinked with melamine or isocyanate crosslinking agents<sup>1,2</sup> and therefore its technological importance is extremely high. In a previous work<sup>3</sup> we studied the effect of the different transesterification parameters on the synthesis of high-solids hydroxyl-terminated isophthalate-based oligoesters. The investigation of the effect that the different reaction parameters had on the properties of the synthesized isophthalate-based oligoesters and the optimization of the experimental data resulted to a profound knowledge of the way through which high-solids hydroxyl-terminated oligoesters with enhanced processability can be obtained in high yields. The result of that investigation was the preparation of a new-synthesized high-solids hydroxyl-terminated isophthalate-based liquid oligoester, the L-311, which presented enhanced processability than its predecessor,<sup>3,4</sup> a reference solid oligoester (RefOL). At the same time the high-solids (NVW ~ 82%) clearcoats<sup>5</sup> prepared from the L-311 as a binder and an hexakis(methoxymethylol)melamine resin (HMMM) as crosslinker, showed comparable or even enhanced film properties to those of a reference clearcoat (CRO) formulated from the RefOL and the same melamine resin.

In the present work we used the L-311 as a binder and an hexakis(methoxymethylol)melamine resin (HMMM) (R-747) as a crosslinker to formulate a series of high-solids clearcoats (CL-series) varying (a) the amount of the catalyst (a solution of dinonylnaphthalene disulfonic acid in isopropanol) and (b) the quantity of the melamine resin (R-747). In our attempt to find the optimum conditions for the crosslinking of the L-311 with the melamine resin R-747, we not only compared their film properties (pencil hardness, knoop hardness, adhesion, flexibility, impact resistance, solvent and gasoline resistance as well as mar resistance) to those of a reference clearcoat (CRO)

prepared from the RefOL, but we also proceeded to a further investigation of the effect that the amounts of the catalyst and those of the melamine resin had on the physical and mechanical properties of the clearcoats.

One such very important property, resistance to marring of crosslinked polymeric surfaces coatings, is a highly desired characteristic of coatings with enormous technological importance especially for the coatings used in the automotive, glazing, and flooring industries.<sup>6-11</sup> The terms "mars" and "marring" are used to describe surface damage that is usually shallow and narrow. The severe damage resulting in visible, deeper, and wider trenches in which fracture or cracking is involved is usually termed "scratch" and "scratching." Although a single mar may not be noticeable, the existence of groups of mars (these mars can be made by car washing, polishing, etc.) does degrade the appearance of coatings. The depth of most of the mars ranges from a couple of dozen to several hundred nanometers, while the depth ranges from a couple of hundred up to two micrometers. It is difficult to set a clear demarcation line between the mars and scratches. A statistical survey relating the damage, the visibility, and the appearance was conducted by Lin and his colleagues.<sup>11</sup> In previous publications<sup>12-15</sup> we described studies of marring of automotive coatings for plastic substrates. Model compound studies led to the working conclusion that a good, and arguably the most viable, approach to making mar-resistant coatings for plastics is to use highly elastic, densely crosslinked coatings with the singular structural feature of having long, flexible spacers separating the resin from the crosslink site. Suitable flexible spacers include  $-\text{O}(\text{CH}_2)_n\text{O}-$  with  $n = 4$  or greater and  $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_m-$  with  $m = 2$  or greater.

The novelty of the present investigation is the correlation of the whole surface of a crosslinked polymer network (crosslink density, distance between the crosslink sites, as well as crosslinking kinetics and orientation of the resulted crosslinked polymer network) to the film properties and more specifically to mar resistance. In other words, the introduction of flexible spacers among crosslink "joints" (triazine rings) seems not to be the only factor that could influence the mar resistance.<sup>4</sup> In our present work we had strong experimental indications that the crosslinking kinetics and the crosslink density, as well as the formation and orientation of the

crosslink polymer network, played an important role in the mar resistance of the polymers.

The mar resistance results we obtained for the clearcoats of the new-formulated CL-clearcoats series are of significant technological importance because it became evident that the preparation of a glossy high-solids clearcoat, which would present enhanced processability, relatively high pencil hardness, and at the same time very good mar resistance is feasible.

## EXPERIMENTAL

### Characterization Methods

Fourier transform infrared (FTIR) and attenuated total reflectance FTIR (ATR-FTIR) spectra were obtained from a Nicolet 510P FT-IR spectrometer.  $^1\text{H-NMR}$  (nuclear magnetic resonance) spectra were recorded using a Bruker AC-250 spectrometer at 250 MHz.  $^{13}\text{C-NMR}$  and  $^{13}\text{C}$ -Distortionless Enhancement by Polarization Transfer (DEPT) spectra were recorded on a Bruker AC-250 spectrometer at 60 MHz. Modulated differential scanning calorimetry (MDSC) analyses were performed with a DuPont TA 2100 Thermal Analyzer using a high-temperature (600°C) cell in a  $\text{N}_2$  atmosphere at a heating rate of 5°C/min. The clearcoats samples for MDSC were prepared as follows: The clearcoats formulations were applied on unprimed plastic panels. After baking at 120°C for 30 min, the films were separated from their plastic substrates and used for MDSC analysis. Gel permeation chromatography (GPC) analyses were carried out with a Hewlett Packard 1050 series Liquid Chromatograph with an HP 1047A differential refractometer as detector. Tetrahydrofuran (THF) was used as a solvent at a flow rate 0.9 mL/min through a series of three Phenogel columns (pore size:  $10^5$ ,  $10^3$ ,  $10^2$  Å) and polystyrene was used for the standardization. Gas chromatography (GC) analyses were performed using a Hewlett-Packard 5809A Gas Chromatograph with a flame ionization detector (FID). 1,4-Butanediol was used as internal standard and the silate agent was a mixture 80/20 v/v of hexamethyldisilazane (HMDS) and N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA). The viscosities  $\eta$  (cP) of the oligomers and their corresponding coatings were determined using a Brookfield DV-II+ Viscometer, at 25°C and at a spindle rate of 6 rpm (Spindle No. 31). The Non Volatiles by Weight (NVW) of the synthesized oligomers and their

corresponding clearcoats were determined upon heating at 110°C for 1 h, of a sample placed in an aluminum dish, in an air-circulated oven (ASTM D2369-95).

The film thickness was measured with a Microtest magnetic thickness gauge. The pencil hardness (PE.H) and both the direct (DIR) and reverse (RIR) impact resistance (inch-lbs.) were measured according to the ASTM D-3364 and D-2794 methods, respectively. The Knoop hardness was tested on a Tukon Microhardness Tester (Wilson Instrument Division) and the Knoop hardness number (KHN) was determined with a load of 0.1 kg according to the ASTM D-1474 method. The Knoop hardness number can be calculated as follows:

$$\text{KHN} = L \times (I^2 \times C_p)^{-1}$$

where  $L$  is the load applied to the indenter (kg),  $I$  the measured length of indentation's long diagonal (mm), and  $C_p$  the indenter constant ( $7.028 \times 10^{-2}$ ).

Elongation tests (ELONG) that consist a measure of the film's flexibility and elasticity were performed on a mandrel tester according to the ASTM D-522-93a method. Gloss measurements were performed using a pocket gloss meter, the BYK-Gardner "micro-TRI-gloss." Methyl ethyl ketone resistance (MEK) was tested by double rubbing with MEK saturated no woven paper (Kimwipe); the no woven paper was kept saturated by MEK during the measurement. Adhesion (ADHES) was tested according to the ASTM D3359-95a. Gasoline resistance (GASOL) was tested using panels aged by crosshatching through a coating on a steel panel and immersed the panel in "CE-10 gasoline" (a mixture of 10 wt % ethanol to 90 wt % reference fuel "C," a 50/50 w/w blend of toluene and isooctane) at ambient temperature. The panel was removed and inspected at four 15-min intervals and then immersed again. Results were recorded as percentage of the cells that had been blistered or lifted after each immersion period. The fewer are the blistered or lifted cells at a specific immersion time, the better is the sample's gasoline resistance.

Mar resistance (MR) was tested on a AATCC Crockmeter Apparatus model CM-1 from Atlas Co. The test procedure was as follows: A coated black aluminum panel was immersed in dry "Bon-Ami" cleaning powder so that the panel was covered with the powder and the excess powder was

gently poured off. The apparatus was modified by gluing a magnetic strip in front of the panel on the test bed to hold the panel in place during test. A fresh green  $50 \times 50 \text{ mm}^2$  felt pad was placed over the probe (diameter of 15 mm) of the tester and secured with a spring clip. The test probe was moved back and forth over a portion of the panel in ten double strokes; the frequency was about one double stroke per second. The result was a marred area on the panel about  $13 \times 220 \text{ mm}$ . The panel was then cleaned in a stream of a cold tap water, gently wiped with a wet wiper, and dried with a soft towel. The  $20^\circ$  gloss of the marred part and the two sides of unmarred part was measured using the "micro-TRI-gloss" pocket gloss meter. The percentage of  $20^\circ$  gloss retention was recorded as MR of the coatings. The higher is the percentage  $20^\circ$  gloss retention, the better is the sample's mar resistance.

The study, characterization, and measurements of micro mar resistance (MMR) and micro indentation hardness (MIH) were performed using a Digital Instruments "Nanoscope III, Scanning Probe Microscope, modified as described hereafter. The test employed a modified Scanning Probe Microscope (SPM) to mar the material and conventional scanning probe microscope to measure and characterize the results. The modification consisted of installing on the SPM a specially fabricated probe consisted of a diamond tip mounted on a high-modulus tungsten cantilever; this probe is stiff enough to indent most polymer surfaces under the normal forces that can be applied with a SPM and to mar surfaces when normal force is combined with lateral movement. Thus, it can be used both as a micro hardness tester and as device for marring polymer surfaces with known force and velocity. More particularly, the custom-made probe consists of a diamond tip glued to a rectangular-shaped tungsten cantilever with epoxy resin. Our diamond tips were purchased from Imetra, Inc. (Elmsford, NY), whose manufacturer is in Switzerland. The tips of Imetra have well-defined shape and sharpness. A  $90^\circ$  conical-shaped diamond tip with a  $1 \mu\text{m}$  radius at its apex was used in most of the tests described. The cantilevers are cut from tungsten foils and their spring constants range from 400 to 4000 N/m, three to four orders of magnitude larger than conventional SPM probes. The SPM equipped with such a probe is capable of making artificial mars, under well-controlled conditions with the same dimensions as the mars encountered in the field. The coatings panels tested were

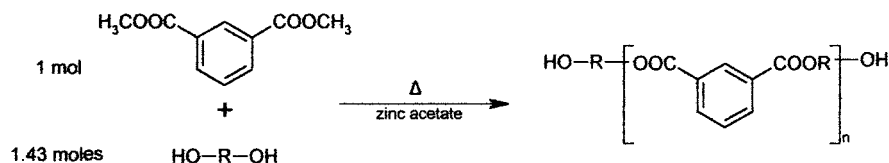
cut into a  $10 \times 10 \text{ mm}^2$  piece by a shear cutter to fit the sample stage of the SPM. Before the test, the samples were washed in an ultrasonic bath with a mild solvent-free detergent, rinsed in a stream of cool tap water, gently dried with soft tissue, and then were blown dry with high pressure nitrogen gas. In the MMR measurement, the tip under a fixed normal force ranging from about 400 to 800  $\mu\text{N}$ , depending on the property of the tested coating, was moved laterally along the surface and made a single scrape of about 70  $\mu\text{m}$  long. After scraping, the tip was lifted and the sample was moved. A second mar was then made under an increased normal force, parallel to the first one at a distance of about 10  $\mu\text{m}$ . After 5 mars were made under different normal forces, the marred sample was again washed in an ultrasonic bath without detergent, rinsed in a stream of cool tap water, gently dried with soft tissue, and blown dry with high-pressure nitrogen gas to remove the broken material. Then the marred surface was imaged with an SPM equipped with a conventional high-resolution tip. The average values over 200–400 data points along the mar were used to calculate the MMR (see Scheme 5), which is defined by the cross-section area of the trough, and the percentage of elastic, plastic, and abrasive responses at different normal forces (see Scheme 5). For the MIH measurements, the same cone-shaped diamond tip used for the MMR measurements was pushed into the surface of a sample and the depth of indentation was measured. Using the normal force divided by the contact area of the tip and sample ( $A_{\text{cnt}}$ ), we obtained the sample's MIH under various normal forces.

Conventional contact AFM topographic images of the unmarred and marred clearcoats surfaces were obtained with an E scanner and a V-shaped silicon nitride cantilever with a length of 100  $\mu\text{m}$ , a constant of 0.58 N/m, and a sharpened tip. The scan size was 10  $\mu\text{m}$  and the scan rate was 2.001 Hz.

## Materials

Dimethyl isophthalate (DI) (99%), 1,6-hexanediol (HD) (97%), 2-methyl-1,3-propanediol (MP) (99%), zinc acetate dihydrate (99+%), and dibutyltin dilaurate (95%) were purchased from the Aldrich Chemical Company. A monomeric methylolated melamine–formaldehyde resin "Resimene-747" (R-747) [HMMM, for hexakis(methoxymethyl)melamine] was obtained from the Monsanto Co. (now Solutia, Inc.). A fluoropolymer surface





where R:  $\text{---}(\text{CH}_2)_6\text{---}$

**Scheme 1** Synthesis of the reference oligoester RefOL.

tension modifier, the Fluorad (FC-430), was obtained from 3M Industrial. The Nacure-155 (dinonylnaphthalene disulfonic acid, DNNDSA, 50% w/w solution in isopropanol) was obtained from King Industries. All materials were used as supplied.

Steel and aluminum  $3 \times 6$  in. panels were purchased from the Q-panel Company. Black panels were made by casting, using a No. 26 draw-down rod a commercial black paint, "Rust Scat" from Colorado Paint Co., on aluminum panels and subsequent baking at  $150^\circ\text{C}$  for 30 min.

### Synthesis of Oligoesters (Scheme 1)

#### Synthesis of the Reference Oligoester (RefOL)

Dimethyl isophthalate (582.57 g, 3.00 mol), 1,6-hexanediol (508.17 g, 4.30 mol), and zinc acetate dihydrate (2.18 g, 0.20% w/w of total reactants weight) were charged into a reactor equipped with a Dean-Stark trap, mechanical stirrer, thermometer,  $\text{N}_2$  inlet, and a condenser. The mixture was flushed with  $\text{N}_2$ , heated to  $140^\circ\text{C}$ , and then gradually to  $200^\circ\text{C}$  for 5 h, while collecting methanol in the Dean-Stark trap. When visible

methanol collection ended, the temperature was increased to  $210^\circ\text{C}$  for 30 min. The warm product was poured into a metallic container before it solidified to a white partly crystalline low-melting solid (942.91 g, yield = 98.9%, NVW = 98%).

$$M_n = 1385, M_w = 2439, M_p = 2420, M_z = 3654, \\ M_{z+1} = 4878, M_v = 2273, D = 1.76$$

Excess of HD = 1.60% w/w

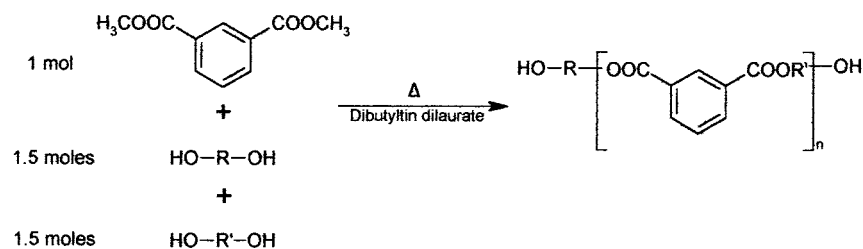
HO-value = 164 mg KOH equivalent to 1 g sample

$T_g = -37^\circ\text{C}$ ,  $T_m = 39^\circ\text{C}$  (onset temperatures determined by MDSC)

FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and  $^{13}\text{C-DEPT}$  data of the RefOL have been reported and extensively discussed in our previous work.<sup>3</sup>

#### Synthesis of the Oligoester L-311 (Scheme 2)

Dimethyl isophthalate (582.57 g, 3.00 mol), 1,6-hexanediol (531.81 g, 4.50 mol), 2-methyl-1,3-propanediol (405.54 g, 4.50 mol), and a catalytic amount of dibutyltin dilaurate (1.52 g, 0.10%



where R:  $\text{---}(\text{CH}_2)_6\text{---}$

where R':  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{---C---C---C---} \\ | \quad | \quad | \\ \text{H}_2 \quad \text{H} \quad \text{H}_2 \end{array}$

**Scheme 2** Synthesis of the oligoester L-311.

**Table I** The Formulation and the Chemical, Physical, and Mechanical Properties of the Reference Clearcoat CRO and the New-Formulated CL-Clearcoats Series (CL8501, CL8510, CL8520, CL8001, CL8010, CL7510, and CL7010)

Formulation and Properties	Clearcoats							
	CRO	CL8501	CL8510	CL8520	CL8001	CL8010	CL7510	CL7010
Oligoester/R-747 <sup>a</sup>	65/35	85/15	85/15	85/15	80/20	80/20	75/25	70/30
FC-430 <sup>b</sup>	10	10	10	10	10	10	10	10
Nacure-155 <sup>c</sup>	1	0.1	1.0	2.0	0.1	1.0	1.0	1.0
Solvent <sup>d</sup>	Xylene	No	No	No	No	No	No	No
<i>n</i> (cP)	300	490	490	490	490	490	485	480
NVW (%)	69	80	80	80	80	80	80	80
<i>T<sub>g</sub></i> <sup>e</sup> (°C)	2.3	-28.6	-18.6	-14.4	-28.5	-16.4	-1.3	1.9
Film Thickness (mil)	0.80	0.76	0.78	0.77	0.77	0.75	0.80	0.77
PE.H	F	F	F	2H	2H	2H	2H	2H
KHN <sub>0.1Kgr</sub>	46.1	48.1	43.8	23.7	20.1	19.8	22.2	25.6
DIR (inch-lbs.)	160	160	160	160	160	160	150	60
RIR (inch-lbs.)	150	160	160	150	160	160	150	60
ELONG (%)	>32	>32	>32	>32	>32	>32	>32	>32
ADHES	0	5B	3B	0	0	0	0	0
MEK (double rubs)	>200	>200	>200	>200	>200	>200	>200	>200
GASOL <sup>f</sup> (%)	100	45	38	25	30	24	15	8
MR <sup>g</sup> (%)	98.5	98.4	98.3	92.3	98.3	98.2	98.0	86.1

<sup>a</sup> %, w/w.<sup>b</sup> %, w/w on (oligoester + R-747) weight (surface tension modifier).<sup>c</sup> %, w/w on (oligoester + R-747) weight (dinonylnaphthalene disulfonic acid, DNNDSA, 50% w/w solution in isopropanol) (catalyst).<sup>d</sup> 40% w/w on (oligoester + R-747) weight.<sup>e</sup> Onset temperature determined by MDSC.<sup>f</sup> The % blistered or lifted cells correspond to an immersion time of 30 min.<sup>g</sup> The % of 20° gloss retention was recorded as MR of the coatings.

w/w of total reactants weight) were placed in a round-bottom flask equipped with a Dean-Stark trap, mechanical stirrer, thermometer, N<sub>2</sub> inlet, and a condenser. The mixture was heated under a stream of N<sub>2</sub> at 200–210°C for 5 h, from the moment methanol began to collect. The transparent liquid product was quickly poured into a steel container to cool and then kept in a vial at room temperature (1305 g, yield = 98.3%, NVW = 82%,  $\eta_{25^\circ\text{C}} = 2010$  cP,  $d_{25^\circ\text{C}} = 1.0984$  g/cm<sup>3</sup>, VOC = 1.66 lbs/gal).

$$M_n = 538, M_w = 719, M_p = 388, M_z = 1016,$$

$$M_{z+1} = 1343, M_v = 710, D = 1.33$$

Excess of diols = 1.98% w/w (HD 1.49% w/w, MP 0.49% w/w)

HO-value = 355 mg KOH equivalent to 1 g sample

*T<sub>g</sub>* = -72°C (onset temperature determined by MDSC)

FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and <sup>13</sup>C-DEPT data of the L-311 have been reported and extensively discussed in our previous work.<sup>3</sup>

## Preparation of Clearcoats

### Clearcoats Prepared from the Liquid Oligoester L-311 as Binder (CL-Clearcoats Series)

Solutions of the L-311 with the R-747 in various % weight ratios L-311/R-747 (85/15, 80/20, 75/25, and 70/30), FC-430 (10% w/w on total weight of the L-311 and the R-747, of a 2.5% xylene solution) were prepared at room temperature in 50-mL beaker. Just before application Nacure-155 was mixed thoroughly into the solution, in various (0.1, 1.0, and 2.0) % weight on total weight of the L-311 and R-747. Coatings with thickness of 0.75–0.80 mil were prepared by casting the above solution on steel and black aluminum panels using a No. 26 draw-down rod. Panels

were baked at 120°C for 30 min. All panels were kept at ambient temperature for one day before testing.

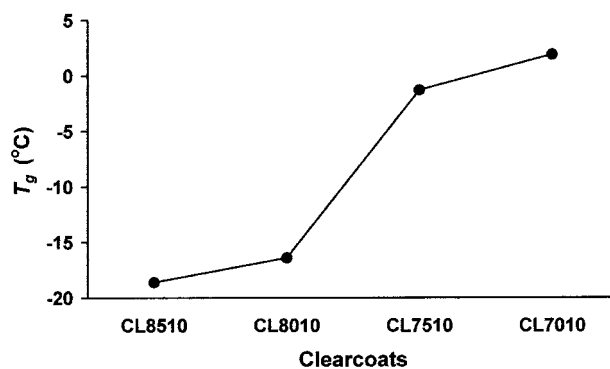
#### Reference Clearcoat Prepared from the Solid Oligoester RefOL as Binder (CRO)

Solution was prepared by warming the RefOL (6.50 g), R-747 (3.50 g), and FC-430 (10% w/w on total weight of the RefOL and the R-747, of a 2.5% xylene solution), and xylene (4.00 g), to about 50°C, in 50-mL beaker. Just before application Nacure-155 (1% w/w on total weight of the RefOL and the R-747) was mixed thoroughly into the solution. Coatings with thickness of 0.80 mil were prepared by casting the above solution on steel and black aluminum panels using a No. 26 draw-down rod. Panels were baked at 120°C for 30 min. All panels were kept at ambient temperature for one day before testing.

## RESULTS AND DISCUSSION

A series of high-solids clearcoats (CL-series) was prepared from the new-synthesized<sup>3</sup> liquid oligoester L-311 as binder and the HMMM, the R-747, varying the percentage of the acid catalyst (Nacure-155) and the quantity of the melamine resin, R-747 (crosslinker). The percent weight ratios L-311/R-747 that we experimented with were 85/15, 80/20, 75/25, and 70/30. Four numbers named each clearcoat of the CL-series. The first two numbers correspond to the weight percentage of the L-311 on the total weight of both the L-311 and R-747, and the subsequent two correspond to the catalyst's weight percentage multiplied by 10, used for their preparation (e.g., the clearcoat CL8510 represents a clearcoat derived upon crosslinking of the L-311 with the R-747 under a weight ratio of 85/15, respectively, and the percent weight of the Nacure-155 was equal to 1.0% w/w on the total weight L-311 and R-747). A reference clearcoat CRO was prepared from the reference oligoester RefOL<sup>3</sup> and the R-747 (see Experimental) under such conditions that were found<sup>4</sup> to contribute to the best performance of the specific clearcoat. The properties of the CL-clearcoats were compared to those of the reference clearcoat CRO.

We focused our tries on the investigation of the mar resistance of the new-formulated clearcoats, and we measured it applying both the crockmeter test and a novel method involving a modified



**Figure 1** The changes in the  $T_{g,s}$  (°C) of the clearcoats CL8510, CL8010, CL7510, and CL7010. The clearcoats have been formulated with the same amount of catalyst (1% w/w on total weight of L-311 and R-747) and different amounts of melamine resin (15, 20, 25, and 30% w/w on total weight of L-311 and R-747, respectively).

scanning probe microscope.<sup>12–15</sup> The results regarding the mar resistance are discussed separately from the other chemical, physical, and mechanical properties.

Table I presents the chemical, physical, and mechanical properties of the CL-clearcoats series as well as those of the reference clearcoat CRO.

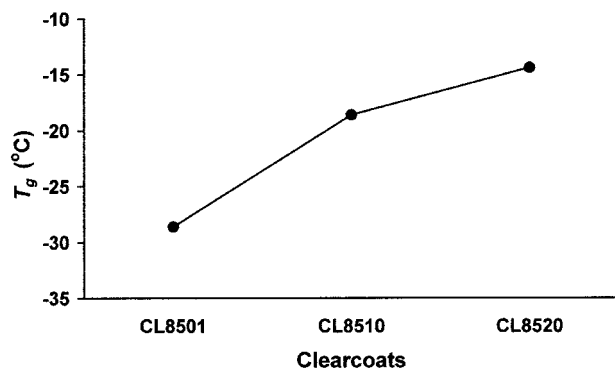
The CL-clearcoats series presented significant differences in their  $T_g$ s, when the amount of catalyst used for the crosslinking was the same. More particularly, an increase in the  $T_g$  was recorded as the amount of the melamine increased in the clearcoats CL8510, CL8010, CL7510, and CL7010 (Fig. 1):

$$T_{g \text{ CL8510}} < T_{g \text{ CL8010}} < T_{g \text{ CL7510}} < T_{g \text{ CL7010}} \quad (1)$$

This is due to the fact that higher melamine concentration in the coatings leads to a more extent self-polymerization<sup>16</sup> of itself, resulting therefore in a higher degree of crosslinking (significant increase of the molecular weight) and subsequently to higher  $T_g$ s<sup>17</sup>. The following equation describes exactly this relation:

$$T_g = T_g^{00} - K \times M_n^{-1}$$

where  $K$  is a constant and  $T_g^{00}$  corresponds to the glass transition temperature of a polymer with theoretically infinite  $M_n$ . According to this equation there is a linear dependence between the  $T_g$  and the  $M_n^{-1}$  of a polymer. The lower the  $M_n$  of a polymer, the lower is also its glass transition temperature (Fig. 1). So it seems that the



**Figure 2** The change in the  $T_g$ s (°C) of the clearcoats CL8501, CL8510, and CL8520. The clearcoats have been formulated with the same amount of melamine resin (15% w/w on total weight of L-311 and R-747) and different amounts of catalyst (0.1, 1, and 2% w/w on total weight of L-311 and R-747, respectively).

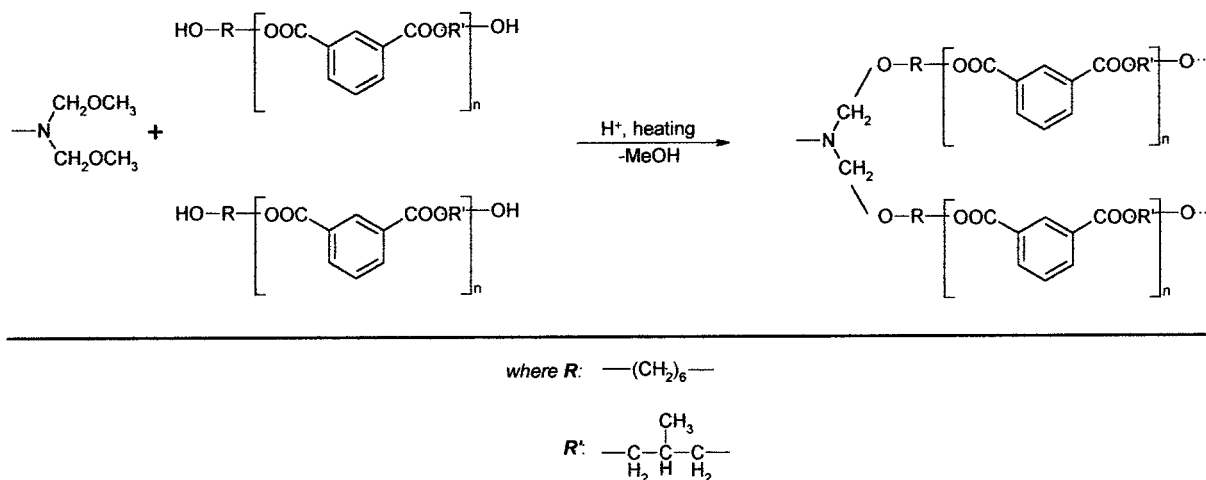
molecular weights of the aforementioned clearcoats upon the heat curing followed the same order as the one described in relation (1) and regarded their  $T_g$ s.

The differences in the  $T_g$ s of the clearcoats CL8501 ( $T_g = -28.6^\circ\text{C}$ ), CL8510 ( $T_g = -18.6^\circ\text{C}$ ), and CL8520 ( $T_g = -14.4^\circ\text{C}$ ), which are presented in Figure 2, we believe are of great interest and need to be discussed further. In these clearcoats the amount of melamine used for their preparation was the same but that of the catalyst differed (0.1, 1, and 2% w/w on total weight of L-311 and R-747, respectively). The different amounts of catalyst used for the crosslinking could only be related to the rate of the formation of the crosslinked

polymer network. We may therefore assume that the higher the amount of catalyst, the less “selective” became the crosslinking reaction, the faster the polymer network was formed, and the highest was the contribution of the melamine molecules in the molecular weight of the resulted crosslinked polymer network. Thus, higher amounts of catalyst led to relatively higher molecular weights of the crosslinked polymer network. That is the reason why the clearcoats CL8501 and CL8520 presented about  $15^\circ\text{C}$  of difference in their corresponding  $T_g$  values. These results were also verified by the clearcoats CL8001 and CL8010 that presented  $T_g$ s of  $-28.5$  and  $-16.4^\circ\text{C}$ , respectively.

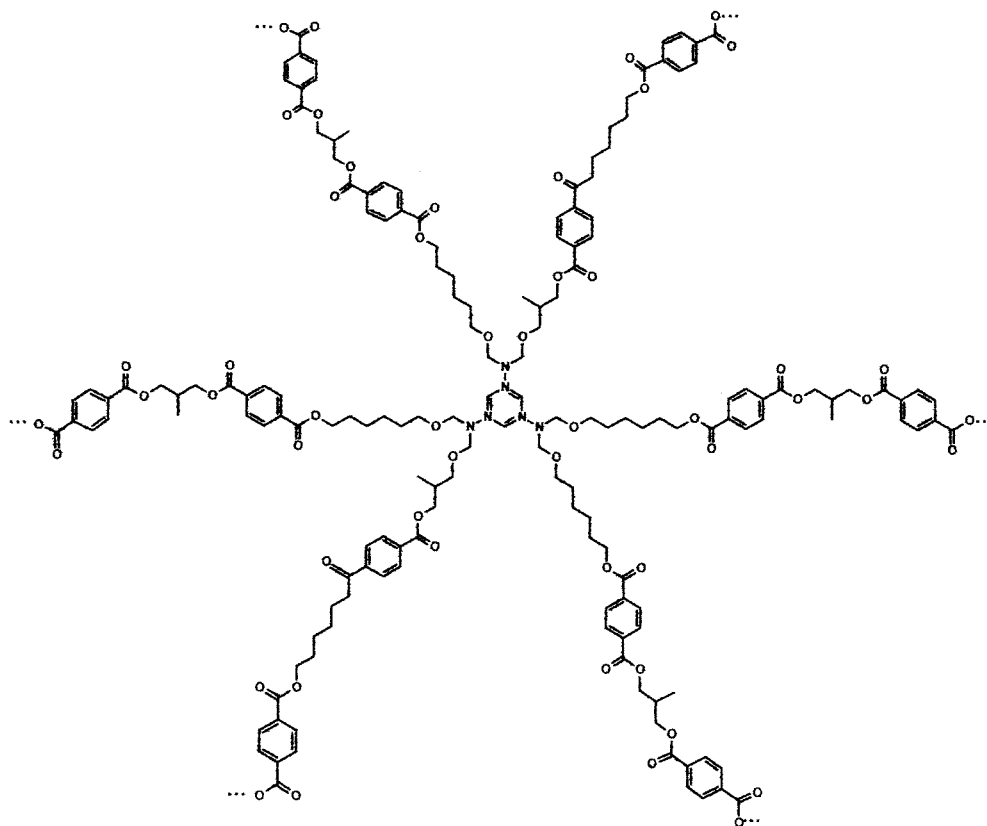
The heat curing process that proceeds via an acid-catalyzed etherification reaction among the hydroxyl groups of the binder (L-311) and the methoxymethylol groups of the crosslinker (melamine resin, R-747) (Schemes 3 and 4) could be monitored by MDSC analyses and/or FTIR spectroscopy. More specifically, the MDSC analyses could monitor the progress of the crosslinking by performing measurements at different reaction times of the  $\Delta H_{\text{exoth}}$  of the exothermic peak attributed to the crosslinking among the aforementioned groups. Previous studies<sup>5</sup> on similar formulations to the present CL-clearcoats revealed and documented the high reaction rate of the etherification reaction of the L-311 with the R-747.

The FTIR spectra of the oligoester L-311, the melamine resin R-747, and the ATR-FTIR spectra of the clearcoats CL8010 (uncured), CL8010 (cured at  $120^\circ\text{C}$  for 30 min), and CL7010 (cured at



**Scheme 3** The heat curing of the oligoester L-311 with the R-747 melamine resin via acid catalyzed etherification reaction in the presence of DNNSA used as catalyst.

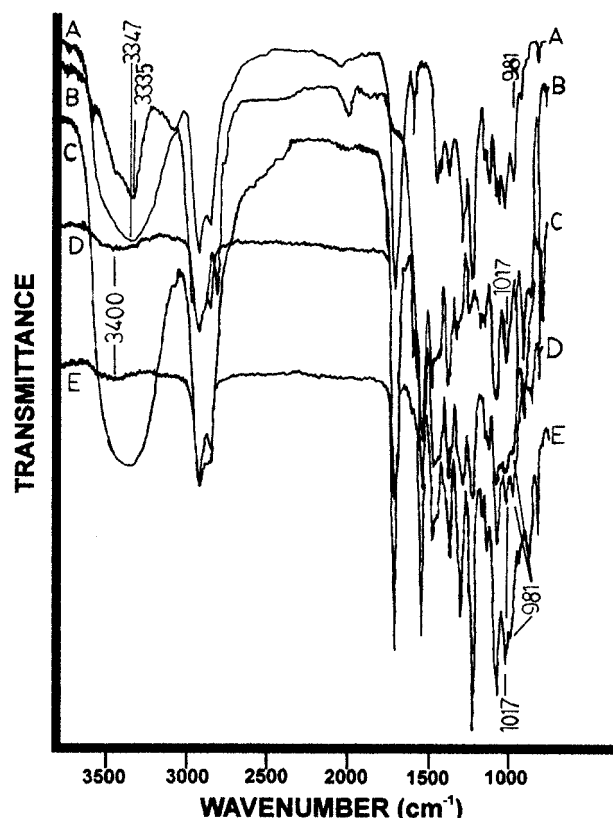




**Scheme 4** A random crosslinked polymer unit derived upon crosslinking of the L-311 with the melamine resin R-747.

120°C for 30 min) are presented in Figure 3. In the spectra of the L-311 and the R-747, the broad absorbancies at 3347 and 3335  $\text{cm}^{-1}$ , respectively, are attributed to the O—H stretching. The absorbance of the melamine resin R-747 at 3335  $\text{cm}^{-1}$  is not surprising [although it is an hexakis-(methoxymethylol)melamine resin] because it is very well known that no commercial product of the kind is practically fully methylolated.<sup>16</sup> Thus, there are some unmethylolated hydroxyl groups that absorb in that wavenumber. The broad band at 3379  $\text{cm}^{-1}$  presented in the FTIR spectrum of the CL8010 (uncured) and attributed to the O—H stretching of both the hydroxyl groups of the L-311 and the R-747, almost disappeared in the spectra of the clearcoats CL8010 and CL7010, indicating the consumption of the “free” hydroxyl groups of the melamine resin (due to its self-polymerization) and of course those of the oligoester through the crosslinking reaction presented in Scheme 3, where the melamine resin is considered to be fully methylolated for simplicity reasons. A slight residue at the aforementioned infrared region ( $\sim 3400 \text{ cm}^{-1}$ ), presented in the

ATR-FTIR spectra of the cured clearcoats CL8010 and CL7010, is probably an indication of the existence of some uncrosslinked (“free”) hydroxyl groups. This is due to the fact that for the preparation of the CL-clearcoats series not a high stoichiometric excess of melamine resin was used. We could also conclude that these “free” hydroxyl groups are those of the oligoester because the absorbance at 981  $\text{cm}^{-1}$  is due to the O—H deformation of the HO-terminated groups of the oligoester L-311 (see Fig. 3, spectra A, C, E, and D). The pattern of the change of the absorbancies at 981 (O—H deformation of the hydroxyl groups of the L-311) and 1017  $\text{cm}^{-1}$  (triazine ring of the melamine molecule) was being changing as the percentage of the melamine resin varied in different clearcoat formulations, as well (see Fig. 3, spectra D and E). Moreover, the absorbance at 981  $\text{cm}^{-1}$  of the CL7010 is less intense than the corresponding one of the CL8010, and also the ratio between the absorbancies at 1017 and 981  $\text{cm}^{-1}$  in the spectra of the aforementioned clearcoats is very different (see Fig. 3, spectra D and E). This is strong evidence that the higher the



**Figure 3** The FTIR spectra of the L-311 (A), the melamine resin R-747 (B), the uncured clearcoat CL8010 (C), and the ATR-FTIR spectra of the cured (at 120°C, for 30 min) clearcoats CL8010 (D) and CL7010 (E).

weight percentage of the melamine used in the crosslinking formulation, fewer were the remained uncrosslinked (“free”) hydroxyl groups of the oligoester L-311 (binder), the higher were the crosslink density, the molecular weight, and their corresponding  $T_g$ s (see Fig. 1).

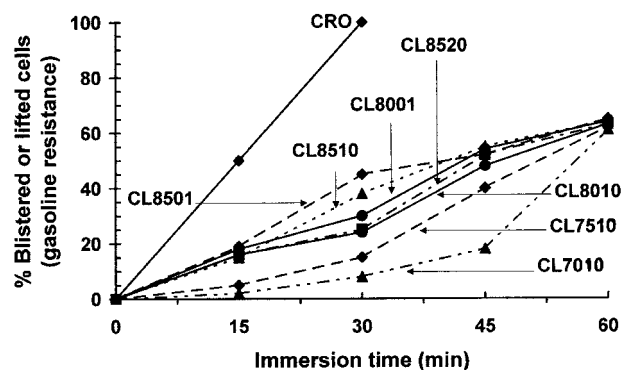
The clearcoats of the CL-series presented very good mechanical properties (e.g., impact resistance and flexibility) although the  $M_n$  (=538) and  $M_w$  (=719) of their binder (L-311) were almost 1/3 of the corresponding values of the reference oligoester RefOL<sup>3</sup> ( $M_n$  = 1385 and  $M_w$  = 2439). This could be probably attributed to the following two reasons. The first has to do with the assumption we made in a previous paper<sup>3</sup> and regarded the probability that the new-synthesized liquid oligoester L-311 present some higher degree of liquid crystallinity than the one presented in the RefOL. If this is the case, then we may hypothesize that the much higher density of the formed mesogenic units could be responsible for the good

mechanical properties of the CL-clearcoats series, as these crystalline units act as energy “absorbers.” The second explanation that could be given is that the percentage of the self-polymerization of the melamine resin was relatively diminished by the high hydroxyl value of the L-311 (355 mg KOH equivalent to 1 g sample) and thus a more elastic film was obtained in the case of the CL-clearcoats series. The elevated by  $\times 2.16$ , hydroxyl value of the L-311 upon comparing to that of the RefOL (164 mg KOH equivalent to 1 g of sample) can be attributed to the much lower  $M_n$  and the slightly higher % w/w of unreacted diols (excess of 1,6-hexanediol and 2-methyl-1,3-propanediol) of the L-311 in comparison to the corresponding values of the RefOL (see Experimental).

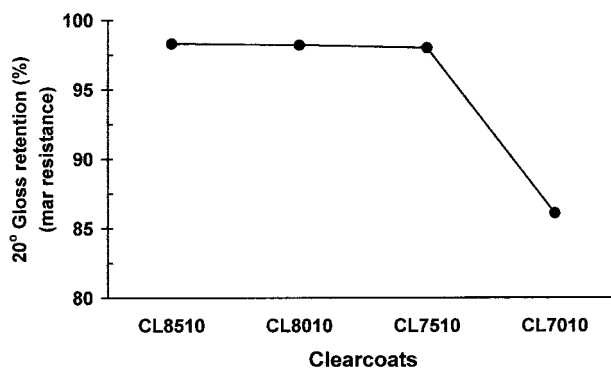
Certain clearcoats of the CL-series, the CL8501 and CL8510, presented very good adhesion equal to 5B and 3B respectively (see Table I) when little amount of melamine resin and catalyst were used in their formulations. The amount of catalyst can be certainly correlated to the crosslinking reaction rate, while the way the crosslinked polymer network is being formed and also its chemical composition (e.g., percentage of uncrosslinked potential “reactive” groups like the hydroxyl groups of the binder are), can be attributed to the quantity of the melamine resin (crosslinker). It is well known that highly oriented polymers present enhanced physical and mechanical properties (adhesion is one of them) than those with higher disorientation. This assumption could be also certified from the fact that when more melamine and catalyst were used for the crosslinking, the adhesion decreased dramatically from 5B to 3B and finally to zero. Probably in the case of the clearcoats CL8520, CL8001, CL8010, CL7510, and CL7010, remained relatively less uncrosslinked hydroxyl groups upon the heat curing and/or the crosslinked polymer network was formed faster, and therefore its orientation was limited. The ATR-FTIR spectra of certain clearcoats presented in Figure 3, verify the existence of some uncrosslinked (“free”) hydroxyl groups in the crosslinked polymer network which results upon the heat curing. It seems that in the clearcoats CL8501 and CL8510 the percentage of those uncrosslinked (“free”) hydroxyl groups were high enough to enhance the affinity of the crosslinked polymer network with the metal substrates (steel panels). Given the results from the adhesion tests and the  $T_g$  values of the aforementioned clearcoats, another hypothesis can be made regarding the formation and the orientation of the resulted

crosslinked polymer network. From the data collected, it is evident that the lower was the amount of the catalyst used for the crosslinking, the highest was the percentage of the uncrosslinked ("free") hydroxyl groups (network with lower molecular weight, lower  $T_g$ , and also O—H stretching absorbencies at the region of  $\sim 3400$  as well as O—H deformation at  $\sim 980$   $\text{cm}^{-1}$ ). Therefore, these "free" uncrosslinked hydroxyl groups could also contribute to a different and probably better orientation of the polymer network through intermolecular hydrogen bonding. As these hydroxyl groups were diminished when more catalyst was being added, the crosslinked polymer network was being formed faster resulting to a less oriented and stiffer structure. The macroscopic result is a decrease in the adhesion.

After 60 min of immersion in reference fuel "CE-10" (see Experimental) during the gasoline resistance test of the clearcoats of the CL-series (Fig. 4), they all presented almost the same percentage of blistered or lifted cells (61–65%). This result was not surprising because they were all prepared from the liquid oligoester L-311 and therefore they all had the same specie of chemical bonds and groups in their structure. Here, it has to be stressed the significant difference between the gasoline resistance result of the CRO, which after only 30 min of immersion in reference fuel "CE-10" gasoline presented 100% blistered or lifted cells. The corresponding values of the CL-clearcoats series after half an hour of immersion time varied from 8 to 45% (see Table I). In the case of the CL-clearcoats the different amount of melamine resin and catalyst used for their prep-



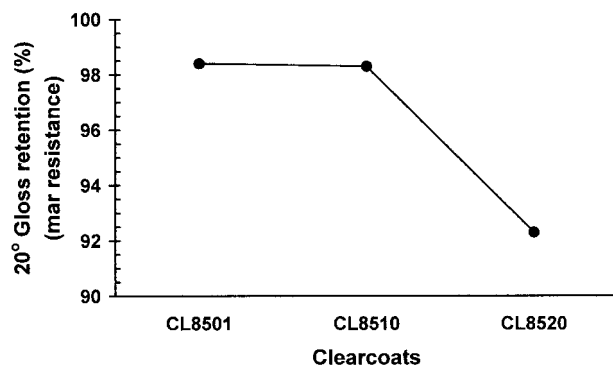
**Figure 4** The percent blistered or lifted cell of the reference clearcoat CRO and the clearcoats CL8501, CL8510, CL8520, CL8001, CL8010, CL7510, and CL7010 versus the immersion time in reference fuel "CE-10" (gasoline resistance test).



**Figure 5** The changes in percentage 20° gloss retention (mar resistance) of the clearcoats CL8510, CL8010, CL7510, and CL7010. The clearcoats have been formulated with the same amount of catalyst (1% w/w on total weight of L-311 and R-747) and different amounts of melamine resin (15, 20, 25, and 30% w/w on total weight of L-311 and R-747, respectively).

aration obviously resulted in different crosslinked densities, and did not seem to affect their gasoline resistance. The latter was probably affected only from the chemical structure of the binder and not from the different crosslink densities of the CL-clearcoats. It seemed that the crosslink density affected only the penetration rate of the gasoline molecules into the clearcoat's network. The higher the crosslink density (higher molecular weights and higher  $T_g$ s), the lower was the penetration rate of the gasoline molecules into the crosslinked polymer network and of course the better was the gasoline resistance of the corresponding clearcoats. The enhanced gasoline resistance of the CL-clearcoats is of great interest for the automotive industry and more specifically for clearcoats for plastic parts (e.g., bumpers).

The mar resistance of the clearcoats CL8510, CL8010, CL7510, and CL7010, recorded as the percentage 20° gloss retention (98.3, 98.2, 98.0, and 86.1%, respectively), are presented in Figure 5. In this case the quantity of the melamine resin R-747 was the only parameter of which mar resistance was affected. The mar resistance decreased as the amount of the melamine resin increased. High concentrations of melamine favor the self-polymerization of the melamine molecules. This results in a polymer network in which the percentage contribution of the self-polymerized melamine molecules is higher. A decrease in the elasticity of the network is inevitable and subsequently a decrease in the mar resistance was recorded (the mar resistance of a coating derived upon R-747's self-crosslinking, was very



**Figure 6** The changes in percentage 20° gloss retention (mar resistance) of the clearcoats CL8501, CL8510, and CL8520. The clearcoats have been formulated with the same amount of melamine resin (15% w/w on total weight of L-311 and R-747) and different amounts of catalyst (0.1, 1, and 2% w/w on total weight of L-311 and R-747, respectively).

poor, just 47.8%, 20° gloss retention). This is another proof of how important is in a crosslinked polymer network the introduction of polymer segments of a certain length and flexibility between the crosslink sites (triazine rings), for a good mar resistance. These results came to certify once more previous experimental results,<sup>4,5</sup> and the straight correlation between the chemical structure of the binder and its clearcoats measured mar resistance.

Figure 6 presents the change of the percentage 20° gloss retention (mar resistance) of the clearcoats CL8501, CL8510, and CL8520 that were 98.4, 98.3, and 92.3%, respectively. The quantity of the catalyst used in the crosslinking reaction was the only parameter of which the mar resistance was affected. Three different amounts of catalyst were used: 0.1, 1, and 2% w/w on the total weight L-311 and R-747. The mar resistance decreased as the amount of the catalyst increased. It seems that higher concentrations of catalyst significantly “accelerate” the formation of the crosslinked polymer network and lead to a less well-formed and/or less well-oriented polymer network. The resultant crosslinked polymer network is under relatively higher stress, which in its turn is responsible for a decrease in the elasticity of the network. Subsequently, the result is a decrease in mar resistance. The same changes of mar resistance (% 20° gloss retention) were also recorded for the clearcoats CL8001 (98.3%) and CL8010 (98.2%).

We also investigated the mar resistance and quantified the physical response (elastic, plastic,

or fracture) of the surfaces of certain CL-clearcoats and that of the CRO, by the use of a modified scanning probe microscope<sup>18–20</sup> (see Experimental). Scheme 5 is a schematic illustration of how to calculate the MIH, the MMR, and the different responses of a coating to marring stress. The cross-section area of the trough is the cross-section area of the ditch plus the cross-section area between the two shoulders, if any. In order to be more consistent with the optical evaluation and visual judgment of the coating surface, the cross-section area of the trough is used to calculate the MMR instead of the cross-section area of the ditch.

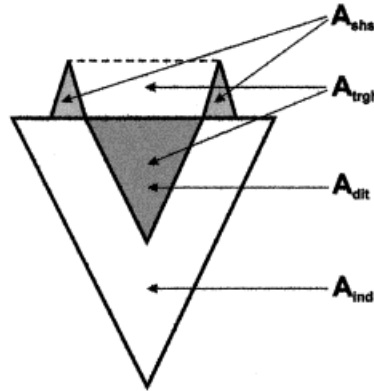
Although the physics of marring has been widely studied<sup>21</sup> there have been relatively few published theories<sup>22–24</sup> of how specific chemical structures affect mar resistance. We think that structural features associated with exceptional mar resistance are as follows:

1. Optimized crosslink density, high enough to promote a highly elastic response but not so high that the materials is readily fractured by marring stress, and
2. Presence of highly flexible  $—O(CH_2)_nO—$  units with  $n =$  at least 4 and preferably  $>4$  between the resin to the crosslinker.

The desirability of the first of these structural features is in harmony with the theories of Courter<sup>21</sup> (derived mainly from an analysis of scattered data published by various sources) and of Hill<sup>25</sup> (derived mainly from theoretical considerations) and that was the reason we investigated the effects of the amounts of the catalyst and melamine resin on the films properties. The second desirable structural feature is less well established. It is presaged by a statement by Betz and Bartelt.<sup>22</sup> Several patents claim good mar resistance of acrylic coatings based on 4-hydroxybutyl (meth)acrylates or on acrylics having side chains derived from caprolactone. It was clearly postulated in one of our publications<sup>4</sup> and that was the reason we preferred to work with the 1,6-hexanediol as one of the basic structural components of the binder (oligoester L-311). Study of additional materials with flexible side chains may yield exceptions to this generalization, but for now it can be used as a working hypothesis for further development of highly mar resistant coatings.

Thus, we characterized the mar resistance and identified the different responses (elastic re-





$A_{ind}$ : Cross-section area of the indentation

$A_{dit}$ : Cross-section area of the ditch

$A_{shs}$ : Cross-section area of the shoulders

$A_{trgh}$ : Cross-section area of the trough

% Elastic Response:  $(A_{ind} - A_{dit}) \times A_{ind}^{-1} \times 100$

% Plastic Deformation:  $A_{shs} \times A_{ind}^{-1} \times 100$

% Abrasion Wear:  $(A_{dit} - A_{shs}) \times A_{ind}^{-1} \times 100$

Micro Indentation Hardness (MIH):  $F_N \times A_{cnt}^{-1}$

Micro Mar Resistance (MMR):  $F_N \times A_{trgh}^{-1}$

**Scheme 5** Schematic illustration of how to measure (a) different responses to marring in a quantitative way, (b) the micro indentation hardness (MIH), and (c) the micromar resistance (MMR).

sponse, plastic deformation, and abrasion wear) of the reference clearcoat CRO and clearcoats CL8501, CL8010, and CL7010 to marring stress. It is very well known<sup>12–15,21–24</sup> that only the plastic deformation and abrasion wear are marring mechanisms, while the elastic response contributes to the “recovery” of a marred coating’s area. In other words, of the three responses, the elastic response is one of the parameters that can determine the ability of a certain film’s surface to resist marring stress (instant recovery). Table II presents the MIH (MPa), MMR (in GPa), and the percentage of elastic response, plastic deformation, and abrasion wear of the reference clearcoat CRO and of the three aforementioned clearcoats of the CL-series, when normal forces of 432, 526,

620, 713, and 806  $\mu\text{N}$  were applied for marring their surfaces.

Figure 7 presents conventional contact AFM images of the unmarred surface of the clearcoat CL8010 and a top-down view of its marred surface when 5 different normal forces of 432, 526, 620, 713, and 806  $\mu\text{N}$  were applied onto its surface from left to right. It is obvious that when a normal force of 432  $\mu\text{N}$  (first scratch from the left) applied on the surface of the CL8010, the latter behaved as an elastomer and its surface recovered in full. But, when it was marred with a normal force of 806  $\mu\text{N}$  (the first scratch from the right), the CL8010 did not recover in full due to some plastic deformation (0.20% of total response) and some abrasion wear (0.40% of total

**Table II** The MIH (in MPa), the MMR (in GPa), and the % of Elastic, Plastic, and Abrasive Responses of the Clearcoats CRO, CL8501, CL8010, and CL7010, when the Normal Forces Applied Were 432, 526, 620, 713, and 806  $\mu\text{N}$ 

Clearcoats	Normal Forces ( $\mu\text{N}$ )	MIH (MPa)	MMR (GPa)	Elastic Response (%)	Plastic Deformation (%)	Abrasive Wear (%)
CRO	432	5.68	$\infty$	100.00	0.00	0.00
	526	6.01	$\infty$	100.00	0.00	0.00
	620	6.37	$\infty$	100.00	0.00	0.00
	713	6.64	$\infty$	100.00	0.00	0.00
	806	6.83	$\infty$	100.00	0.00	0.00
CL8501	432	3.37	155.00	100.00	0.00	0.00
	526	3.44	100.00	100.00	0.00	0.00
	620	3.47	98.50	100.00	0.00	0.00
	713	a	a	a	a	a
	806	a	a	a	a	a
CL8010	432	74.30	$\infty$	100.00	0.00	0.00
	526	66.60	1490.00	99.90	0.00	0.10
	620	64.20	340.00	99.80	0.00	0.20
	713	66.60	149.00	99.50	0.00	0.50
	806	69.90	76.20	99.40	0.20	0.40
CL7010	432	393.00	14.50	84.40	15.60	0.00
	526	354.00	10.40	82.40	17.60	0.00
	620	292.00	8.60	81.50	18.50	0.00
	713	237.00	7.50	83.00	17.00	0.00
	806	196.00	6.50	83.90	16.10	0.00

<sup>a</sup> Out of test limit.

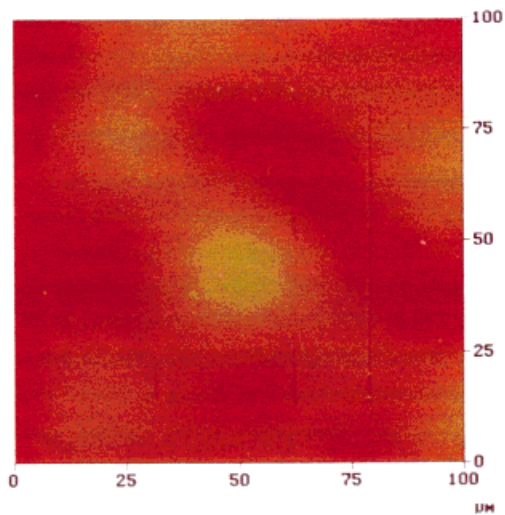
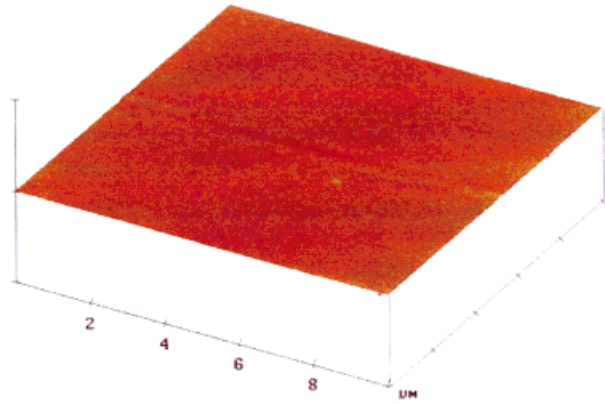
response) that are both marring mechanisms as previously mentioned. That is the reason why the scratch corresponding to the normal force of 806  $\mu\text{N}$  can be seen on the surface of the CL8010 while the one that corresponds to the normal force of 432  $\mu\text{N}$ , cannot be detected upon a conventional contact AFM imaging.

Figure 8 presents the change in MIH of the clearcoats CL8010 and CL7010. While the pattern of the changes of the MIH of the CRO and CL8501 was almost the same, those of the other two clearcoats of the CL-series were much different. It is of interest that the high MIH values of the CL8010 decreased for applied normal forces up to 620  $\mu\text{N}$  and increased for applied normal forces higher than 620  $\mu\text{N}$ . The fact that the MIH values of all the tested clearcoats were being changed by varying the applied normal forces is a strong indication of how much different can the properties of the coating's hard crust (top layer) be, from those obtained underneath the surface.<sup>26</sup> Moreover, the different ways that the tested clearcoats responded to marring stresses proba-

bly unveils differences in their crosslinked polymer networks, something that is in good agreement with the other experimental data mentioned here above.

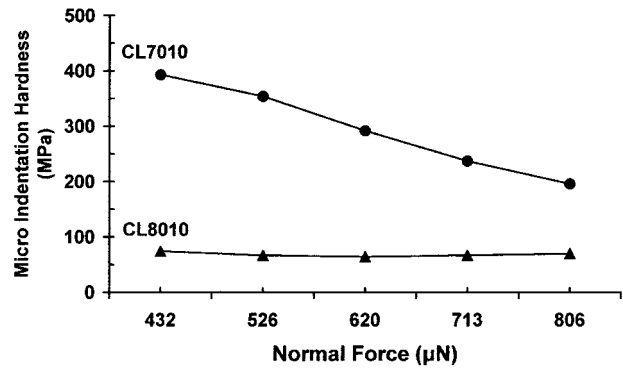
The changes in MMR of the clearcoats CL8501, CL8010 are presented in Figure 9. The MMR of the CRO was infinite and the corresponding values of the CL7010 were very small and so both could not be presented in Figure 9 along with the MMR values of the CL8501 and CL8010. Both the CL8501, CL8010 presented a decrease in their MMR as the applied normal force increased but, from the two, the clearcoat CL8010 showed the most dramatic decrease in its micro-mar resistance.

The changes in the percentage of the elastic responses of the clearcoats CRO, CL8501, CL8010, and CL7010 are presented in Figure 10. When the aforementioned clearcoats were marred under a normal force of 620  $\mu\text{N}$ , presented elastic responses of 100, 100, 99.8, and 81.5%, respectively. They all presented the same pattern of change, except the CL7010. The percent elastic



**Figure 7** Contact AFM images (scan size 10.00  $\mu\text{m}$ , set point 0 V, scan rate 2.001 Hz, number of samples 512) of the unmarred surface (top) of the clearcoat CL8010 ( $x = 2.00 \mu\text{m}/\text{div}$  and  $z = 400.00 \text{ nm}/\text{div}$ ) and its marred surface (bottom) when 5 normal forces of 432, 526, 620, 713, and 806  $\mu\text{N}$  were applied from left to right, respectively.

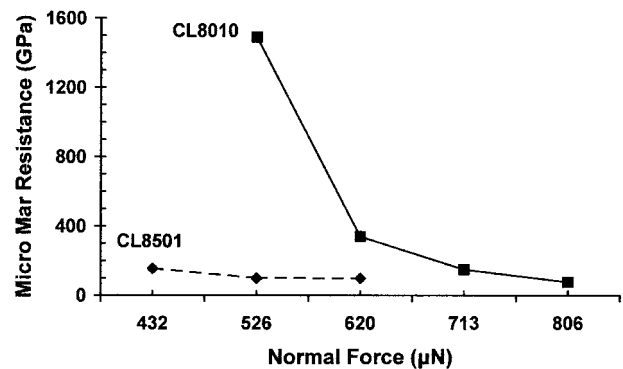
response of the latter decreased for applied normal forces up to 620  $\mu\text{N}$  and increased for normal forces higher than this value. These data come to verify our assumptions made in previous paragraphs and regarded probable differences in their crosslinked polymer networks. It seems that the tested clearcoat formulations had major differences in their crosslinking reaction rates and also in the orientation of their corresponding cross-linked polymer networks that afforded films with significantly different film properties and perfor-



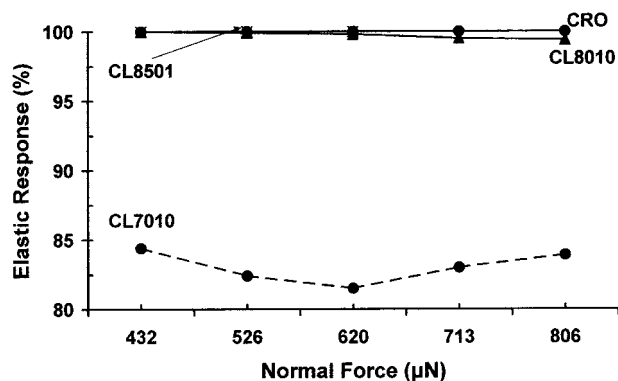
**Figure 8** The changes in the MIH (MPa) of the clearcoats CL8010 and CL7010 when normal forces of 432, 526, 620, 713, and 806  $\mu\text{N}$  were applied for marring their surfaces.

mance. And in addition it becomes evident that the crosslinking reaction parameters (e.g., amounts of catalyst and melamine resin, etc.) may determine or even predetermine certain film properties.

Upon comparing the mar resistance results obtained from the crockmeter test (Table I) to those of the SPM analysis (Table II) as well as the relative Figures 7–10, we can conclude that generally the results of the crockmeter test were qualitatively confirmed by the SPM measurements. In addition, it seems that the percentage of the elastic response of a coating as this was determined by the SPM method, could be somehow related to the percentage of 20° gloss retention (crockmeter test), in the following sense: high values of a film's percentage 20° gloss retention are certainly translated to high percentages of a



**Figure 9** The changes in the MMR (GPa) of the clearcoats CL8501 and CL8010 when normal forces of 432, 526, 620, 713, and 806  $\mu\text{N}$  were applied for marring their surfaces.



**Figure 10** The changes in percent elastic responses of the reference clearcoat CRO and the clearcoats CL8501, CL8010, and CL7010 when normal forces of 432, 526, 620, 713, and 806  $\mu\text{N}$  were applied for marring their surfaces.

film's elastic response at least for applied normal forces up to 806  $\mu\text{N}$ . The lower was the applied normal force in the SPM method for the characterization of the mar resistance, the closer was the result of the mar resistance, we obtained from the crockmeter test (see Table I and II, and compare the corresponding data of the clearcoat CL7010 when the applied normal force was 432  $\mu\text{N}$ ). But the potential ability of the SPM method to go deeper into the polymer mass and to characterize better the mar resistance is indisputable when even higher normal forces will be applied from the tip of the scanning probe microscope onto a coating's surface. And from all the experimental data regarding the mar resistance, and obtained from the investigation we carried out applying the method involving the use of a modified SPM, the following became evident: (a) the existence of a hard crust at the top layer of all the tested clearcoats, and (b) the significant different responses of a coating's main mass upon comparing to the corresponding responses of its crust, to marring stress. This is another—indirect of course—proof of how much important is the role of the whole three-dimensional crosslinked polymer network (chemical composition and structure, orientation, etc.) underneath coating's crust for a good mar resistance. The results obtained from the clearcoat CL8010 came to reinforce our expectations for the preparation of a film, which could combine relatively high pencil hardness, high MIH, and at the same time would respond as an elastomer (very good elastic recovery) to marring stress.

An effort should be also anticipated to the evaluation of the mar resistance of novel classes of

pigmented coatings formulated with the new-synthesized liquid oligoester L-311 and various fillers (e.g. talcs,<sup>27</sup> kaolins,<sup>28</sup> calcium metasilicates,<sup>28</sup> etc.).

## CONCLUSIONS

1. A series of high-solids (low-VOC content) clearcoats (CL-series) was prepared by crosslinking the new-synthesized liquid HO-terminated isophthalate-based liquid oligoester L-311 with an hexakis(methoxymethyl)melamine resin (HMMM). The chemical, physical, and mechanical properties of the new-formulated clearcoats were compared to those of a reference clearcoat CRO.
2. We studied the effect that the amounts of catalyst and melamine resin used in their formulations had on the chemical, physical, and mechanical properties of the clearcoats. More specifically, it seems that the amount of the catalyst affects seriously the mar resistance while the quantity of the melamine resin has a serious influence on both the mar resistance and the impact resistance.
3. An attempt was made to correlate the crosslinking reactions, kinetics, and density as well as the chemical structure, composition, formation, and orientation of the crosslinked polymer network to films properties. Strong indications were obtained regarding the important role of the three-dimensional structure of the clearcoat's main mass on its measured chemical, physical, and mechanical properties.
4. It became evident that varying the amounts of catalyst and melamine resin used for the preparation of a coating, it is possible to control the molecular weight (different  $T_g$ s) of the resultant crosslinked polymer network.
5. Upon comparing the properties of the reference clearcoat CRO to those of the CL-clearcoats, it was found that the latter presented enhanced processability, were more environmentally friendly as no solvent was used for their preparation and had also higher NVW values ( $\sim 10\%$ ) (lower VOC content) than the reference clearcoat CRO. Their mechanical properties were en-



hanced or at least comparable to those of the CRO.

6. We have used a modified scanning probe microscope equipped with a custom-made probe to measure mar resistance and identify different responses of polymeric surfaces (coatings) to marring stress. The knowledge gained will be very helpful in understanding the marring mechanism and developing high mar resistant surface coatings. The SPM has been proven a very useful instrument in studying mechanical properties of coatings on the micron and submicron scale.
7. The mar resistance of the clearcoats was investigated by applying both the crockmeter test and a method involving a modified scanning probe microscope. The results of the crockmeter test were generally in qualitative agreement with those of the SPM method. Moreover, the results of the mar resistance that we obtained for the clearcoats CL8501 and CL8010 came to justify our expectations for the possibility of preparing a clearcoat that would present relatively high pencil hardness, high MIH, and very good elastic recovery (the response of their surfaces to physical stress was >99.40% elastic at all normal forces applied) along with all the aforementioned chemical, physical, and mechanical properties mentioned here above (conclusion 5) for the new-formulated high-solids CL-clearcoats. In other words, the clearcoats CL-8501 and CL-8010 are suitable prototypes for further development because they combine a good balance of film physical properties with extraordinary mar resistance.

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