

High Performance Radiation-Curable Ink and Coating Resins for Thermoforming and In-Mold Decoration

Chris W. Miller
Surface Specialties Inc., Smyrna, GA USA

I. Introduction

I.A. Thermoforming

Thermoforming comprises a process by which a solid substrate is formed into a desired shape through sequential application of heat and pressure. Thermoforming is used in the plastics industry to manufacture a wide variety of structural and functional plastic parts including automotive body parts, children's toys, athletic equipment, sporting goods, and packaging materials. Additionally, thermoforming is used to create three-dimensional (3-D) objects that are useful, for example, as decorative art and signage. For graphics applications, the basic thermoforming process may be described as follows:

Thermoforming Process Steps

- a) *A graphic design is applied to a sheet of polymeric substrate by multi-color screen-printing.*
- b) *The printed sheets are stacked, packaged, and shipped to a forming location.*
- c) *Hydrophilic substrates such as polycarbonate then must be preheated to $>100^{\circ}\text{C}$ for ~ 1 hour to remove water from the polymer prior to forming.*
- d) *The dried sheet is placed in a thermoforming unit and heated by radiant (infrared) heating to a temperature at which the polymer is pliable, but remains sufficiently stiff to resist gravitational force. The temperatures and heating times vary widely, depending upon the type of polymer and the thickness of the sheet. Thermoforming sheet temperatures for commonly used substrates are shown in Table 1.*
- e) *The mold form is rapidly pressed into the bottom of the hot sheet. The sheet is then conformed to the mold shape by application of low-level vacuum to the mold chamber, which shrink-wraps the substrate onto the mold form. Clear substrates (e.g. PC, PET, etc.) are formed with the printed side of the sheet touching the mold. Opaque substrates (e.g. polystyrene) are typically formed with the non-printed side touching the mold.*
- f) *Cool air is injected into the mold chamber to release the vacuum and harden the sheet.*
- g) *The formed sheet is then trimmed prior to final assembly.*

Table 1. Thermoforming sheet temperatures of commonly used polymers.¹

Material	Common Abbreviation	Thermoforming Sheet Temperature ($^{\circ}\text{C}$)
Poly(vinyl chloride)	PVC	121 – 177
Acrylonitrile-butadiene-styrene copolymer	ABS	121 – 188
Poly(ethylene terephthalate); glycol modified	PET; PET-g	129 – 163
Poly(methyl methacrylate)	PMMA	135 – 177
Poly(styrene)	PS	143 – 177
Poly(propylene)	PP	154 – 199
Bis-phenol-A polycarbonate	PC	182 – 216

The printing and thermoforming processes oblige control of several aspects of resins, inks, and coatings used for thermoforming applications. A number of these are cited below, and must be kept in proper balance to provide the necessary performance in the final product.

Ink Performance Aspects for Thermoforming

- a) *Raw materials used in the ink must be relatively easy for the ink-formulator to handle with regards to viscosity, shelf life, compatibility, etc.*
- b) *Fully formulated inks must exhibit the rheology, pigment dispersion, curing characteristics, shelf-stability, and various other ink properties that allow easy printing of multiple colors and multiple layers.*
- c) *The cured ink must have excellent adhesion to the plastic substrate as well as excellent intercoat adhesion.*
- d) *The cured ink must exhibit sufficient scratch and mar resistance to allow handling and stacking, while also exhibiting little or no surface tackiness.*
- e) *The prints must remain sufficiently tack-free to resist blocking (sticking to adjacent sheets) when stacked hot (up to 60 °C) immediately after printing and after thermoforming.*
- f) *The cured ink must have good temperature stability to avoid decomposition, adhesion loss, or discoloration during the drying or heating stages.*
- g) *The cured ink must have excellent flexibility and retain excellent adhesion to the plastic substrate during extension. It must not crack or delaminate upon thermoforming of shallow (1:1) or deep (8:1) draws.*
- h) *The thermoformed ink must maintain scratch and abrasion resistance, gloss, and other desirable ink properties. Scratch and abrasion resistance, chemical resistance, and long-term light stability are more crucial in cases where the ink is on the exterior surface of the formed object. Performance requirements are less rigorous when the ink is on the interior of translucent substrates where the ink is protected by the polymer substrate.*

Five critical performance factors for thermoforming resins and inks that must be kept in balance include:

Critical Factors for Thermoforming Resins

- Oligomer viscosity*
- Adhesion to substrate*
- Post-cure thermal stability*
- Post-cure flexibility*
- Post-cure surface tack*

I.B. In-Mold Decoration

In-Mold Decoration is a process in which a decorative layer is fabricated into a laminated structure through injection molding of a thermoplastic layer onto the face-side or the back-side of a printed substrate. IMD can be utilized on flat substrates, although more typically a thermoformed printed sheet is used as the substrate. The resulting laminate structures offer several potential advantages including: (1) protection of the ink surface from degradation due to physical, chemical, or photolytic exposure, (2) fabrication of thick 3-D parts using thermoplastics that are difficult to thermoform directly in thick sections (ex. PC), and (3) utilization of multiple thermoplastics to create laminates which could be difficult to make directly by thermoforming of pre-formed or co-extruded laminates. Examples of laminate products prepared via thermoforming / IMD processing include: cellular phone covers, automotive interior trim parts and exterior fascia, electronic keypad covers, and athletic headgear such as bicycle helmets

and hockey masks. The IMD process is described using polycarbonate as an example substrate:

In-Mold Decoration Process Steps

- a) *Polycarbonate substrate is printed and thermoformed via the process described previously.*
- b) *The formed part is placed into a mold on an injection-molding machine.*
- c) *The mold is clamped shut and molten polycarbonate (275-300°C) is injected under pressure onto the cured ink surface to fill the mold cavity over a period of a few seconds. Many solvent-borne and water-borne inks are washed away from the substrate during this stage as the molten thermoplastic sweeps rapidly across the ink surface. The washout tendency can be somewhat mitigated by utilization of different types of gates and/or multiple gates in the mold which can more evenly distribute the flow across the part.*
- d) *After a few seconds, the part solidifies, is “popped out” of the mold, and trimmed to remove the sprue etc.*
- e) *The final part is a laminate wherein the ink is sandwiched between two layers of polycarbonate.*

The printing, thermoforming, and IMD processes oblige control of several performance aspects for resins, inks, and coatings used for IMD applications. A number of these are cited below, and must be kept in the proper balance to meet the requirements of the final product.

Performance Requirements in Printing for In-Mold Decoration

- a) *The raw materials used in the ink must be relatively easy for the formulator to handle, specifically with regards to viscosity, shelf-life, compatibility, etc.*
- b) *Fully formulated inks must exhibit the rheology, pigment dispersion, curing characteristics, shelf-stability, and various other ink properties that allow easy printing of multiple colors and multiple layers.*
- c) *The cured ink must have excellent adhesion to the initial thermoplastic substrate, excellent inter-coat adhesion, and must exhibit adequate scratch and mar resistance for handling and stacking of printed sheets.*
- d) *The cured ink must have little or no surface tackiness up to ~ 60°C to avoid blocking when they are stacked hot immediately after printing, and also to avoid sticking to the mold during thermoforming.*
- e) *The cured ink must have excellent thermal stability to avoid decomposition or discoloration during the drying or heating stages and to avoid being washed away from the sheet surface during injection of the molten thermoplastic.*
- f) *The cured ink must have good flexibility and retain excellent adhesion to the plastic substrate during thermoforming and during the injection molding stage.*
- g) *The ink must not crack, split, peel, or delaminate upon thermoforming during shallow (1:1) or medium (4:1) draws.*
- h) *The ink must have very good adhesion to the injected thermoplastic layer. The initial peel strength for delamination of the printed sheet from the injected polycarbonate should be at least 8lb/linear inch.*
- i) *The laminate should maintain adhesion during thermal cycling designed to mimic the end-use environment so that the part does not delaminate due to thermal shock upon rapid cooling or heating under the use conditions of the final product.*
- j) *There are many variables in the printing, thermoforming, and injection molding processes, which may vary significantly from one location to another. If possible, resin performance should be sufficiently robust to provide adequate performance under all conditions; however,*

this is difficult. Variables include: type of thermoplastic substrate; additives such as mold release, silicone copolymers, and plasticizers in the thermoplastic; ink additives and formulation differences; printing and curing conditions; thermoforming temperature and depth of draw; mold temperature, injection time and temperature, cycle time, mold depth, gate type, etc. on the injection machine; and number and types of layers of ink and/or coatings.

Seven critical performance factors for IMD resins and inks that must be kept in balance include:

*Critical Factors for IMD
Oligomer viscosity
Initial adhesion to substrate
Post-cure thermal stability
Post-cure flexibility
Post-cure surface tack
Intercoat adhesion
Adhesion to injected thermoplastic*

II. Experimental

II.A. Materials

Urethane acrylate oligomers were synthesized via standard processes involving reaction of hydroxy-acrylate, isocyanate, and oligomeric polyols at elevated temperatures in the presence of catalyst and stabilizers. Viscosities were measured using Brookfield viscometers at various temperatures. Oligomers used in the example formulations in this paper are listed in Table 2. Elongation at break values for several urethane acrylate oligomers evaluated during this study are given in Figure 1. Commercial materials were used as received. Additional components used in the ink and coating formulations are listed below.

Polymerizable monomers

Isobornyl acrylate (IBOA) (SSI); N-vinylpyrrolidinone (NVP) (ISP); experimental monomers XM-1, XM-2, XM-3 (SSI).

Additives

Ebecryl[®] 7100: amine-functional acrylate monomer to promote adhesion (SSI); TEGO[®] Foamex N (Degussa) used as defoamer; TEGO[®] Rad 2250 (Degussa) flow aid and anti-blocking agent; TS-100 precipitated silica (Degussa); Zonyl[®] FSG (Dupont); Fluorad[™] FC-4430 (3M[™] Corporation); various standard process pigments for white, black, cyan, magenta, yellow.

Photoinitiators

Darocur[®] 1173 photoinitiator (Ciba); ViaCure DX and ViaCure LX photoinitiator blends (SSI).

Table 2. Selected examples of urethane acrylate oligomers examined in this study.

Resin	Theoretical Oligomer MW (g/mol)	Polyol Backbone Type and Diluent	Viscosity (cP)
UA-1	2,000	Aliphatic polyester	5,800 (60°C)
UA-2	4,100	Mixed aliphatic/aromatic polyester	42,000 (90°C)
UA-3	7,500	Mixed aliphatic/aromatic polyester	42,000 (90°C)
UA-4	6,200	Mixed aliphatic/aromatic polyester, polyether	31,000 (90°C)
UA-5	4,500	Mixed aliphatic/aromatic polyester, polycarbonate	35,000 (90°C)
UA-6	4,500	Polyether, polycarbonate	23,000 (90°C)
UA-7	4,600	Mixed aliphatic/aromatic polyester, polyether	45,000 (90°C)
UA-8	4,300	Mixed aliphatic/aromatic polyester, polyether, polyurethane	46,000 (90°C)
UA-9	6,900	Mixed aliphatic/aromatic polyester, polycarbonate	66,000 (90°C)
UA-10	8,800	Mixed aliphatic/aromatic polyester, alkoxyated Bisphenol A	47,000 (90°C)
UA-11	7,600	Mixed aliphatic/aromatic polyester, polyether	26,000 (90°C)
UA-12	7,800	Mixed aliphatic/aromatic polyester, polyester	29,000 (90°C)
UA-13	10,600	Mixed aliphatic/aromatic polyester, polyether, 10% IBOA	40,000 (90°C)
UA-14	10,600	Mixed aliphatic/aromatic polyester, polyether, 30% IBOA	7,100 (90°C)
UA-15	7,500	Mixed aliphatic/aromatic polyester, 20% IBOA	--
UA-16	8,700	Mixed aliphatic/aromatic polyester, polyether, 30% IBOA	--
UA-17	9,300	Mixed aliphatic/aromatic polyester, polyether, 28% IBOA	21,000 (60 °C)
UA-18	10,000	Mixed aliphatic/aromatic polyester, polyether, 30% IBOA	19,000 (60 °C)
UA-19	9,100	Mixed aliphatic/aromatic polyester, polyether, 49% IBOA	3,000 (60 °C)
UA-20	9,100	Mixed aliphatic/aromatic polyester, polyether, 49% IBOA	--
UA-21	8,100	Mixed aliphatic/aromatic polyester, polyether, 35% IBOA, 19% XM-2	--
UA-22	7,800	Mixed aliphatic/aromatic polyester, polyether, 35% IBOA, 12% XM-2	--
UA-23	9,400	Mixed aliphatic/aromatic polyester, polyether, 27% IBOA	--
UA-24	9,400	Mixed aliphatic/aromatic polyester, polyether, 49% IBOA	--
UA-25	9,100	Mixed aliphatic/aromatic polyester, polyether, 28% IBOA	--
UA-26	9,200	Mixed aliphatic/aromatic polyester, polyether, 33% IBOA	29,000 (60°C)
UA-27	8,200	Mixed aliphatic/aromatic polyester, polyether, 35% IBOA, 19% XM-2	3100 (60°C)
UA-28	7,100	Polycarbonate	6000 (60°C)
UA-29	3,400	Polyester	--
UA-30	4,900	Aliphatic polyester, 20% IBOA	6500 (65.5 °C)
UA-31	9,100	Mixed aliphatic/aromatic polyester, polyether, 28% IBOA	23,000 (60 °C)
UA-32	4,900	Polyester	--
UA-33	7,800	Mixed aliphatic/aromatic polyester, polyether, 23% IBOA	--
UA-34	9,900	Mixed aliphatic/aromatic polyester, polyether, 30% IBOA	--
UA-35	8,100	Mixed aliphatic/aromatic polyester, polyether, 25% IBOA	--
UA-36	7,100	Mixed aliphatic/aromatic polyester, 20% IBOA	--

II.B. Thermoforming and IMD Formulations

Inks and clear coating compositions were prepared by standard methods. Samples were printed by hand using a Durometer A70 squeegee and a 355/34pw or 390/31pw mesh screen

with 15-19 N/cm tension. Prints were cured by 2-3 passes through a Fusion UV-Systems curing unit equipped with two 600 watt H-bulbs and belt speed of 80-120 ft/min. Substrates for thermoforming PS, Lexan® SP 8010 PC, 4 mm and 500 µm PET-g, PET, and rigid PVC without any surface treatment. IMD samples were printed exclusively on Lexan® SP 8010 PC. Samples for crosshatch adhesion testing and blocking testing were about 1.5 x 1.5 inch square prints on 2 x 2 inch square substrate pieces. Exemplary ink formulations selected from among the 720 formulations that were tested are given in Tables 3.1 and 3.2.

Surface tack and blocking characteristics of selected inks were tested by stacking about ten 1.5x1.5 inch samples of the printed substrates front to back. A cover sheet of polycarbonate and a 1 kg weight was placed on top of the stack with the force applied to the face of the printed samples. The stack was then placed at 25°C at 48% relative humidity for 24 hours and then evaluated for tack and blocking. This test was then repeated at 35, 45, 55, and 65 °C. None of the samples tested showed any increase in surface tack or tendency to stick to or transfer to the bottom of the substrate above it.

Table 3.1. Ink and clear-coat formulations for thermoforming and IMD.

Component	Formulation (weight %)									
	1	2	3	4	5	6	7	8	9	10
UA-5			24.18			40.76			40.76	
UA-15	31.54	6.08		40	23.87					
UA-16					19.89					
UA-17		43.24								
UA-18	15.14									
UA-32			11.38							
UA-33								47.69		
UA-34										
UA-35							45.9			44.06
XM-1			32.72			19.88			24.85	
XM-2	8.88	16.22	22.76	11.6	13.26	24.85	13.87	9.08	24.85	13.32
IBOA	20.83	18.72		29.2	21.88		15.23	18.13		19.02
NVP	3.78				3.98	4.97	4.17	4.08		4
Ebecryl 7100	7.57	5.41	4.27	2.8	6.63	4.97	7.29	8.16	4.97	7
TEGO Foamex N	0.5	0.54	0.43	0.4	0.53	0.6	0.52	0.51	0.6	0.4
Zonyl FSG	0.53									
Fluorad FC-4430								0.1		0.2
TS-100					1.33		0.52			
Silica										
Magenta pigment	1.89	3.04		4	1.99		4.17	4.08		4
ViaCure DX/LX blend	9.34	6.75		10	6.64		8.33	8.17		8
Darocur 1173			4.26	2		3.97			3.97	

Table 3.2. Ink and clear-coat formulations for thermoforming and IMD, continued.

Component	Formulation (weight %)										
	11	12	13	14	15	16	17	18	19	20	21
UA-3				42.91							
UA-5		30.92									
UA-15			31.6								
UA-18			15.17								
UA-30											63.91
UA-31						43.03	43.73	43.73	43.03	26.81	
UA-32		9.45									
UA-34					20.2						
UA-36	40.8				24.1						
XM-1		5.3									
XM-2	11.8	17.67	8.92	22.44	25.3						
IBOA	26.8	24.73	20.81	22.44	10.6	34.97	34.77	34.27	35.47	21.19	5.46
NVP		3.53	3.79	3.59	4	2	2	2	2	2	13
Ebecryl 7100	6	4.42	7.58	4.49	6.6	7	7	7	7	7	5
TEGO Foamex N	0.4	0.44	0.51	0.54	0.5	0.7	0.7	0.7	0.7	0.7	0.18
TEGO RAD 2250						0.3	0.3	0.3	0.3	0.3	
Fluorad FC-4430			0.36								
Silica						1.5	1.5	1	1.5		
Magenta pigment	4		1.9		2.1	4.5					4.45
Cyan pigment							4				
Black pigment									4		
Yellow pigment								5			
White pigment										36	
ViaCure DX						6	6	6	6		
ViaCure LX										6	
ViaCure DX/LX blend	10.2		9.36		6.6						8
Darocur 1173		3.54		3.59							

II.C. Physical Characterization

Tensile Properties

Tensile properties of selected neat oligomer samples cured with photoinitiator were measured at room temperature using an Instron® Series IX automated materials testing system with sample rate of 10 points/s, 4 in gap width, and crosshead speed of 20 in/min to test ½ x 6.5 in free films. The samples were prepared by curing about 10 mil films between Mylar® sheets using 2 passes on a Fusion UV-Systems curing unit equipped with two 600 watt H-bulbs with belt speed of 80-120 ft/min. As can be seen in Figure 1, many oligomers showed high elongation at break.

Modulus values ranged from 500 – 27,000 psi, though most oligomers showed values in the range 600 – 9,000 psi. Glass transition temperatures were measured by Dynamic Mechanical Analysis for a few representative oligomers, and ranged from -41 to -8 °C.

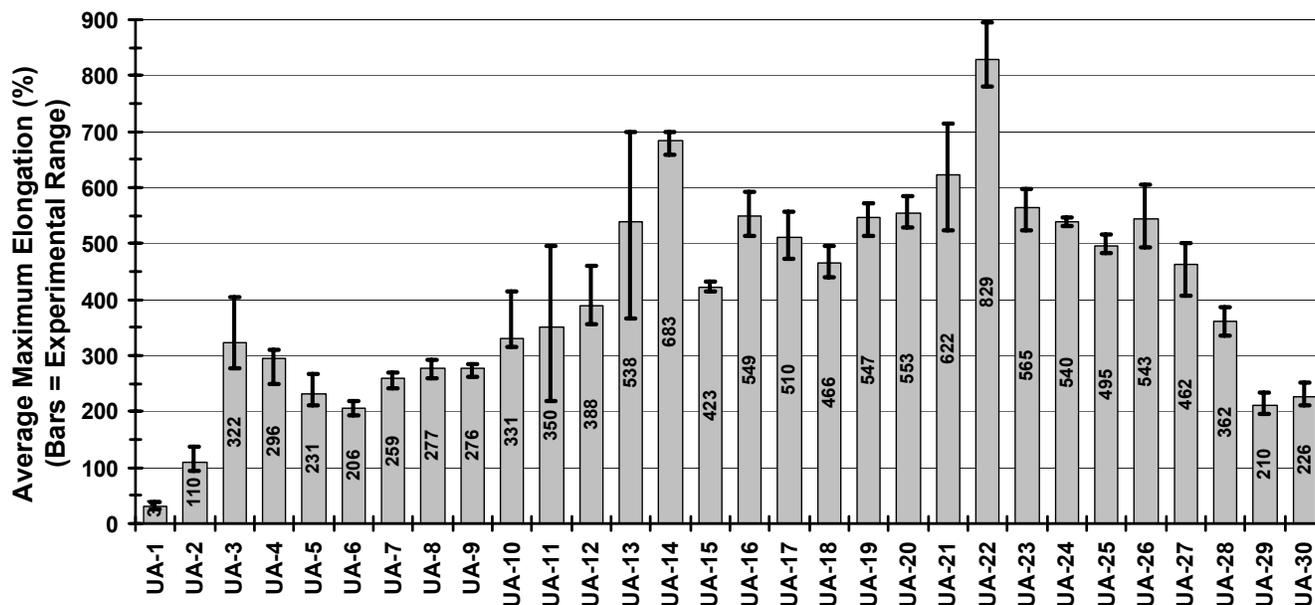


Figure 1. Elongation at break values of selected urethane acrylates evaluated during this study. Measurements made at 25°C on free films.

Solubility Parameter Calculations

Semi-empirical solubility parameter calculations were performed using three methods for selected examples of the oligomers to correlate structural characteristics with adhesion results and surface energy measurements. The first method was based upon group contribution factors taken from Van-Krevelen's semi-empirical analysis² to calculate the polar, dispersive, hydrogen-bonding, and total solubility parameters. The remaining two methods were used from a solubility parameter spreadsheet obtained from SolventCentral, also involving semi-empirical group contributions. Calculated solubility parameter values are given in Table 4.

As can be observed by examining the data in Table 4, the largest contribution to the overall solubility parameter for all of the urethane acrylate resins was the dispersive factor. Due to the oligomers' relatively high molecular weight and the high molecular weight of the starting polyols, aliphatic and aromatic hydrocarbon was by far the most numerous type of group, hence the high contribution from dispersive forces. Thus, even with very significant chemical changes in the oligomer backbones, e.g. changing from polyester to polycarbonate to polyurethane, etc., the total solubility parameters did not vary widely. Dilution with IBOA also did not significantly affect the theoretical solubility parameters, as the total solubility parameter of IBOA was also dominated primarily by dispersive force contributions. These data suggest that to significantly alter the solubility parameter characteristics of formulations based upon these oligomers, it would be necessary to incorporate a high percentage of polar and/or hydrogen-bonding functionality in the oligomers and/or monomer diluents.

Table 4. Solubility parameter calculations for high elongation urethane acrylate oligomers. Calculations were performed using three separate methods. Data given below represent the averages of values from the three methods.

Resin (oligomer portion only)	Solubility Parameter Calculations (cal ^{1/2} cm ^{-3/2}) Average of values from three methods.			
	Dispersive δ_d	Polar δ_p	Hydrogen Bonding δ_H	Total δ_T
UA-3	8.42	1.57	3.55	9.34
UA-4	8.51	1.49	3.40	9.36
UA-5	7.69	0.84	3.00	8.35
UA-6	7.75	0.91	2.90	8.39
UA-7	8.21	1.31	3.33	9.02
UA-8	8.12	1.48	3.50	9.05
UA-9	7.95	1.08	3.23	8.71
UA-10	8.23	1.56	3.55	9.18
UA-11	8.27	1.73	3.06	9.07
UA-12	6.78	1.20	3.12	7.61
UA-13	8.39	1.47	3.38	9.23
UA-16	9.30	1.66	3.49	10.15
UA-28	8.25	1.90	3.10	9.10
UA-30	7.85	1.54	3.60	8.85

Contact Angle Measurements

Contact angle measurements were performed on two samples of cured UV inks and injection-molded polycarbonate to examine the differences in the surface energy of representative cured urethane-acrylate based ink formulations and the commercial grade polycarbonate resins used in the IMD testing. Measurements were made using a Dataphysics Contact Angle System OCA 20. Ink CA-1 was formulated using UA-30 in combination with a bisphenol-A epoxy acrylate, while CA-2 was formulated using UA-30 in combination with a significant NVP content. White and magenta inks based on CA-1 and CA-2 were tested. The polycarbonate sheet was Lexan[®] 8010, and the injected polycarbonate was standard IMD PC either Lexan[®] SP1010 or Lexan[®] SP1010R.

Contact angle (CA) measurements involved placing a 1-2 μ L drop (sessile drop) of the probe fluid on the substrate at room temperature (23°C). De-ionized filtered water (Milli-Q purification system), 1-bromonaphthalene (Merck), and dimethylsulfoxide (DMSO) were used as probe fluids. The drop image was taken by a camera and then transferred into a software program where it was fitted with an ellipsoid contour from which the contact angles were calculated. Surface free energies (SFE) were calculated using the Owens-Wendt & Koelble method using surface tension values [total (T), dispersive (D) and polar (P)] given below for the probe liquids. The dispersive component represented the contribution of induced dipole-dipole interactions, while the polar component represented contributions from hydrogen bonding and permanent dipole-dipole interactions. Prior to measurement, the polycarbonate samples were washed with isopropanol to remove residue from the protective film with which they were shipped. This washing resulted in a small decrease in the water CA from 82.7° to 78.1°. Measured surface energy values are given in Table 5 (water and 1-bromo naphthalene as probe fluids) and Table 6 (water, 1-bromonaphthalene and DMSO as probe fluids). Values are given as (average +/-

standard deviation), calculated on about 10 to 20 counts of contact angle values of the probe fluids.

$$\begin{aligned} \text{Water: } & \sigma = 72.1 \text{ mN/m, } \sigma_d = 19.9 \text{ mN/m, } \sigma_p = 52.2 \text{ mN/m} \\ \text{1-bromonaphthalene (1-bN): } & \sigma = 44.4 \text{ mN/m, } \sigma_d = 44.4 \text{ mN/m, } \sigma_p = 0 \text{ mN/m} \\ \text{Dimethylsulfoxide: } & \sigma = 44 \text{ mN/m, } \sigma_d = 38 \text{ mN/m, } \sigma_p = 6 \text{ mN/m} \end{aligned}$$

Table 5 shows that polycarbonate surfaces were observed to have total surface energies of about 46 - 47 mN/m, with the PC plate showing a polar component of 4.6 mN/m vs 2.4 mN/m for the PC sheet. This was significantly higher than the values reported in a technical datasheet published by the CA station manufacturer where total, dispersive, and polar components were given as 34.2, 27.7, and 6.5 mN/m respectively. Therefore, further CA measurements were carried out with another reference fluid, DMSO. Table 6 reports the SFE values calculated on the basis of all possible combinations of water, 1-bN and DMSO CA values. The calculated SE values were smaller than the ones previously obtained, i.e. 36 – 41 mN/m for the dispersive component and 2 - 4 mN/m for the polar component.

Table 5. Surface free energy values of PC surfaces and printed PC surfaces, involving water and 1-bromonaphthalene as probe fluids.

Material	Water CA (°)	1 bromo-Naphthalene CA (°)	Surface free energy (and components)		
			γ_s (mN/m) (mean \pm st. dev.)	γ_d (mN/m) (mean \pm st. dev.)	γ_p (mN/m) (mean \pm st. dev.)
PC sheet (foil removed)	82.7 (\pm 0.6)	8.4 (\pm 2.4)	46.3 (\pm 0.3)	43.9 (\pm 0.3)	2.4 (\pm 0.1)
PC plate (cleaned with isopropanol)	76.3 (\pm 0.8)	16.2 (\pm 2.1)	47.2 (\pm 1.0)	42.7 (\pm 0.4)	4.6 (\pm 0.2)
CA-1 Magenta on PC sheet	87.0 (\pm 1.1)	17.5 (\pm 0.4)	43.9 (\pm 0.3)	42.4 (\pm 0.1)	1.5 (\pm 0.3)
CA-2 Magenta on PC sheet	90.9 (\pm 0.6)	27.5 (\pm 0.8)	40.6 (\pm 0.1)	39.5 (\pm 0.1)	1.1 (\pm 0.1)
CA-1 White on PC sheet	90.4 (\pm 1.1)	25.0 (\pm 1.5)	41.4 (\pm 0.6)	40.3 (\pm 0.5)	1.1 (\pm 0.1)
CA-2 White on PC sheet	87.3 (\pm 0.6)	37.3 (\pm 1.4)	38.1 (\pm 0.7)	35.8 (\pm 0.6)	2.3 (\pm 0.1)

In comparison, crosslinked UV inks CA-1 and CA-2 in white and magenta showed slightly lower total surface energy values, ranging from 38 – 44 mN/m. Dispersive components were similar and ranged from 36 – 55 mN/m, while the polar components ranged from 1 - 2.5 mN/m. These data qualitatively were in agreement with the semi-empirical solubility parameter calculations, which also predicted that the surface characteristics of inks based upon the high molecular weight urethane acrylate oligomers reported herein would be dominated by dispersive forces and have minor contributions from polar forces.

Both the polycarbonate and the inks had the largest surface energy component contribution from dispersive forces (i.e. aliphatic, aromatic hydrocarbon). For wetting to occur in the IMD application wherein molten polycarbonate is injected onto the surface of the cured ink, the

change in free energy upon exchanging relative amounts of ink/air interface, PC/air interface, and PC/PC interface for new ink/PC interface must be negative. Generally, this means that the surface energy of the substrate must be equivalent to or higher than the surface energy of the liquid material being applied to the surface. These measurements suggest that with these basic formulations, combinations of certain polycarbonates and certain radiation curable inks may exist that will not bring good wetting and therefore will not provide adhesion in the IMD laminates. This further suggests that adding components that raise the total surface energy of the cured ink may increase the probability to obtain wetting and adhesion.

Table 6. Surface free energy values of PC surfaces using water, 1-bromonaphthalene and DMSO as probe fluids.

Material	Water CA (°)	1 bromo-Naphthalene CA (°)	DMSO CA (°)	Surface free energy (and components)		
				γ_s (mN/m) (mean \pm st. dev.)	γ_d (mN/m) (mean \pm st. dev.)	γ_p (mN/m) (mean \pm st. dev.)
PC sheet (foil removed)	82.7 (\pm 0.6)	8.4 (\pm 2.4)		46.3 (\pm 0.3)	43.9 (\pm 0.3)	2.4 (\pm 0.1)
	82.7 (\pm 0.6)	8.4 (\pm 2.4)	28.2 (\pm 1.4)	43.9	41.3	2.6
		8.4 (\pm 2.4)	28.2 (\pm 1.4)	44.3	43.9	0.3
	82.7 (\pm 0.6)		28.2 (\pm 1.4)	39.6	35.9	3.7
PC plate (cleaned with IPA)	76.3 (\pm 0.8)	16.2 (\pm 2.1)		47.2 (\pm 1.0)	42.7 (\pm 0.4)	4.6 (\pm 0.2)
	76.3 (\pm 0.8)	16.2 (\pm 2.1)	29.1 (\pm 2.1)	43.9	38.8	5.0
		16.2 (\pm 2.1)	29.1 (\pm 2.1)	43.2	42.7	0.5
	76.3 (\pm 0.8)		29.1 (\pm 2.1)	38.6	31.2	7.4

Thermo-Mechanical Analysis (TMA)

The linear and volumetric thermal expansion coefficients of various types of polycarbonate are affected by differences in molecular weight distributions, additives that affect the temperature and breadth of the glass transition and secondary and tertiary thermal transitions, the thermal history of the samples, and other factors.³ Potential differences in thermal expansion characteristics of polycarbonate compared to that of a UV-cured ink based upon flexible urethane acrylate oligomers were evaluated by TMA. Characterization was performed using a TA Instruments TMA 2940 Thermomechanical Analyzer. Measurements were made on a polycarbonate substrate and on a sample of the same substrate screen-printed with a 10 μ m thick ink layer and with a 41 μ m ink layer. The experiment involves using a probe with a force displacement arm that moves in the z dimension normal to the face of the substrate. The probe is rested on the surface and is monitored as it is displaced negatively or positively from its initial location due to expansion or contraction of the sample as a function of temperature to generate a plot as shown in Figure 2.

Data extracted from the TMA curve shown in Figure 2 show that very slow expansion of the polycarbonate is observed in the range 0 – 120 °C with a linear expansion coefficient of about 0.026 $\mu\text{m}/^\circ\text{C}$, followed by the onset of softening of the PC at about 130 °C. In comparison, the PC sheet with a 10 μm thick (1 print layer) ink layer showed expansion in the range 0 - 75 °C with a linear expansion coefficient of 0.036 $\mu\text{m}/^\circ\text{C}$, followed by possible softening of the ink layer at 70 °C and then softening of the PC layer around 120 - 130 °C. In contrast, the PC sheet with a 41 μm ink layer (4 print layers) showed non-linear expansion in the range 0 - 75 °C with a much larger linear expansion coefficient of 0.213 $\mu\text{m}/^\circ\text{C}$ in the range 0 - 40 °C, followed by probable softening of the ink layer at 70 °C and then softening of the PC around 120 – 130 °C.

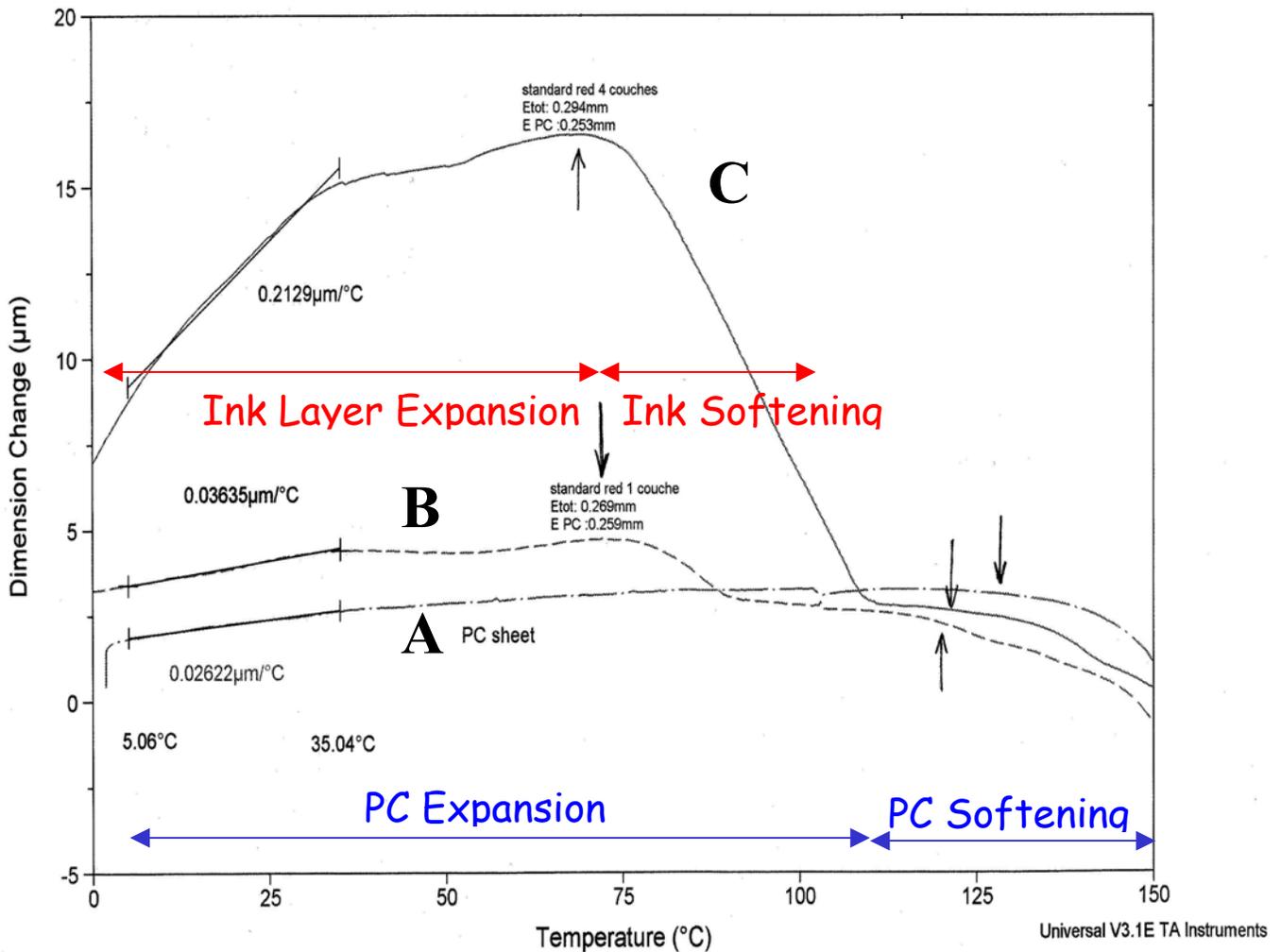


Figure 2. TMA curve illustrating the linear expansion of a PC substrate (A), PC substrate with a 10 μm ink layer (B), and PC substrate with 41 μm ink layer (C).

II.D. Photopolymerization Kinetic Studies on Monomers

Kinetics of homopolymerization of monomers XM-2 and XM-3 were characterized by Real-Time Fourier Transform Infrared Spectroscopy (RT-FTIR) using the experimental conditions described following. The infrared spectra were recorded in real-time at room temperature using a scan speed of 20 spectra per second at a resolution of 16 cm^{-1} , using a Perkin-Elmer

Spectrum GX FTIR spectrometer equipped with a TGS detector. 10 μ m-thick samples containing 5% Darocur 1173 photoinitiator were sandwiched between a KRS-5 crystal and an oriented polypropylene sheet. Full arc ultraviolet (UV) radiation from a Philips 400 W medium-pressure mercury lamp was introduced into the sample chamber through a flexible light guide, with irradiance (on-sample light intensity) values of about 25 mWcm⁻². Conversions of the acrylate double bonds were followed via the decay of the absorption band of the C=CH-H_{out-of-plane} stretching mode at 809 cm⁻¹ by integration of the peak areas. Conversion versus time data were converted into rate versus time by taking the numerical 3-point average first derivative of the conversion plot and multiplying by the molar volume. Data are presented in Figures 3 and 4.

III. Results for Thermoforming

III.A. Thermoforming Resin and Formulation Design

Resin design to meet the requisite levels of performance for thermoforming formulations is very much a matter of balance. For example, increasing the flexibility can increase post-cure surface tack, decrease thermal stability, and increase oligomer viscosity. Significantly decreasing surface tack can decrease flexibility and affect adhesion to the substrates. Decreasing formulation viscosity by adding monofunctional monomers or decreasing the oligomer molecular weight can significantly decrease flexibility. Finding an acceptably optimized combination involves not only oligomer design but also formulation strategy.

The obvious primary considerations for thermoformable inks are that they must have good adhesion to the substrate(s) and that they must be very flexible. For IMD, extreme flexibility is not necessary because the depth of the forms are usually shallow (cellular phone covers, instrument panels, etc.). However, for decorative thermoforming, the depth of the forms can be quite deep (8:1 draw ratios or higher), depending upon the substrate. Additionally, most ink additives, particularly solids such as pigments, photoinitiators, and fillers, can significantly decrease the flexibility of the final inks. This is particularly problematic in white inks, which may contain up to 40-50% by weight titanium dioxide to reach the necessary opacity.

The oligomer design in this study was limited to urethane acrylates, which are relatively easy to synthesize, offer many potential structural variations, and show good utility in screen inks. A target range of 500 – 700 percent elongation at break was chosen to address the flexibility requirements of the thermoforming applications. Oligomers synthesized during this study showed average elongation at break values in the range 30 – 830% as shown in Figure 1.

During this study a number of polyol types were evaluated including: polyether, linear aliphatic and cyclo-aliphatic polyester, aliphatic polycarbonate, aliphatic polyurethane, and mixed aliphatic/aromatic polyester. These were used in combination with aliphatic isocyanates to maintain flexibility and potential for outdoor weatherability. The high molecular weight oligomers (7,000 – 10,000 g/mol) resulting from these syntheses were quite viscous such that they would have been intractable in formulation work without a diluting monomer or solvent. Isobornyl acrylate (IBOA) was selected as a diluent of choice because it did not significantly decrease elongation at break of cured thin films containing the oligomers.

III.B. Summary of Thermoforming Application Results

A number of common polymeric substrates were utilized as substrates including: PET, 4 mm and 500 μ m PET-g, polycarbonate, polystyrene, PVC, thick-sheet acrylic, and GE's SolIX[®]

modified polycarbonate material. All substrates were untreated. None of the inks showed sensitivity to high temperatures in the thermoforming testing. Adhesion to thermoforming substrates was easiest on polycarbonate, while adhesion to polystyrene, acrylic, and PET was more challenging. Performance of example formulations in thermoforming testing is given in Table 7.

Most of the inks showed relatively slow cure speeds, which was anticipated due to the high resin molecular weight and to formulation with monofunctional acrylate monomer. Low acrylate functionality results in lower cure speed due to the lower average concentration of acrylate groups, while the concomitant low crosslink density yields higher flexibility. Cure speed may be increased by the addition of multifunctional or rapid-curing acrylate monomers; however, cure speed must be balanced against ultimate flexibility of the cured ink.

In some instances, adhesion and scratch resistance were observed to improve significantly after thermoforming compared to the freshly printed samples. This may be due to additional polymerization taking place at elevated temperature. If so, a slight under-curing of the ink may allow a tack-free surface with the bulk of the ink remaining highly flexible due to plasticization by unreacted monomer and/or oligomer. The ink may then reach full cure during thermoforming, potentially reducing the stress caused by the elongation of the ink.

Table 7. Thermoforming testing results.

Formulation	Surface Tack*	Adhesion	Thermoforming Observations
1	None	Excellent on PC**	Printed in 5 process colors on PC; excellent performance at draw ration up to 8:1
5	None	Excellent on PC**	Printed in 5 process colors on PC; excellent performance at draw ration up to 8:1
7	None	Excellent on PC**	Printed in 5 process colors on PC; excellent performance at draw ration up to 8:1
13	None	Excellent on PC**	Printed in 5 process colors on PC; excellent performance at draw ration up to 8:1
16	None	Excellent on PC; good on PET, PET-g, PVC, PS	Good performance at draw ratios of 1:1 – 4:1***
17	None	Excellent on PC; good on PET, PET-g, PVC, PS	Good performance at draw ratios of 1:1 – 4:1***
18	None	Excellent on PC; good on PET, PET-g, PVC, PS	Good performance at draw ratios of 1:1 – 4:1***
19	None	Excellent on PC; good on PET, PET-g, PVC, PS	Good performance at draw ratios of 1:1 – 4:1***
20	None	Excellent on PC; good on PET, PET-g, PVC, PS	Good performance at draw ratios of 1:1 – 4:1***

* Qualitative observation of tacky to touch or not; ** Not tested on additional substrates; *** Not tested at higher than 4:1 draw ratio.

IV. Results for In-Mold Decoration

IV.A. IMD Resin and Formulation Design

In-Mold-Decoration is significantly more challenging than thermoforming. The crux of the IMD challenge can be visualized by considering that the IMD process proposes to create a decorative laminate object by having a cured, non-tacky, flexible, yet scratch-resistant ink that is strained up to 300%, pressure washed with molten thermoplastic, cooled, and the resulting laminate subjected to thermal and mechanical shock. After this process, the laminate is expected to maintain adhesion during thermal cycling over wide ranges of temperature and relative humidity. Few inks, including solvent-borne, water-borne, and 100% solids systems, have been found that can meet all of the performance requirements. Approaching these requirements with a 100% solids radiation curable ink formulation is particularly challenging and involves careful design of the component resins and the resulting formulations.

The initial formulation efforts were based upon existing Surface Specialties UCB oligomers, monomers, and additives in combination with additives from external sources. Several of these formulations had good adhesion to the initial printing substrate, but none showed adhesion in IMD laminates. Therefore, new oligomers were designed and synthesized to prepare new resins offering good flexibility, low post-cure surface tack, excellent adhesion to polycarbonate, good thermal stability, and potential for good adhesion in the IMD laminates.

Two monomers, XM-2 and XM-3, were tested at various concentrations and in various combinations with the best performing urethane acrylate oligomer/additive package found up to that point. XM-2 was found to show significant benefit for adhesion in the IMD laminates while surprisingly XM-3 showed little or no adhesion benefit in the IMD laminates. Interestingly, XM-2 and XM-3 were quite similar in structure and composition, but exhibited significantly different maximum rates of homopolymerization as described following.

Percent conversion versus time plots for polymerization of XM-2 and XM-3 are given in Figure 3. It is readily apparent that XM-3 homopolymerized much more efficiently than did XM-2 under the conditions of this experiment. This is further illustrated by Figure 4, which provides a plot of rate of polymerization versus time for monomers XM-2 and XM-3. The rate of polymerization of XM-2 is quite low with a maximum rate of polymerization estimated at only about $2 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ as compared to a maximum rate of polymerization of about $12 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ measured for XM-3 under the polymerization conditions described above. NVP was found also to have a beneficial effect on the adhesion in the IMD laminates. Interestingly, NVP has been shown in the literature to have a very low efficiency of homopolymerization, with rates as low as $0.03 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ as measured by RT-FTIR using 11 m W/cm^2 irradiance (on-sample intensity) of a xenon arc lamp to cure NVP containing 1% by weight 2,2-dimethoxy-2-phenylacetophenone as initiator at $25 \text{ }^\circ\text{C}$.

Thermal Expansion Characteristics

A complicating factor with implications for adhesion in IMD laminates demonstrated by the TMA data was that the volumetric thermal expansion coefficient of the initial polymer substrate, the cured ink layers, and the injected thermoplastic layer may be quite different. Data extracted from the TMA curve in Figure 2 show that the linear thermal expansion coefficient of the PC may be almost an order of magnitude less than that of the inks. If the coating is not sufficiently adhered to the layers and sufficiently flexible to absorb physical stresses that arise due to differences in the thermal expansion characteristics of the plastics compared to the ink, then delamination will likely occur upon thermal cycling or thermal shock. It was postulated that the

inks were sufficiently flexible to handle stresses induced by differences in the thermal expansion coefficients of the inks and the PC, which was confirmed by further testing.

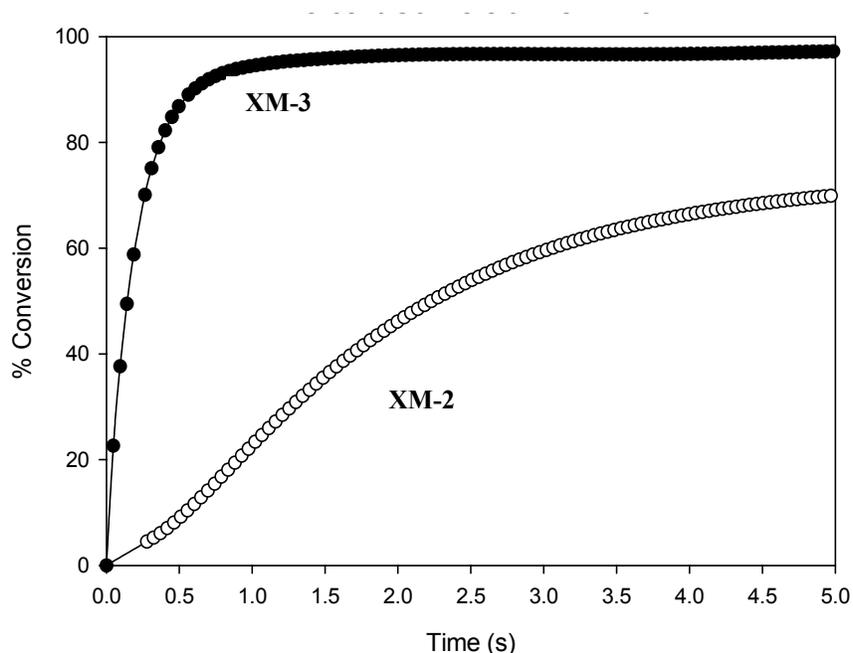


Figure 3. Conversion versus time plots generated from Real-Time FTIR kinetic studies on XM-2 and XM-3.

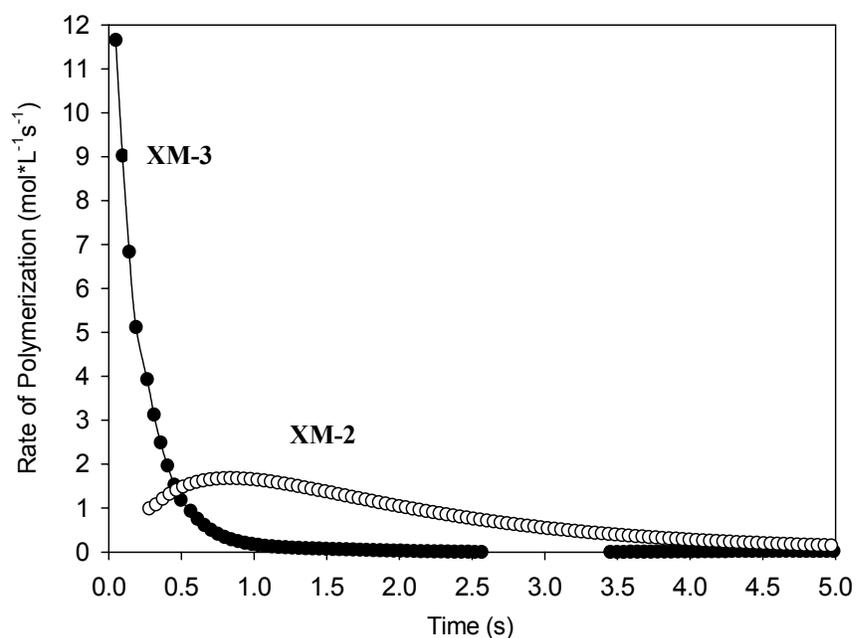


Figure 4. Rate of polymerization versus time generated by taking derivative of plots for conversion versus time for XM-2 and XM-3 shown in Figure 3.

IV.B. Summary of IMD Application Results

The IMD process, from initial printing to trimming of the injection molded laminate article, has many variables in each of the process stages that significantly affect the performance and potential adhesion in the IMD laminate. Design of the oligomer is only one of the many significant variables. It is clear that formulations must be tailored to specific types and grades of thermoplastic and that printing, thermoforming, and injection molding process variables must be consistently controlled in order to achieve and maintain ideal IMD performance.

Qualitative results for 15 representative formulations tested are given in Table 8. These samples all showed good initial adhesion to the polycarbonate substrate, but varied in performance in the final IMD laminates. Two of the formulations met or exceeded the adhesion requirements in the laminates with standard grade Lexan[®] PC, but none passed the demanding thermal cycling testing. Adhesion to silane-modified PC and certain specialty grades of PC was significantly more difficult. As with the thermoforming formulations, the IMD inks showed relatively slow cure speeds due to the high molecular weight of the component oligomers and the relatively low acrylate functionality. Cure speed may be increased by the addition of multifunctional or rapid-curing acrylate monomers; however, cure speed must be balanced against the flexibility of the cured ink as well as adhesion in the IMD laminate.

Table 8. Results from adhesion testing to various IMD injection-molded polycarbonate substrates.

Formulation	Lexan [®] SP 1010	Lexan [®] SP 1010R
1	**	Good adhesion
2	**	Good adhesion
3*	Some adhesion	**
4	**	Good adhesion
5	**	Good adhesion
6*	Some adhesion	**
7	**	Good adhesion
8	**	Good adhesion
9*	Some adhesion	**
10	**	Good adhesion
11	**	Some adhesion
12*	Some adhesion	**
13	**	Good adhesion
14	Good adhesion	**
15	**	Good adhesion

* Printed in two layers as a clear coat over two layers of ink formulation 21.

** Not tested

V. Summary and Conclusions

The most significant attributes for thermoforming formulations include post-cure flexibility, adhesion to the printing substrate, and post-cure surface tack. Significant attributes for IMD formulations additionally include good adhesion to the injection-molded thermoplastic and excellent thermal stability under injection molding conditions. Thermoforming and IMD resins and formulations must be designed to yield inks and coatings exhibiting the appropriate balance of flexibility, surface tack, adhesion, and cure speed in order to achieve optimal applications performance. IMD is a particularly challenging process, and requires careful tailoring of formulation and process variables to produce good performance in the laminate products.

The oligomer development work conducted during this study resulted in a number of highly flexible urethane acrylate oligomer resins that exhibited elongation at break of up to 800%, shrinkage upon cure of less than 2%, and low post-cure surface tack. Significant oligomer and formulation design variables were identified and explored using corroborative techniques including semi-empirical solubility parameter calculations, surface free-energy measurements, thermo-mechanical analysis, and photopolymerization kinetics characterization. Based upon the new highly flexible oligomers, 100% solids UV-curable formulations were developed that showed good adhesion to a variety of polymer substrates including polycarbonate, polystyrene, PVC, acrylic, PET, and PET-g, and excellent thermoforming characteristics at draw ratios up to 8:1. Similar resins and formulations were developed that showed good promise for 100% solids UV-curable in-mold decoration formulations on polycarbonate and potentially additional substrates.

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