Synthesis and Application of Acrylic Colloidal Unimolecular Polymers as a Melamine Thermoset System

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ABSTRACT: Acrylic polymers were synthesized with a ratio of 1 : 7 or 1 : 8 of acrylic acid to acrylic ester monomers to produce an acid-rich resin. The polymers were water reduced and solvent was stripped to produce colloidal unimolecular polymers (CUPs). These particles were typically 3–9 nm in diameter depending on the molecular weight. They were then formulated into a clear coating with melamine as the crosslinker with thermal curing. Compared to commercial latex films, these melamine-cured acrylic CUPs had a distinct advantage of having a near-zero volatile organic compound, better availability of surface functional groups, and improved water resistance. The coatings were evaluated for their **methyl ethyl ketone** resistance, adhesion, hardness, gloss, flexibility, abrasion, and impact resistance properties. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40916.

INTRODUCTION

Water-borne resins typically used in the coatings industry are particles of 25–120 nm in diameter and contain multiple chains entangled into each other. They typically rely on diffusional entanglement to form a film when the water leaves. This research article discusses a water reduction process which is conceptually similar to the current water reducible resin processes, except that the collapse of the chains was unimolecular owing to the low concentration of polymer at the reduction point and that the solvent was stripped off, leaving the particles suspended in water with zero volatile organic compound (VOC) and with the ability to be crosslinked to give films with excellent properties.

Significant effort has been expended on the investigation of nanoscale polymer particles. When polymers containing blocks of both hydrophilic and hydrophobic regions are placed in an aqueous environment at a set pH, the hydrophilic portions of the chains orient into the water phase such that they leave the hydrophobic region in the interior domain forming a macromolecular micelle of many chains with an average diameter of 50–120 nm.[1] Typical surfactant-based micelles are 2–10 nm in diameter or roughly twice the diameter of the surfactant hydrocarbon chain. In a study by Morishima,[2] the micelle behavior of a single polyelectrolyte chain was observed to be "self-assembled" in a poor solvent when the chain collapsed into unimolecular micelles of a diameter of approximately 5.5 nm.

Multiple chain polymer collapse has also been observed in water-borne urethane resins synthesized by reaction of isocyanate by Reichhold when acetone was removed from the resin–water blend, causing the chains to collapse into aggregates with a diameter of approximately 25 nm.[3,4] Water-reducible resins containing ionizable carboxylic acid groups neutralized with amines were synthesized in another study and dissolved in high boiling, water-miscible solvents after which water was introduced into the system until the solvent blend became a less-than theta solvent condition which caused the entangled polymer chains to collapse.[5]

The term colloidal unimolecular polymer[6] (CUP) describes a solid spherical unimolecular particle suspended in a continuous aqueous phase. CUPs contain hydrophilic groups such as carboxylic acid salts and a hydrophobic backbone. CUPs are formed by the process of water reduction, followed by the subsequent removal of a volatile water-loving solvent. Therefore, the CUP solution can be VOC free. The collapsed CUP particles are spheroidal in nature owing to the repulsive nature of the carboxylate groups. As the inside of the particle has low dielectric, the carboxylate groups do not "feel" each other through the particle. But the high dielectric of water causes the adjacent carboxylate groups to feel each other strongly. In an earlier study, the particle diameter of the CUPs was found to be proportional to the molecular weight (MW) of the starting polymers.[7] Unlike the larger latex particles which settle with time,
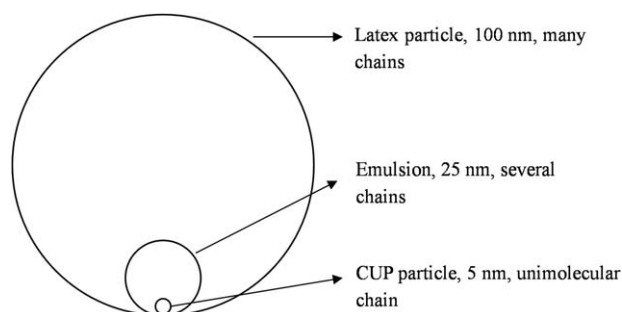
Figure 1. Particle size comparison for water-borne particulate coating resins.

CUP particles are thermodynamically stable owing to the particle's low mass and the Brownian motion of the solvent molecules around them. No change in particle size and aggregation/settling has been observed in the samples of the reduced CUP particle suspensions retained for more than 3 years. In another study, it was reported that polymers with a MW of 13,000 and above formed CUPs with a stable particle size and uniform size distribution.[8] This research article explores the synthesis of acrylic CUPs in true nanoscale range (<10 nm) with particular emphasis on coating performance enhancements offered by the melamine cure of the polymeric films.

Figure 1 shows the particle size comparison between the two conventional small coatings resin particles represented by a latex and a typical water-borne urethane resin with the CUP particle.

In this study, copolymers were synthesized in tetrahydrofuran (THF) using acrylic monomers by free radical polymerization. Four polymers were investigated: two of low glass transition temperature (T_g) that is below room temperature, and two of high T_g that is above room temperature; two of which were of high MW ($\sim$50,000) and the other two of low MW ($\sim$20,000). The low-molecular-weight polymer would require crosslinking to obtain any respectable physical properties, whereas the high-molecular-weight polymer would have marginal lacquer performance. THF was selected as the primary solvent owing to its good solvency for acrylics, its miscibility with water, and low boiling point allowing it to be easily stripped off after water reduction without loss of a significant amount of water. The hydrophilic/lipophilic balance requires that the acid monomer to ester ratio to be in the range of 1 : 7–1 : 8. This ratio yields a monomolecular reduction to the CUP particles. If significantly less acid groups are incorporated, aggregation may be observed. Triethylamine was added to neutralize the carboxylic acid groups on the synthesized polymers during water reduction. Bases such as NaOH and KOH cannot be used for neutralization in coatings as they are not reversibly lost on drying, but these can be used for other applications. Ammonium hydroxide can be used for neutralization but it can react with the free formaldehyde content of the melamine during the crosslinking process. Thus, triethylamine was chosen for this study. Water was added slowly during water reduction to avoid a large regional solvent composition change which causes the formation of more coagulum.[9] This coagulum formation yields visible cloudiness. A modest stirring rate was also essential for avoiding

any regional solvent composition change. The synthesized acrylic CUP resins will give the performance of a lacquer without a crosslinker and therefore to enhance the performance, a commercially available melamine was chosen as the crosslinking resin.

Melamine, which is an organic base and a trimer of cyanamide, is one of the most widely used crosslinkers for baked coating systems. The reaction of melamine with aldehydes, carboxylates, or alcohols yields thermosetting polymers: melamine–formaldehyde (MF) type resins which have various applications such as fabrics, dinnerware, glues, foams, counter tops, and so forth.[10,11] Resin systems with reactive functional groups such as hydroxyl, carboxylic acid, activated aromatics, and urethane can react with MF resins to give crosslinked products.[12] The melamine used in this study to crosslink the acrylic CUPs was Cymel 373 from Cytec Industries: a methylated MF with a medium degree of alkylation, medium to high methylol content, and low imino functionality (Figure 3). The crosslinker Cymel 373 was soluble in water and was compatible with the acrylic CUPs. The acid functionality on the acrylic CUPs was sufficiently acidic to catalyze the curing reaction at a relatively low curing temperature. However, sulfonic acid catalysts are added to the formulation to improve the curing characteristics.[13] The mechanism of crosslinking of Cymel 373 with the carboxylated acrylic CUPs involves the esterification of the methylated group by the acid functionality present in the acrylic polymer backbone.[14] The performance of melamine-crosslinked CUPs is evaluated by means of testing protocols as per the specified ASTMs. The aforementioned acrylic CUP resin crosslinked with melamine was a zero VOC coating system, except for the amine.

EXPERIMENTAL

Materials
Methacrylic acid (MAA), butyl methacrylate (BMA), ethyl acrylate (EA), ethyl methacrylate (EMA), 2-ethylhexyl methacrylate (2-EHMA), 2,2′-azobis(2-methylpropionitrile) (AIBN), and 1-dodecanethiol were obtained from Aldrich. MAA was purified by distillation with copper (I) bromide under vacuum. All other monomers were purified by washing with a 10% w/w solution of sodium bicarbonate, followed by rinsing with deionized water, and brine after which the solution was dried over sodium sulfate, filtered, and purified by distillation under nitrogen with copper (I) bromide as an inhibitor. The initiator AIBN was recrystallized before use from methanol, whereas 1-dodecanethiol was used as received.

Polymer Syntheses
All polymers were synthesized by free radical polymerization in THF. The monomer composition of polymers J-31 and J-32 was in the following range of molar ratios—MAA : EMA : BMA = 1 : 2.5 : 5.5 with the acid: acrylate ratio of 1 : 8, whereas the monomer composition of polymers J-51 and J-52 was in molar ratios—MAA : EA : 2-EHMA : BMA = 1 : 1.5 : 1.5 : 4 with the acid: acrylate ratio 1 : 7 (Table I). The monomer ratios were chosen such that two of those polymers would have a T_g above room temperature and the other two below room temperature for adequate evaluation of the synthesized polyacrylic resins. The molar ratio of dodecanethiol was varied

Table I. Monomer Composition, MAA : Acrylate Ratio, % Yield, T_g, and Molecular Weight of the Synthesized Polymers

Polymer	Monomer composition	MAA : acrylate ratio	% Yield	T_g (°C)[a]	Molecular weight (M_n)
J-31	MAA : BMA : EMA	1 : 5.5 : 2.5	89	55	19,000
J-32	MAA : BMA : EMA	1 : 5.5 : 2.5	93	55	50,000
J-51	MAA : BMA : EA : 2-EHMA	1 : 4 : 1.5 : 1.5	91	21	21,000
J-52	MAA : BMA : EA : 2-EHMA	1 : 4 : 1.5 : 1.5	93	21	51,000

[a] Mid-point of T_g transition range.

to produce a low and a high range of MW. The solvent THF was added in the amount of 2.5 times the total weight of monomers.

Synthesis for Polymer J-32. The monomers BMA (0.477 mol, 67.79 g), EMA (0.217 mol, 24.74 g), and MAA (0.0865 mol, 7.47 g) were charged in a 1000-mL three-neck round-bottomed flask with the initiator AIBN (0.781 mol, 0.094 g) along with chain-transfer agent dodecanethiol (0.0011 mol, 0.257 g) and THF (250 g) and stirred. The flask was fitted with a nitrogen line, condenser, and a gas outlet adapter connected to an oil bubbler to allow a positive pressure of nitrogen throughout the polymerization process. The flask was heated slowly to reflux and allowed to react for 24 h. The polymer solution was then cooled to room temperature, precipitated in cold deionized water under high shear, and then dried to constant weight under vacuum. Polymers J-31, J-51, and J-52 were also synthesized as per the abovementioned protocol.

Polymer Characterization
The ^{1}H NMR was carried out using a Varian 400 MHz FT/NMR spectrometer in a 5-mm outer diameter thin-walled glass tube with sample concentrations around 30 mg/mL in CDCl₃. All spectra were consistent with proposed polymer structures. Absolute number average MWs (M_n) were measured by gel permeation chromatography (GPC) on a Viscotek GPCmax from Malvern instruments coupled with a triple detector array TDA305 (static light scattering, differential refractometer and intrinsic viscosity). Acid value (reported in mg of KOH/g of polymer sample) for all polymers was measured by titration method (ASTM D-974) which was modified by using potassium hydrogen phthalate in place of hydrochloric acid and *phenolphthalein as an indicator in place of methyl orange*. T_g was measured on TA Instruments Q2000 by means of Modulated-Differential Scanning Calorimeter (MDSC) method. Thermogravimetric analysis (TGA) was made on a TA Instrument model Hi-Res-TGA Q50 analyzer. The thermal stability of the MMA–MAA-based CUP was determined under nitrogen by measuring weight loss while heating at a rate of 10°C/min.

CUP Formation by Water Reduction
Polymers were dissolved in a low boiling, water-miscible solvent, THF (20% w/w), and stirred overnight. The acid groups were neutralized by adding triethylamine and then deionized water was added by a *peristaltic* pump at 1.24 g/min. The pH of CUP solution was maintained between 8.3 and 8.7. After the addition of water, the THF was stripped off under vacuum, giving CUPs in VOC-free aqueous solution, except for the added

base, at the desired concentration. Ammonium hydroxide works equally well and makes this system even lower in VOC.

Water-Reduction Process for the Polymer J-32. Polymer J-32 (0.0174 mol, 20 g) was dissolved in THF (80 g) to make a 20% w/w solution; the acid groups were neutralized with triethylamine (0.006 mol, 0.61 g); and deionized water (160 g) was added by means of a peristaltic pump after which the THF was stripped off under vacuum to give a 10% solution of CUPs. The CUP solutions were then concentrated to 20% by stripping off water under vacuum and filtered through 0.45-μm Millipore membrane to remove any foreign materials which were typically measured to be <0.05% by weight. Polymers J-31, J-51, and J-52 were also water reduced as per the abovementioned protocol. Figure 2 shows the process of the formation of CUPs. It was found that the amount of water used as well as the amount of THF was critical as if the collapse from a random coil into a hard sphere occurs at too high a concentration the particle becomes a poly-chain particle instead of a CUP owing to the chain–chain entanglement.

Characterization of CUPs
After the water-reduction process, the measurements of viscosity were carried out by Ubbelohde viscometer method at 25 and 30°C for use in measuring the particle size and reported in the units of centiStokes. The viscosity of 10% of CUP solution in water was done at 25°C on a Brookfield Rheometer model DV-III at a shear rate of 112.5 and reported in centipoise (Figure 4). The sizes of particle were measured by dynamic light scattering (DLS) on a Nanotrac 250 particle size analyzer from Microtrac with a laser diode of 780 nm wavelength and measuring angle of 180°. The principle for the particle size measurement was that the particles in solution were constantly moving owing to collisions by the solvent molecules that is Brownian motion. If the particles or molecules are illuminated with a laser, then the intensity of the back-scattered light that strikes the detector is Doppler shifted and is dependent on the size of the particles. It should be noted that owing to the low scattering ability of CUPs and their ionic charge interacting at the concentration needed to obtain particle size measurements, the solution viscosity instead of the solvent viscosity was used as input to the Nanotrac software.[7] Minimum film formation temperature (MFFT) was measured on Rhopoint WP-Bar90 as per the method described in ASTM D-2354.

CUP Coatings
The CUPs were used at 20% of solids and cured by means of a melamine for evaluating the coating characteristics of the clear
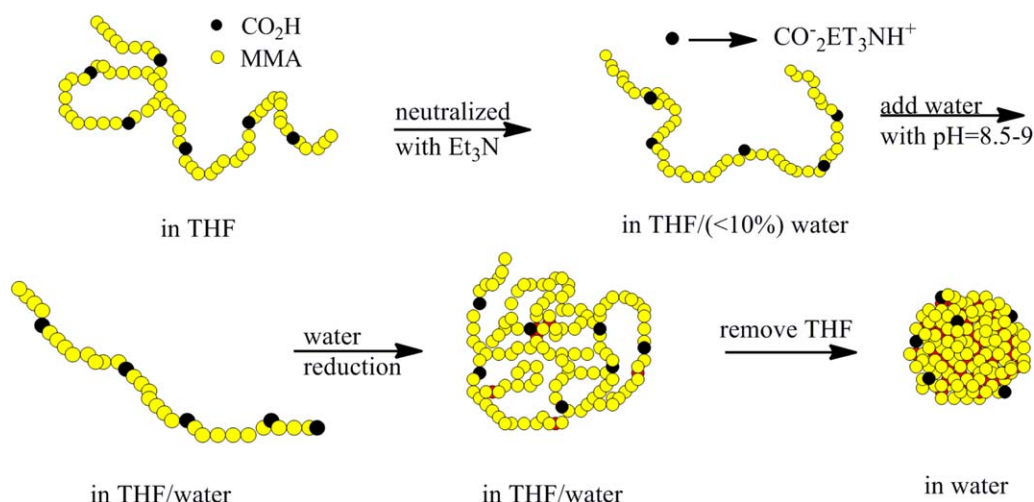
Figure 2. Process of forming CUP particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coat CUPs. The crosslinker was used in a ratio of 1 : 1 of the acid equivalent of the resin. The melamine used to cure CUP clear coats was Cymel-373, which is obtained from Cytec Industries and used as received. The utilizable functionality of the melamine was assumed to be 4.5. The amine-blocked *para*-toluenesulfonic acid catalyst used was Na-Cure 2547 (active, 25%), which was obtained from King Industries and used as received.

CUP Coatings from J-32. For 100 g of water-reduced resin with 20% of solids, 1.39 g (0.004 mol) of Cymel 373 was used along with 0.21 g (1% w/w of total solids of the formulation) of Na-Cure catalyst. The coated samples were cured at 300°F (~150°C) for 30 min.

Testing of the CUP Clear Coats

Aluminum panels (A-36 mill finish) and iron phosphate steel panels (R-36 dull matte finish) from Q-panel were used for the testing of CUP clear coats. The melamine-cured CUP clear coats were baked at 300°F (150°C) for 30 min and tested for: the % active catalyst required for effective curing, optimum curing time and temperature, appropriate functionality of melamine required, methyl ethyl ketone (MEK) resistance, adhesion, hardness, gloss, flexibility, abrasion, and impact resistance properties.
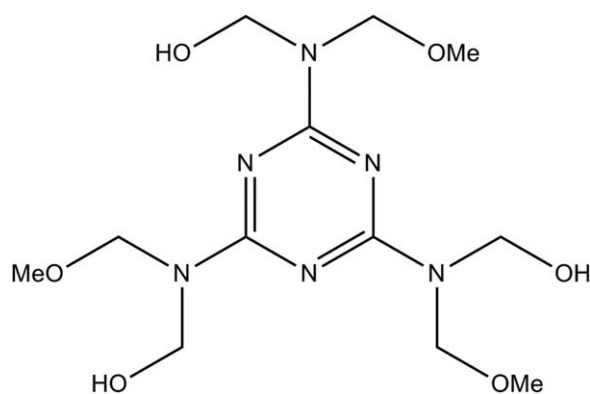

Figure 3. Modified melamine in water.

The controls used for the testing protocol were the CUP clear coats cast on panels without any crosslinker. The amount of catalyst was varied and the samples were cured at a fixed temperature (150°C) and time (30 min) to find out the optimum % active catalyst required for effective curing. The curing time was varied as 10, 20, 30, and 40 min at a fixed curing temperature (150°C) and % active catalyst (0.25% on resin solids) to find out the optimum time required for effective cure. The curing temperature was varied as 100, 125, 150, and 175°C at a fixed curing time (30 min) and at 200°C for a curing time of 20 min with fixed % active catalyst (0.25%) to find out the optimum temperature required for effective cure. The amount of melamine content required to cure the CUPs was changed by estimating a different functionality of melamine as 3.0, 3.5, 4.0, 4.5, and 5 to find out the appropriate amount of melamine (estimated functionality of melamine) required for effective curing of acrylic CUPs. Gloss was measured on the aluminum panels by a Byk-Gardener microgloss meter and an average of three readings with standard deviation of <1 were recorded at three angles: 20, 60, and 85°. MEK double rub test was performed on aluminum panels by employing a lint-free cloth as per ASTM method D-4752. The cloth was dipped in MEK and then rubbed on the test panel with the index finger held at an angle of 45°, with moderate pressure. One forward and back motion constituted one double rub. The cloth was dipped in MEK every 25 double rubs and the number of rubs until the substrate became visible was termed as MEK double rubs. The average of two readings was reported.

Hardness of coating films can be evaluated by various methods such as Knoop hardness, pencil hardness, Taber abrasion, and Tukon hardness. Pencil hardness test was chosen because of its easy interpretation and convenience.[15–17] Pencil hardness tests were performed on aluminum panels as per the ASTM method D-3363 by using pencils of varying hardness in the range of 9B-9H and the average of three readings was reported. The pencil was held against the coating at an angle of 45° and then pushed away from the operator for a 6.5-mm stroke followed by the

Table II. Characterization : Acid Value of the Synthesized Polymers: Charges per Particle, Particle Size, Viscosity, and MFFT of CUPs

Polymer	Acid value theo./exp.	Charges per particle	Particle size (nm) theo./exp.	Kinematic viscosity[a] (cSt)	Viscosity at shear rate of 112.5[a] (cP)	MFFT (°C)
J-31	48.7/48.8	16	3.6/4.0	2.19	2.31	45.2
J-32	48.7/48.7	43	5.0/4.5	2.51	3.82	45.5
J-51	50.9/52.5	19	3.7/3.1	2.45	2.57	12.5
J-52	50.9/51.7	46	5.1/4.7	3.13	3.96	12.4

[a] In total, 10% of solids by weight.

examination of surface for scratch marks. For each sample, the test was started with the hardest pencil and continued down the scale until the pencil which could not produce a visible scratch on the coating. This was reported as the pencil hardness value. Film thickness was measured on aluminum panels by a coating thickness gage by Elcometer-6000 Positector and an average of three readings was reported in mil. Impact testing was done on iron phosphate steel Q-panels as per ASTM D-2794 using Gardner Impact Tester with a 5/8 inch ball indenter of 4-lb weight and results were reported in units of inch–lbs. Flexibility was tested on aluminum Q-panels by mandrel test method as per ASTM D-522 and the results were recorded in inches. Adhesion testing was done as per the ASTM D-4541 on iron phosphate steel Q-panels by prepping the coatings with sandpaper # 320, cleansing with isopropyl alcohol wipe, and gluing the grit-blasted and MEK-cleaned pucks onto the coating with either a Locktite Quick Set 2-ton epoxy or a 3M Scotch Weld DP-460 epoxy. It was allowed to cure for 48 h after which the puck was removed via a nut threaded on the puck and rotating with a torque wrench. ComputorQ-II was used to record the torque and the failure mode was reported through observation. The torque displayed in inch–pound units was recorded in PSI units by appropriate conversion and an average of four readings was reported. Wet adhesion testing was done by immersing one-third of the aluminum panel in deionized water for 1 h and then inspecting the panels for delamination, change in clarity/transparency, and so on. Pencil hardness testing was also performed on those panels. Abrasion resistance testing was performed on 4 inch × 4 inch iron phosphate steel Q-panels, R-44 dull matte finish from Q-panel, by using a Taber Abraser 5150 with a load weight of 1000 g for 100 cycles utilizing H-10 wheels as per the ASTM D-4060.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

The initial study investigated four polymers, two of low T_g that is below room temperature, and two of high T_g that is above room temperature. For both the polymers, two MWs were chosen: one with high MW of ~50,000 and the other with low MW of ~20,000. The MWs chosen here are only examples. The monomer composition can also be varied. Polymers with MWs ranging from 13,000 to 130,000 have been successfully reduced to form CUPs. Polymers with MW lower than 13,000 may form CUPs but they have some aggregation owing to too few stabilizing groups.[8]

The monomers MAA, BMA, EA, EMA, and 2-EHMA were chosen in the particular composition to yield polymers with specified T_g. The actual acid value of the synthesized polymers was found to be slightly higher than the theoretical acid value as expected, because a part of the monomer MMA was lost with nitrogen purging through evaporation with solvent during polymer synthesis (Table II). Good yields are reported for all the synthesized polymers. The MFFT of the synthesized polymers was found to be lower than the T_g as it is typical for polar water-borne resins.[18]

The molar ratio of 8 : 1 and 7 : 1 of the hydrophobic acrylate (or methacrylate) group to the hydrophilic MAA group was based on the typical surfactants having 16–22 carbon atoms (the hydrophobic part) for each hydrophilic acid group. All these polymers underwent water reduction to give a clear, transparent CUP solution without any visible aggregate formation. After reduction, these CUPs were free from any organic solvent and hence have a zero VOC, where the neutralizing amine group was the only air contaminant. The CUP solution was then filtered through a 0.45-μ filter and analyzed further for viscosity and particle size.[19]

The viscosity of water-reduced CUPs was water like and the actual/measured particle sizes were close to the theoretical particle size, indicating the true unimolecular characteristics of the synthesized CUPs (Table II). As shown in Figure 4, the viscosity profile of CUPs, as measured by a Brookfield rheometer, was linear for the graph of square root of shear rate versus square root of shear stress with a slope of 0.1456. Therefore, zero-point viscosity at 25°C was 2.02 cP. This fits with the results of kinematic viscosity, measured by an Ubbelohde viscometer. The viscosity of water-reduced CUPs was basically Newtonian at concentration below 15% of solids by weight. At high concentrations, the polymer does exhibit shear thinning and thus are non-Newtonian owing to the charge–charge repulsion of the particles. The presence of charged groups on the CUP particles lead to the formation of a surface water layer and causes particle repulsion.[20] These two effects lead to the rise in viscosity of CUP solution with increasing concentration of CUP particles. When compared with a latex (typically 100 nm diameter) and a water-borne urethane dispersion (typically 25 nm diameter), at the same volume fraction, the viscosity of CUPs was always higher, which was attributed to the surface charge of the CUPs. According to the Mark–Houwink–Sakurada equation, $\eta = kM^a$, where η is viscosity, "k and a" are the Mark–Houwink
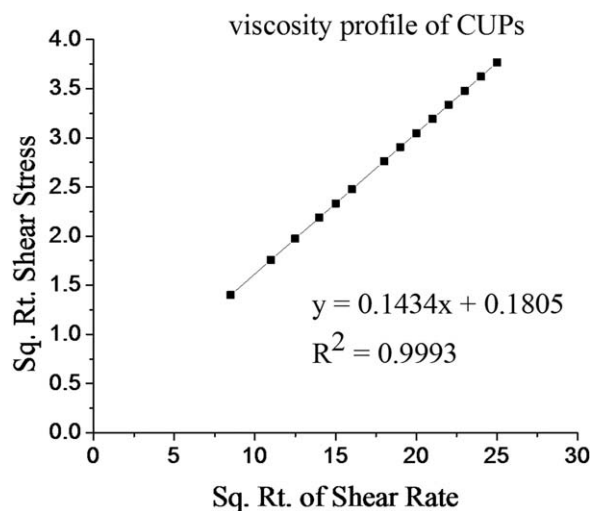
Figure 4. Viscosity of 10% of solution of CUP J-32 in water at 25°C.

Figure 6. Improperly water-reduced CUPs (left); properly water-reduced CUPs (right).

constants, and M is the MW, for spherical uncharged CUPs, the value of "a" would be zero.[21] However, the data indicate that viscosity increased with increasing MW. The viscosity also depends on the surface charge density, increasing with increasing charge density. Hence, the viscosity could increase with a decrease in MW if the surface charge density was increased. As summarized in Table II, CUPs prepared from polymers J-32 and J-52 had higher viscosity than polymer J-31 and polymer J-51, respectively, which was attributed to the higher MW of the corresponding polymers and increased charge density. Polymers J-31 and J-32 were synthesized based on an acid : acrylate ratio of 1 : 8, whereas polymers J-51 and J-52 were based on acid : acrylate ratio of 1 : 7. The number of charged groups per particle was calculated as the MW of one CUP particle divided by the weight of repeating unit. For example, number of charges per particle for J-31 = 19,000/(wt. of MMA + 5.5 × wt. of BMA + 1.5 × wt. of EMA). The particle charge density was also calculated as ρ_{charge} = (number of charges per particle/surface area of the particle). Based on this formula, the charge densities of the four CUPs that is J-31, J-32, J-51, and J-52 were 0.39,

0.55, 0.44, and 0.56 (charges/nm^2), respectively. Hence, CUPs prepared from polymer J-51 had higher number of charged groups per particle and particle charge density than CUPs prepared from J-31, whereas CUPs prepared from polymer J-52 had higher number of charged groups per particle and particle charge density than CUPs prepared from J-32. As a result, CUPs prepared from polymers J-51 had slightly higher viscosity than CUPs prepared from polymer J-31, whereas CUPs from polymer J-52 had slightly higher viscosity than polymer J-32.

The four synthesized polymers were analyzed for comparison between the theoretical particle size calculated from the GPC fractions at different MWs and the actual/experimental particle size as determined by DLS. Figure 5 validates a good agreement between the distribution and the particle diameters, assuming that the density of the bulk polymers was the same as that of CUPs. The presence of THF, if not stripped off completely, influences the measured diameter of the CUPs as it can partition into the CUP particles and give a larger diameter than expected owing to swelling. However, NMR was employed in this research to verify the removal of THF. It should be noted that water must be added in a slow gradient during reduction to avoid regional large solvent compositional changes. If they occur, coagulum may be formed, resulting in a cloudy solution owing to some large aggregates. The water must also be free of polyvalent cations like calcium or magnesium which can bind to the carboxylates and cause gelling. If performed correctly, the solution appears water clear as shown in Figure 6.

Figure 5. Particle size comparison by GPC (calculated) and DLS (measured) for polymer J-32.

Latex particles used in coatings are typically 100 nm in diameter, whereas urethane dispersions can be as small as 25 nm. Polymer chains containing reactive groups such as carboxylic acid or alcohol functionality are taken into account. Only a small percentage of the reactive groups are on or near the surface, whereas the remainders are inside the particle of 25–100 nm. These reactive groups have to diffuse to the surface to react or the crosslinker will need to diffuse deep into the latex particle to react.[22] The catalyst will be in the water phase until the water leaves and also must migrate into the resin to crosslink a latex or dispersion. With CUP particles, most of the carboxylate

Table III. % Active Catalyst Required for Effective Curing of CUPs

Polymer	% Active catalyst	Pencil hardness	MEK double rubs
J-31	0.125	HB	31
	0.25	F	50
	0.375	F	48
	0.5	HB	40
J-32	0.125	HB	43
	0.25	H	82
	0.375	H	82
	0.5	F	84
J-51	0.125	HB	67
	0.25	H	188
	0.375	H	181
	0.5	H	183
J-52	0.125	F	70
	0.25	H	212
	0.375	H	200
	0.5	H	200

Table IV. Curing Time Study for Melamine-Cured Acrylic CUPs

Polymer	Curing time (min)	Pencil hardness	MEK double rubs
J-31	10	HB	30
	20	F	48
	30	F	50
	40	F	50
J-32	10	HB	43
	20	H	79
	30	H	82
	40	H	82
J-51	10	HB	79
	20	H	185
	30	H	188
	40	H	188
J-52	10	HB	96
	20	H	147
	30	H	212
	40	H	211

groups are at the surface and more readily available to react. This gives CUPs a significant kinetic crosslinking advantage.

The MW of the polymer and the temperature of the reaction also affect the diffusion process. For linear polymers, the following correlation has been observed between the diffusion coefficient and the MW of the polymer: $D\alpha\,M^{-2}$.[23] Latex polymers have a high MW typically in the range of 100,000. The CUP resins reported here have MW in the range of 20,000–55,000. The diffusion will possibly be better in the case of CUPs as compared to latex resins. For diffusion to occur, the temperature during the reaction has to be maintained above the T_g of the polymer chains.[24] As the temperature decreases, the viscosity of the system will rise and will oppose the diffusion process. These factors make the latex or dispersed larger particle resin less efficient at forming crosslinks with a water-borne crosslinker.

If we calculate the functionality as carboxylates on CUP J-32, the surface area occupied per carboxylate is 0.67 nm^2. If a latex has the same functionality and is of a 100 nm diameter, the percentage of acid groups on the surface is approximately 9% of the total number of acid groups. Thus, only a fraction of total functionality is available for crosslinking for latexes without chain diffusion. In the case of small-diameter dispersions and CUPs, most of the reactive groups are on the surface and can react without polymer diffusion. Again, as the crosslink density increases for a latex particle, the diffusion slows and will stop short of completion. In CUPs, the crosslink efficacy is high as all the groups are at or near the surface for full reaction without the need for significant slow diffusion. The ester groups of the latex react slowly as compared to the acid groups and the self-polycondensation of melamine also affects the crosslink density, which should not be a significant issue for CUPs.[21]

Melamine-Cured CUP Coatings

The catalysts used for melamine curing are sulfonic acids and although they are blocked in the formulae, after baking they are still free acids and can cause corrosion or degrade the polymer with time. Therefore, the optimum % active catalyst level required for effective curing of CUPs by melamine was determined by carrying out a reaction of the CUP resin with the melamine resin in a 1 : 1 acrylic: melamine (with a functionality of 4.5) equivalents ratio. Typically, for acrylic latex cured with melamine resins, it has been reported that not all the six reactive groups on the melamine react and on an average the melamine has an average functionality of 4.5.[25] As summarized in Table III, the MEK double rubs increased when the % active catalyst was increased from 0.125 to 0.25% and then it plateaued. The level of active catalyst (based on the resin solids) was set at 0.25% as it minimized the acid used and gave the optimum performance for melamine cure of acrylic CUPs when baked at 150°C for 30 min. This was comparable to the amount of catalyst reported in the literature for acrylic latex–melamine resin systems which was between 0.25 and 0.5% based on the resin solids.[26,27] As summarized in Table III, crosslinked films prepared using higher MW polymers (J-32 and J-52) had higher MEK double rubs than those prepared using polymers with low MW (J-31 and J-51). As the MW is increased, the number of crosslinks per chain also increases which provides better solvent resistance. The effect of T_g on the crosslinking of the films was also evident from the MEK double rub values. Polymers with low T_g had better diffusion during curing than the high T_g polymers and hence coalescence and reaction to give films with higher MEK double rubs. The low T_g polymers also had higher surface charge density than the corresponding high T_g polymers

Table V. Curing Temperature Study for Melamine-Cured Acrylic CUPs

Polymer	Curing temp. (°C)[a]	Pencil hardness	MEK double rubs
J-31	100	HB	12
	125	HB	26
	150	F	50
	175	HB	33
	200	HB	30
J-32	100	HB	18
	125	F	32
	150	H	82
	175	H	44
	200	F	41
J-51	100	HB	56
	125	HB	64
	150	H	188
	175	B[b]	12
	200	B[b]	10
J-52	100	HB	62
	125	HB	79
	150	H	212
	175	B[b]	14
	200	B[b]	8

[a] Thirty-minute cure, except at 200°C for which the curing time was 20 min.
[b] Overbake resulted in the color change of the CUP clear coats.

arising from a higher acid : acrylate ratio. This leads to higher crosslink density which contributes to better solvent resistance for low T_g polymers than the corresponding high T_g polymers.

The curing time study was executed by varying the baking time of the panels as 10, 20, 30, and 40 min at a fixed curing temperature (150°C) and 0.25% active catalyst to find out the optimum time required for effective cure (Table IV). For all the four polymers, the MEK double rub values after 10 min curing were poor. This was attributed to the time required for the loss of water, evaporation of the blocking agent of the acid catalyst, reaching the temperature of T_g to allow diffusion and achieving the required temperature for curing. Similar to latex film-formation process, the diffusion of polymer chains would determine the part of the mechanical properties of the cured coating. The performance of the coating reached its peak value after 20 min of curing and plateaued. The values of the MEK rubs measured at different curing times again reflected the effect of MW and the T_g on the mechanical strength of the cured coating. Lower T_g and higher MW of the polymer provided the coating with higher MEK double rubs. The diffusion coefficient (D) is a function of MW and T_g of the polymer with $D_{high\ MW} < D_{low\ MW}$ at equal T_g and $D_{high\ Tg} < D_{low\ Tg}$ at equal MW and as the temperature increases, diffusion increases above the T_g.[23,24] As the MW increases, the number of acid groups per particle also increases, which gives higher crosslink density and better mechanical properties. Both intra- and inter-

molecular crosslinking can occur between the melamine and the CUP resin. The melamine resin could react with one or more carboxylic acid groups on the CUP resin, giving intramolecular crosslinking. For the intermolecular crosslinking, two or more CUP particles could be attached to the same melamine unit. The entanglement of polymer chains and the crosslink density are dependent on diffusion coefficient. If entanglement occurs before crosslinking, the film is more resilient and better performing. Hence, the low T_g and high MW polymer gives better mechanical properties.

To ensure thorough cure, a 30-min curing time for melamine-cured acrylic CUPs was chosen as optimum at 150°C. Typically, solvent-borne polyols as well as OH-functional latexes have been crosslinked with melamine at 150°C for 30 min in the presence of 0.5% of acid catalyst.[28]

A curing temperature study was executed by varying the oven temperature as 100, 125, 150, and 175°C at a fixed curing time (30 min) and at 200°C for a curing time of 20 min, limiting the damage at the higher temperature with fixed % active catalyst (0.25%) to find out the optimum temperature required for effective cure without overbake. For the polymers J-51 and J-52, overbaking of the resin (>125°C) leads to their degradation, most likely via cis-elimination,[29] producing the carboxylic acid and alkene as degradation products. However, optimum performance was recorded at a curing temperature of 150°C (Table V). To further evaluate the overbaking, TGA was performed on the four polymers with and without the presence of acid catalyst. Figure 7 shows the TGA for the four polymers as a plot of weight % against temperature. For all the four polymers that is J-31, J-32, J-51, and J-52 without acid catalyst, significant degradation did not occur until a temperature of 300°C was reached. For polymers J-31 and J-32, in the presence of acid catalyst, thermal stability was slightly reduced and degradation started at about 150°C. But for polymers J-51 and J-52, the presence of acid catalyst significantly reduced the thermal stability and degradation started at about 100°C. Polymers J-51 and J-52 were composed of 2-ethylhexyl methacrylate, which is more prone to cis-elimination as compared to polymers J-31 and J-32 which were based on EMA. To further refine the curing at elevated temperatures, shorter times would need to be employed to define the overbake window. In an independent study on melamine-cured acrylic latex, the optimum cure temperature was found out to be 170°C and appropriate melamine/acrylic mass ratio was identified as 0.45–0.55 based on the pencil hardness, dry/wet heat resistance, adhesion and stain testing results, which is much higher as compared to CUPs (melamine/acrylic mass ratio, 0.1–0.2).[15]

Studies with melamine crosslinked acrylic resins have shown that at optimum cure, about 50–80% of the total functional sites of melamine react with the acrylic resin. Hence, out of the six functional groups on melamine, 3–4.5 react at optimum cure which corresponds to a functionality of 3–4.5 for the melamine resin.[25] To find out the appropriate amount of melamine (estimated functionality of melamine) required for effective curing of acrylic CUPs, the amount of melamine content was changed by estimating a different functionality of melamine as
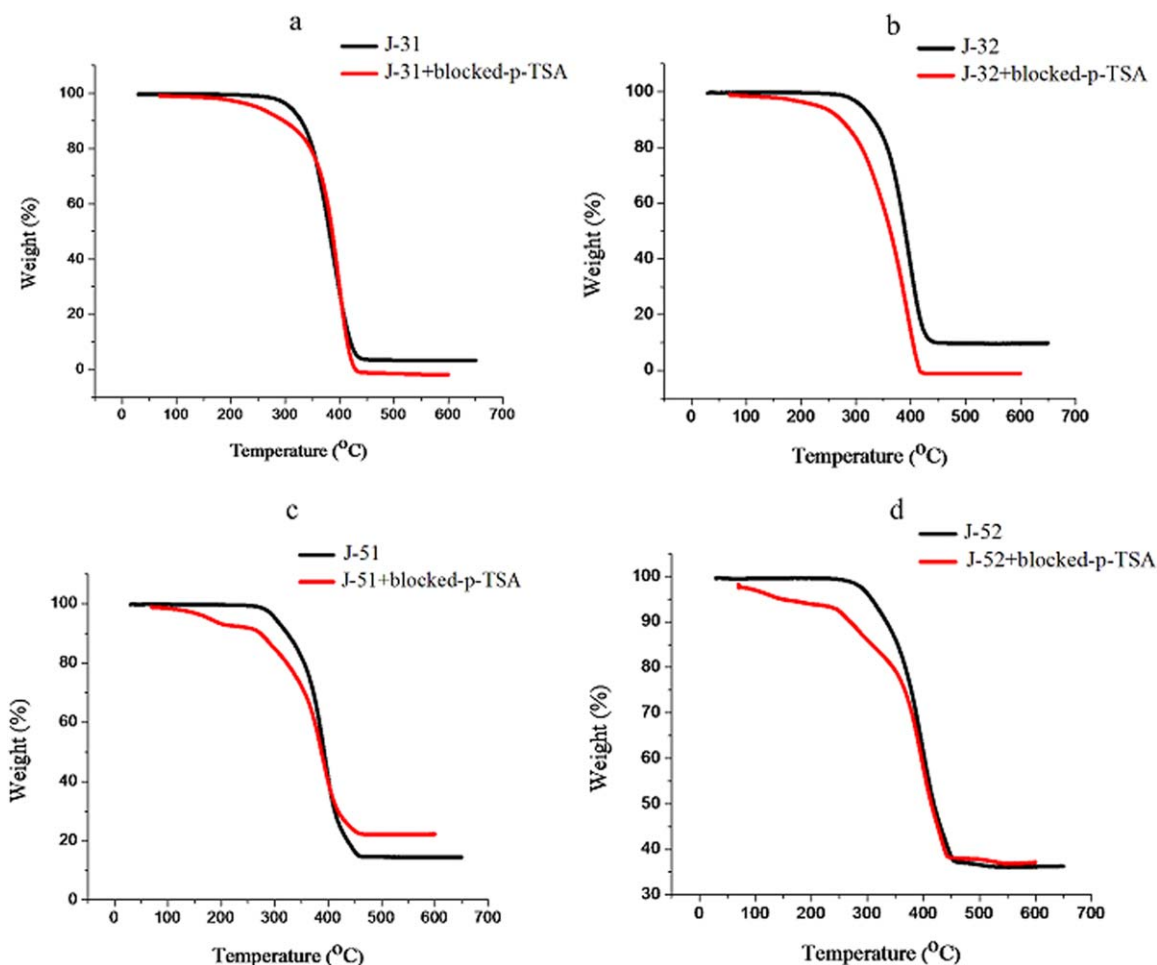
Figure 7. TGA of polymers with and without catalyst (a) polymer J-31, (b) polymer J-32, (c) polymer J-51, and (d) polymer J-52. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3.0, 3.5, 4.0, 4.5, and 5. As summarized in Table VI, optimum performance for all the four polymers was observed when the assumed functionality of melamine was 4.5, above which, the pencil hardness values and MEK double rubs for the cured films plateaued. Using the higher functionality of the melamine cross-linker, there will be improvement in the crosslink density, hardness, and MEK double rubs. If more flexibility is desired, a lower value may be targeted which will give lower crosslink density. Polymer J-51 had better MEK double rubs than polymer J-31 and polymer J-52 had higher than polymer J-32. This was attributed to the low T_g of polymer J-51 and J-52 than the corresponding polymers J-31 and J-32. Lower T_g would result in better coalescence of the films. Polymers J-31 and J-32 were based on acid : acrylate ratio of 1 : 8, whereas polymers J-51 and J-52 had an acid : acrylate ratio of 1 : 7. This resulted in a shorter linear backbone distance between the crosslinks (i.e., higher crosslink density) for polymers J-51 and J-52 and hence better mechanical properties as compared to polymers J-31 and J-32.

The acrylic–melamine films were then cast using the optimum catalyst level, curing time, curing temperature, and melamine functionality, and evaluated for pencil hardness, MEK double

rubs, flexibility, impact resistance, and dry and wet adhesion testing.

The MEK double rubs were higher than the controls for all of the melamine-cured CUP clear coats (Table VII). The low T_g CUPs (J-51 and J-52) cured by melamine showed excellent curability/crosslinkability and solvent resistance. The lack of any crosslinker would render the coating a lacquer, and thus resulting in lower hardness and solvent resistance as seen from the results of the control. It was observed that melamine-cured CUP clear coats had good hardness characteristics. Crosslink-ing with melamine provided a three-dimensional network structure which improved the mechanical properties. On a quantitative study of the performance characteristics of water-borne melamine–acrylic emulsions, the pencil scratch hardness was found to be 1 (on a scale of 1–6, 6 being the best).[15] Compared to these, the pencil hardness values of the CUP resin were better possibly owing to better availability of surface functional groups of CUPs, leading to higher crosslink density. The CUP clear coat made from all the four polymers gave good gloss with the low T_g polymers (J-51 and J-52) having slightly higher gloss values than the high T_g polymers (J-31 and J-32). This gives an indication of good flow and leveling

Table VI. Optimum Melamine Functionality Assumed for Effective Curing of CUPs

Polymer	f of Melamine	Pencil hardness	MEK double rubs
J-31	3	HB	12
	3.5	HB	14
	4	HB	38
	4.5	F	50
	5	F	50
J-32	3	HB	36
	3.5	F	39
	4	F	55
	4.5	H	82
	5	H	81
J-51	3	HB	42
	3.5	F	47
	4	F	95
	4.5	H	188
	5	H	185
J-52	3	F	57
	3.5	F	61
	4	F	104
	4.5	H	212
	5	H	212

Figure 8. High impact resistance and flexibility of melamine-cured CUP clear coatings.

Mandrel Flexibility and Impact Resistance Results of the Clear Coats Formulated from CUPs. Both impact and flexibility require elongation of the polymer. If the polymer has low tensile strength, then it will lead to failure in the flexibility and the impact testing. Similarly, if the coating is highly crosslinked, it will be brittle and will fail. The flexibility and impact strength are related to each other via the brittleness. Brostow and Lobland[31,32] have shown that more brittle the material (less flexible), lower its impact strength. Hence, coatings with lower flexibility will have low impact strength. Typical polyesters have equivalent weight of 200–700 per functional group, whereas CUPs J-31/32 have an equivalent weight of 1166 and CUPs J-51/52 have an equivalent weight of 1115. The higher MW per functional group results in larger separation between the adjacent functional groups and greater distance between the crosslinked chains which gives flexibility to CUPs. CUPs prepared from polymers J-31 and J-32 had larger distance between the crosslinks as the acid : acrylate ratio was 1 : 8, whereas polymers J-51 and J-52 had acid : acrylate ratio of 1 : 7. It was observed that all the formulated CUP clear coats (the control as well as the melamine-crosslinked CUPs) passed the 1/8″ mandrel flexibility and the forward/reverse impact rating of 160+ inch–lbs. This excellent flexibility and impact resistance can be attributed to the adhesion promoting carboxylate and amine groups of the acrylic–melamine resin. Typically, the strength of

of all the four resins. The difference in the gloss values, though not significant, could possibly be owing to the slight surface unevenness, likely owing to the reaction before full flow and thus slightly reduced coalescence. The gloss values were comparable to the typical acrylic–melamine coil coatings, (gloss, 20/60°–65/89).[30] Jones et al.[26] indicated that acrylic latexes crosslinked with melamine resins gave a pencil hardness value of H and MEK double rubs were above 200. The CUP resin crosslinked with melamine gave comparable pencil hardness and MEK double rubs. As summarized in Table VII, crosslinking the CUPs gives significant boost to the performance characteristics of the resin, as measured by the MEK double rubs and pencil hardness.

Table VII. Film Thickness, Gloss, MEK Double Rubs, and Pencil Hardness Results of the CUP Clear Coats

Polymer	Cure type	Film thickness (mil)	Gloss 20°/60°/85°	MEK double rubs	Pencil hardness
J-31	Control	0.5	81/83/90	5	B
	Melamine	0.5	85/89/93	50	F
J-32	Control	0.5	87/91/93	7	B
	Melamine	0.5	84/90/93	82	H
J-51	Control	0.7	90/93/97	5	B
	Melamine	0.7	90/91/95	188	H
J-52	Control	0.5	90/94/97	7	B
	Melamine	0.5	91/94/98	212	H

Table VIII. Adhesion Testing Results of the Clear Coats Formulated from CUPs

Polymer	Cure type	Epoxy adhesive used	Torque (PSI)	Failure[a]
J-31	Control	Locktite	810	C/s[b]
	Melamine	3M	4025	C/s
J-32	Control	Locktite	1021	C/s
	Melamine	3M	4655	C/s
J-51	Control	Locktite	838	C/s
	Melamine	3M	4133	C/s
J-52	Control	Locktite	1065	C/s
	Melamine	3M	5070	C/s

[a] All panels exhibited 100% adhesive failure.
[b] Mode of failure: C/s, coating to substrate; E/c, epoxy to coating.

the film increases with increasing crosslink density. But this could lead to brittleness in the film.[33,34] This problem is avoided in CUP resins as the distance between the crosslinks is high. Figure 8 is the evidence of the high flexibility and impact resistance of the resin developed.

When the puck adhesion was measured for these coatings, the Locktite quickset 2-ton epoxy adhesive failed for all the coatings except the control, indicating that the polymeric films had better adhesion than the adhesive (Table VIII). Therefore, to evaluate the actual adhesion potential of melamine cured acrylic CUPs, a higher strength adhesive, DP-460 by 3M, was used. The actual adhesion of the melamine-crosslinked CUP system was very high in all cases with failure occurring as coating adhesion failure to the substrate. Typically for adhesives, their bonding strength is directly related to the MW, increasing with increasing MW up to a certain point after which it levels off. Higher MW increases the chain entanglement which gives better adhesion.[35–37] Hence, the higher MW polymers displayed slightly higher adhesion than the low MW polymers.

Wet Adhesion Test Results. For latex resins with carboxylic acid groups, it has been reported that the presence of unreacted, resid-

Table IX. Abrasion Resistance Test Results of the Clear Coats Formulated from CUPs

Polymer	Cure type	MIlligram lost/100 cycles[a]	Wear index[a]
J-31	Control	39	390
	Melamine	14	140
J-32	Control	27	270
	Melamine	13	130
J-51	Control	22	220
	Melamine	10	100
J-52	Control	23	230
	Melamine	12	120

[a] Using H-10 wheels and 1000 g of load.

ual acid groups increased the water sensitivity of cured films.[38] The CUP resins were evaluated for the wet adhesion. The lower one-third of the CUP-coated panels was immersed in deionized water for 1 h followed by 1 h of air drying. No visible change was observed on any of the polymeric films nor was there any hazing or change in pencil hardness. This would possibly be owing to increased crosslink efficiency as most of the carboxylic acids are on the surface of the resin free to react with melamine.

It was observed that the wear index of the control was usually high, indicating low abrasion resistance, whereas the wear index of melamine-cured CUPs indicated a moderate abrasion resistance of the clear coats formulated from CUPs (Table IX). This corroborates that crosslinking the CUPs with melamine occurred and enhanced its abrasion resistance.

CONCLUSIONS

The true nanoscale nature of CUPs, with all the acid groups on the surface, can result in a well-crosslinked acrylic clear coat with good mechanical properties. Compared to commercial latex films, they have a distinct advantage of having a near-zero VOC, better crosslink efficiency, and improved water resistance. Melamine-cured CUP coatings produced well-crosslinked films that were found to be hard and effectively crosslinked. This study illustrates the advantages of the nano–unimolecular nature of CUPs and its low viscosity. These near-zero VOC systems offer a potential high-performance technology option for future coatings for original equipment manufacturing applications.

Over the last few years, the development of acrylic CUPs has moved from the realm of laboratory investigation to the point today at which they can be tested and developed commercially in numerous applications. Thus, the utilization of melamine-curing agents for water-reduced acrylic CUPs has illustrated their usefulness and potential in many applications.

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