ACRYLATE-BASED FLUORINATED COPOLYMERS FOR HIGH-SOLIDS COATINGS

Abstract
A series of low, medium, and high molecular weight copolymers containing methyl methacrylate, n-butyl acrylate, 2-hydroxyethyl methacrylate, and 2,2,2-trifluoroethyl methacrylate were synthesized by solution polymerization under monomer-starved conditions. The copolymers were crosslinked with a methylated melamine formaldehyde resin in order to obtain thermosetting acrylics. Lower wettability, higher oxygen permeability, and lower refractive index were observed for higher concentrations of fluorinated monomer in the copolymer composition and high number-average hydroxyl functionality of the high molecular weight copolymers increased the crosslink density of the acrylic films, thereby resulting in improved tensile strength and tensile modulus.

(a)

(b)
Fig. 1
Fig-2
**Fig-3**

MF Resin Structure

![Chemical structure of MF resin](image)

Triazine Ring

![Chemical structure of triazine ring](image)

Comprised Structure

![Chemical structure of comprised structure](image)

Acrylic Copolymer

![Chemical structure of acrylic copolymer](image)

Crosslinking Reaction

![Chemical structure of crosslinking reaction](image)
Fig-4

(a)

Tensile Strength (MPa)

0 10 20 30 40

vol% TFEMA

- Low Mw
- Medium Mw
- High Mw

Fig-5

(b)

Tensile Modulus (MPa)

0 500 1000 1500 2000 2500 3000 3500

vol% TFEMA

- Low Mw
- Medium Mw
- High Mw
ACRYLATE-BASED FLUORINATED COPOLYMERS FOR HIGH-SOLIDS COATINGS

REFERENCE TO RELATED APPLICATION


FIELD OF THE INVENTION

[0002] The present invention is related to acrylate copolymers, and in particular, to acrylate fluoropolymers used for coatings.

BACKGROUND OF THE INVENTION

[0003] Fluoropolymers are considered an ideal solution for coatings applications requiring chemical resistance (to acids, bases, solvents, and hydrocarbons), high thermal stability [1], low friction [2], and excellent weatherability. The unique combination of optical and electrical characteristics, low dielectric constant, low dissipation factor [3], and low surface energy [4, 5] has also led to growing interest in fluorine chemistry for a wide range of applications. In addition to the fluorinated olefin-based polymers, step growth fluoropolymers have been developed to obtain similar performance characteristics as well as to expand the potential scope of coatings applications. Even low fluorine content results in substantial beneficial properties [6]. Acrylates are non-yellowing and resist chemicals, i.e. gasoline, salt, oil, anti-freeze. Thus, in commercial coatings, fluorinated acrylics are used in the automotive industry, especially for automotive clearcoat formulations.

[0004] Fluoroacrylic copolymers have been extensively researched to discover applications in optics [7, 8], electronics [9], and construction (protective [10-12] and high performance coatings [13]). There have been various reports of fluoroacrylates prepared by emulsion polymerization [14-18], atom transfer radical polymerization [19-21], and high radiation polymerization [22, 23]. Furthermore, fluorinated methacrylates have been investigated for the synthesis of fluoropolymers with reduced polymerization shrinkage and improved strength [24]. The effect of fluorinated monomers on reduction of surface energy and surface wettability has also been published elsewhere [25, 26].

[0005] A number of fluorinated coatings have also been recently reported. Wynne et al. [27] focused on the surface modification of polyurethanes with short fluorinated side chains. The fluorinated groups improved the hydrophobicity, while retaining the bulk properties of a conventional polyurethane. They also demonstrated that the effectiveness of antimicrobial coatings was dependent on the nature of both fluorinated side chains and quaternary alkylation side chains [28]. Ober et al. [29] reported the anti fouling coatings based on both hydrophobic (fluorinated) and hydrophilic functionalities as surface domains. They explored the marine organisms’ settlement behavior on surface domains with distinct wettability. Deluccci et al. [30] studied the fluoropolyether coatings based on perfluorooether oligomeric diols cured with isocyanates. They concluded that fluorine content is not always the dominating parameter since other physical factors, such as the crosslink density, phase separation, and glass transition temperature, can play major roles on coating performance.

[0006] Solventborne high-solids acrylic technology is still widely used in the coatings of automotive and general industrial plastics. The primary advantages of solventborne acrylic technology are adhesion, quick drying, and durability [31]. On the other hand, the requirements of several government regulations have resulted in the product development to improve the environment, which is one of the main drivers in the coatings industry. Therefore, high-solids acrylics have been the subject of continuing research [32-36]. However, a very comprehensive study on synthesis and characterization of fluorinated acrylic copolymers for high-solids coatings has not yet been reported. Since the coating industry still relies on conventional free radical-initiated polymerization for the production of acrylates, it is important to obtain high-solids (60 wt. %) surface active acrylics with moderate polydispersity by a technique capable of economically producing functional acrylic copolymers.

SUMMARY OF THE INVENTION

[0007] A series of low, medium, and high molecular weight copolymers containing methyl methacrylate, n-butyl acrylate, 2-hydroxyethyl methacrylate, and 2,2,2-trifluoroethyl methacrylate were synthesized by solution polymerization under monomer-starved conditions. The acrylate-based copolymers were characterized by FTIR; 1H, 13C, and 19F NMR, and MALDI-TOF mass spectrometry. The molecular weights and the glass transition temperatures of the copolymers were determined using Gel Permeation Chromatography (GPC) and Differential Scanning calorimetry (DSC). The copolymers were crosslinked with a methylated melamine formaldehyde resin in order to obtain thermosetting acrylics. Surface, optical, barrier, mechanical, and viscoelastic properties of the acrylic coatings were investigated. An enrichment of fluorinated units at the acrylic surface was directly verified measuring dynamic contact angles. Lower wettability, higher oxygen permeability, and lower refractive index were observed for higher concentrations of fluorinated monomer in the copolymer composition. High number-average hydroxyl functionality of high molecular weight copolymers increased the crosslink density of the acrylic films, resulting in improved tensile strength and tensile modulus.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 is a schematic illustration of molecular structures for: (a) fluorinated; and (b) non-fluorinated acrylic copolymers;

[0009] FIG. 2 is a Fourier transform infrared spectroscopy (FTIR) spectrum of the F10-CTA5 designated copolymer;

[0010] FIG. 3 is a mass spectrometry spectrum of the F10-CTA5 designated copolymer;

[0011] FIG. 4 is a schematic representation of a crosslinking reaction by melamine formaldehyde resin with a hydroxyl group in a copolymer under acid catalyst according to an embodiment of the present invention; and

[0012] FIG. 5 is a graphical plot of: (a) tensile strength; and (b) tensile modulus as a function of TFEA content for copolymers according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The present invention discloses a top coat composition and a process for making the top coat composition. The
The top coat composition may or may not be used as part of a self-stratifying coating and the composition has utility as a coating for a motor vehicle.

[0014] The top coat composition can be a copolymer that includes an acrylate and/or a methacrylate, for example a fluorinated acrylate, fluorinated methacrylate or fluorinated hydrocarbons that are copolymerized with a methacrylate or acrylate. In addition an initiator, a solvent, a chain transfer agent, a catalyst and/or a crosslinking agent can be included in the top coat composition and/or the process for making the top coat. In some instances the acrylate can be a plurality of acrylates, illustratively including two or more of the following: methyl methacrylates, n-butyl acrylate, 2-hydroxyethyl methacrylate, 2,2,2-trifluoroethyl methacrylate and the like. In addition, the acrylate can be between 1 to 25 wt % of the top coat composition, between 2.5 and 15 wt % or between 5 and 12.5 wt %.

[0015] The crosslinking agent can be a methylated melamine formaldehyde, or in the alternative be a formaldehyde-free resin. For example and for illustrative purposes only, the crosslinking agent can be ethylene glycol acrylate, a methylenebisacrylamide, a methylenebisacrylamide and the like.

[0016] In order to better illustrate, but in no way limit the scope of the invention, example top coat compositions and a process for making a top coat composition are provided below.

### Materials

- **Methyl methacrylate (MMA)**
- **n-butyl acrylate (BA)**
- **2-hydroxyethyl methacrylate (HEMA)**
- **p-toluene-sulfonic acid monohydrate (ACS reagent, ≥98.5%)**
- **2-hydroxyethyl mercaptan, 2,2'-azobis(2-methylpropionitrile) (AIBN)**
- **methyl ethyl ketone (MEK)**
- **n-hexane (ACS reagent, ≥99.0%)**

[0017] Methyl methacrylate (MMA), n-butyl acrylate (BA), 2-hydroxyethyl methacrylate (HEMA), p-toluene-sulfonic acid monohydrate (ACS reagent, ≥98.5%), 2-hydroxyethyl mercaptan, 2,2'-azobis(2-methylpropionitrile) (AIBN), methyl ethyl ketone (MEK) (ACS reagent, ≥99.0%), and n-hexane (ACS reagent, ≥99.0%) were purchased from Aldrich Chemical Company, 2,2,2-trifluoroethyl methacrylate (TFEMA; trade name: Fluororster) was provided by Tosoh F-Tech, Inc. Methanol-etherified melamine formaldehyde resin (trade name: Luwipal 072) was obtained from BASF Corporation. All of the materials were used as received without further purification.

[0018] The chemical structures of monomers, solvents, initiator, chain transfer agent, and catalyst are shown in Table 1.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Nomenclature</th>
<th>Structure</th>
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<tbody>
<tr>
<td>Monomer</td>
<td>Methyl Methacrylate (MMA)</td>
<td><img src="image1" alt="Methyl Methacrylate" /></td>
</tr>
<tr>
<td>Monomer</td>
<td>n-Butyl Acrylate (BA)</td>
<td><img src="image2" alt="n-Butyl Acrylate" /></td>
</tr>
<tr>
<td>Monomer</td>
<td>2-Hydroxyethyl Methacrylate</td>
<td><img src="image3" alt="2-Hydroxyethyl Methacrylate" /></td>
</tr>
<tr>
<td>Monomer</td>
<td>2,2,2-Trifluoroethyl Methacrylate (TFEMA)</td>
<td><img src="image4" alt="2,2,2-Trifluoroethyl Methacrylate" /></td>
</tr>
<tr>
<td>Initiator</td>
<td>2,2'-Azobis(2-methylpropionitrile) (AIBN)</td>
<td><img src="image5" alt="2,2'-Azobis(2-methylpropionitrile)" /></td>
</tr>
<tr>
<td>Solvent</td>
<td>Methyl Ethyl Ketone (MEK)</td>
<td><img src="image6" alt="Methyl Ethyl Ketone" /></td>
</tr>
<tr>
<td>Solvent</td>
<td>n-Hexane</td>
<td><img src="image7" alt="n-Hexane" /></td>
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TABLE 1-continued

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Nomenclature</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chain Transfer Agent</td>
<td>2-Hydroxyethyl Mercaptan</td>
<td>![Structure Image]</td>
</tr>
<tr>
<td>Catalyst</td>
<td>p-Toluenesulfonic Acid Monohydrate</td>
<td>![Structure Image]</td>
</tr>
</tbody>
</table>

General Synthesis Procedure

[0019] Solution polymerization was conducted in a 500-mL, round bottom, four-necked flask immersed in a constant temperature water bath and equipped with a thermometer, a mechanical stirrer, a nitrogen gas inlet, and a reflux condenser. Methyl ethyl ketone was used as a solvent. Half of the solvent (60 mL, 48.24 g) was initially charged to the reaction flask and heated to a temperature of 60°C. The remaining solvent (60 mL, 48.24 g) was added to the monomer solution along with the chain transfer agent (2-hydroxyethyl mercaptan), and the initiator (2,2'-azobisis(2-methylpropionitrile). A syringe/needle/pump setup was used to feed the mixture to the reaction flask with a constant feed rate over one hour. Afterwards, 10 wt. % of the original amount of the initiator was dissolved in the solvent (5 mL) and added to the system through the condenser. Further stirring was conducted for several hours (See Table 2). Unreacted monomers and solvent were first removed without excessive heating, using a rotary evaporator. The solution was washed with excess n-hexane (2x500 mL) to completely eliminate the residual monomers and other impurities that were present. The precipitated copolymer was dried in a vacuum oven at 40°C for 96 h. Later, the product was re-dissolved into methyl ethyl ketone to obtain a 60 wt. % high-solids solution. Fourier Transform Infrared (FTIR) spectroscopy verified the disappearance of C–C bond stretching peaks resulting from vinyl groups of monomers, after further rotary evaporation and n-hexane extraction.

[0020] A series of low, medium, and high molecular weight copolymers were synthesized with the amounts of chemicals used in the synthesis shown in Table 2. The copolymer compositions were found by 1H NMR spectroscopy using integral area of chemical shifts of monomer functional groups for quantitative analysis and the yields were determined to be 90±4.5%.

TABLE 2

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>MMA (g, mL)</th>
<th>BA (g, mL)</th>
<th>HEMA (g, mL)</th>
<th>TFEEMA (g, mL)</th>
<th>Chain Transfer Agent (g, mL)</th>
<th>Initiator Solvent (g, mL)</th>
<th>Initiator (g, mL)</th>
<th>Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0-CTA5</td>
<td>59.41 g</td>
<td>56.57 g</td>
<td>57.83 g</td>
<td>—</td>
<td>8.82 g, 8.62 mL</td>
<td>2.61 g, 96.48 g</td>
<td>0.261 g</td>
<td>2</td>
</tr>
<tr>
<td>Low M0</td>
<td>63 mL</td>
<td>63 mL</td>
<td>54 mL</td>
<td></td>
<td>120 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F0-CTA2.5</td>
<td>59.41 g</td>
<td>56.57 g</td>
<td>57.83 g</td>
<td>—</td>
<td>4.41 g, 4.31 mL</td>
<td>2.61 g, 96.48 g</td>
<td>0.261 g</td>
<td>3</td>
</tr>
<tr>
<td>Medium M0</td>
<td>63 mL</td>
<td>63 mL</td>
<td>54 mL</td>
<td></td>
<td>120 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F0-CTA0.5</td>
<td>59.41 g</td>
<td>56.57 g</td>
<td>57.83 g</td>
<td>—</td>
<td>0.89 g, 3.47 g, 96.48 g</td>
<td>—</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>High M0</td>
<td>63 mL</td>
<td>63 mL</td>
<td>54 mL</td>
<td></td>
<td>0.87 mL, 120 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F5-CTA5</td>
<td>42.44 g</td>
<td>64.66 g</td>
<td>57.83 g</td>
<td>10.63 g, 9 mL</td>
<td>8.91 g, 8.71 mL</td>
<td>2.63 g, 96.48 g</td>
<td>0.263 g</td>
<td>2</td>
</tr>
<tr>
<td>Low M0</td>
<td>45 mL</td>
<td>72 mL</td>
<td>54 mL</td>
<td></td>
<td>120 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F5-CTA2.5</td>
<td>42.44 g</td>
<td>64.66 g</td>
<td>57.83 g</td>
<td>10.63 g, 9 mL</td>
<td>4.45 g, 2.63 g, 96.48 g</td>
<td>0.263 g</td>
<td></td>
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</tr>
<tr>
<td>Medium M0</td>
<td>45 mL</td>
<td>72 mL</td>
<td>54 mL</td>
<td></td>
<td>120 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F5-CTA0.5</td>
<td>42.44 g</td>
<td>64.66 g</td>
<td>57.83 g</td>
<td>10.63 g, 9 mL</td>
<td>0.89 g, 3.51 g, 96.48 g</td>
<td>—</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>High M0</td>
<td>45 mL</td>
<td>72 mL</td>
<td>54 mL</td>
<td></td>
<td>0.87 mL, 120 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F10-CTA5</td>
<td>42.44 g</td>
<td>56.57 g</td>
<td>57.83 g</td>
<td>21.24 g</td>
<td>9.04 g, 8.84 mL</td>
<td>2.67 g, 96.48 g</td>
<td>0.267 g</td>
<td>2</td>
</tr>
<tr>
<td>Low M0</td>
<td>45 mL</td>
<td>63 mL</td>
<td>54 mL</td>
<td>18 mL</td>
<td>120 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F10-CTA2.5</td>
<td>42.44 g</td>
<td>56.57 g</td>
<td>57.83 g</td>
<td>21.24 g</td>
<td>4.51 g, 2.67 g, 96.48 g</td>
<td>0.267 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium M0</td>
<td>45 mL</td>
<td>63 mL</td>
<td>54 mL</td>
<td>18 mL</td>
<td>120 mL</td>
<td></td>
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<tr>
<td>F10-CTA0.5</td>
<td>42.44 g</td>
<td>56.57 g</td>
<td>57.83 g</td>
<td>21.24 g</td>
<td>0.91 g, 3.56 g, 96.48 g</td>
<td>—</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>High M0</td>
<td>45 mL</td>
<td>63 mL</td>
<td>54 mL</td>
<td>18 mL</td>
<td>0.89 mL, 120 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[10-CTA0.5 = 10 vol.% TFEEMA (2,2,2-trifluoroethyl methacrylate) - 0.5 wt. % CTA (chain transfer agent), based on total amount of the reaction monomers and the initiator.]
The nomenclature for the copolymers is focused on the concentration of the monomer, 2,2,2-trifluoroethyl methacrylate (TFEMA), and the chain transfer agent, 2-hydroxyethyl mercaptan, in the composition. The designation consists of two terms and two numbers. As an example, for copolymer F5CTA2.5 in Table 2, the first term “F” represents the TFEMA monomer and the number “5” next to the letter “F” indicating the concentration of TFEMA monomer in the feed is 5 vol.%. The second term “CTA” designates the chain transfer agent and the following number “2.5” indicates the chain transfer agent concentration (2.5 wt.%). 

TABLE 3

<table>
<thead>
<tr>
<th>Structural Group</th>
<th>¹H NMR (ppm)</th>
<th>Structural Group</th>
<th>¹³C NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–CH₂–CH₂–OH</td>
<td>3.0-4.3</td>
<td>O–CH₂–OH</td>
<td>77-78</td>
</tr>
<tr>
<td>O–CH₃</td>
<td>3.0-4.3</td>
<td>O–CH₂–OH</td>
<td>60-66</td>
</tr>
<tr>
<td>O–CH₂–OH</td>
<td>3.0-4.3</td>
<td>O–CH₂–CH₂–CH₂–CH₃</td>
<td>66-66</td>
</tr>
<tr>
<td>O–CH₃–OH</td>
<td>3.0-4.3</td>
<td>O–CH₂–CH₂–CH₂–CH₃</td>
<td>66-66</td>
</tr>
<tr>
<td>O–CH₂–CF₃</td>
<td>4.4-5.3</td>
<td>O–CH₂–CF₃</td>
<td>77-78</td>
</tr>
</tbody>
</table>

Film Preparation

Film formation was performed by crosslinking the copolymers with melamine formaldehyde (MF) resin. 60 wt. % high solids acrylic copolymer solution (10 g) was mixed with MF resin (2.406 g) based on 2:1 equivalence ratio of methoxy groups in MF resin to hydroxy groups in the copolymer. Equivalent weight of MF resin was taken as 80 g/eq, resulting from the presence of dimers, trimers, and higher oligomers [37]. As a strong acid catalyst, p-toluenesulfonic acid monohydrate, 1 wt. % (0.02406 g) of MF resin was added to the formulation. The mixture was stirred for 1 h under ambient conditions (1 atm, 24±2°C); later, thin films were cast on steel and glass panels by a draw-down bar with a wet thickness of 125 μm. The films underwent evaporation at room temperature for 12 h, and were cured at 120°C for 1 h. The films cast on glass panels were prepared for viscoelastic properties, tensile tests, oxygen permeability and refractive index measurements, peeling off the films from the glass panels. The films cast on steel panels were used for coating tests such as pencil hardness (ASTM D3363), cross-hatch adhesion (ASTM D3359), pull-off adhesion (ASTM D4541), impact resistance (ASTM D2794), Taber abrasion (ASTM D4060), gloss (ASTM D523), and solvent resistance (ASTM D4752). Dry film thickness was typically 50-80 μm. All films were kept at room temperature for 7 days before any tests were performed.

Instruments

Fourier transform infrared (FTIR) spectroscopy was performed with 32 scans in 4000-600 cm⁻¹ on a Thermo Scientific Nicolet 380 FTIR with a diamond crystal UATR.

¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Gemini-300 MHz spectrometer (Varian) in chloroform-d as a solvent.

A Waters system was used for gel permeation chromatography (GPC) with a HR4, HT2, HR1, HR0.5 styragel, and 500 Å ultrastraygel columns connected in series. Gel permeation chromatography (GPC) analyses were performed at room temperature on 0.1% (w/v) sample solutions in distilled tetrahydrofuran (THF). Solutions were filtered on 0.45 μm membrane syringe filters and 200 μL was injected into the chromatograph with an eluent flow rate set at 1.0 mL/min⁻¹. The calibration curve was obtained with polystyrene (PS) standards.

Mass spectral experiments were performed to assist in determining the chemical structure of copolymers, using a Bruker REFLEX-III time-of-flight matrix-assisted laser desorption ionization mass spectrometer (Bruker Daltonics, Billerica, Mass.) equipped with an LSI model VSL-337ND pulsed nitrogen laser (337 nm, 3 nm pulse width), a two-stage gridless reflector and a single stage pulsed ion extraction source. Separate THF (anhydrous, ≥99.9; Aldrich) solutions of dithranol matrix (20 mg/mL) (>97%; Alfa Aesar), sodium trifluoroacetate (10 mg/mL) (>98%; Aldrich) and copolymer (10 mg/mL) were mixed in a ratio of matrix-cationizing salt: copolymer (10:1:2), and 0.5 μL of the resulting mixture was introduced onto the MALDI target plate. The spectra were obtained in the reflectron mode. The attenuation of the nitrogen laser was adjusted to minimize unwanted copolymer fragmentation and to maximize the sensitivity. The calibration of mass scale was carried out externally using poly(methyl methacrylate) standard (Fluka) with a similar molecular weight as the sample.

The glass transition temperatures (Tg) were measured by differential scanning calorimeter (DSC) (2920, TA Instruments), employing approximately 10 mg of the encapsulated sample. The data were chosen by a second scan performed under a dynamic nitrogen flow (40 mL/min) by first cooling to ~50°C and then heating to 200°C at a scanning rate of 10°C/min. The first scan was run to remove the thermal history. The value of glass transition temperature (Tg) was taken as the midpoint of the heat capacity transition region.

A Brookfield LV DV II+Pro Digital viscometer was used to evaluate the effect of the molecular weight of the solid (copolymer) content on the viscosity of the copolymer solutions (60 wt. % solid content). Small sample adapter accessory in combination with disposable sample chamber was utilized to measure the viscosity at a very small sample volume of 16 mL. The measurements were performed under ambient condition (1 atm, 24±2°C), using SC-25 spindle with a shear rate constant of 0.22. The shear rate is dependent...
on the rotational speed of the spindle, the size and the shape of the spindle and the sample chamber, and thus the distance between the chamber wall and the spindle surface. Consequently, the shear rate was calculated by multiplying the shear rate constant of the spindle (SRC = 0.22) with the selected spindle speed of 100 rpm, which gave a precise shear rate of 22 s⁻¹.

[0028] Contact angles were measured using deionized water and ethylene glycol with a Dake-Hart contact angle goniometer, model 100-00. Silicon wafers were cut into small square pieces and were cleaned in a solution of H₂SO₄ (70 wt. %) and H₂O₂ (30 wt. %), using a reflux condenser at a steam bath for an hour. Afterwards, wafers were washed with distilled water and dried with nitrogen gas. Later, silicon wafers were spin coated with diluted copolymer solutions. Six images of advancing and receding angles on three randomly chosen spots from each sample were taken using image-capturing equipment (Dazzle DVC, Dazzle media). The contact angles on both sides of the droplet were measured using the Scion Image. The average value of all the contact angles was used in calculating surface energy. In addition, the standard deviation of six measurements for each dynamic contact angle (advancing and receding) was calculated and reported as error. The measurements were performed under ambient condition (1 atm, 24±2°C).

[0029] The viscoelastic properties were measured on a dynamic mechanical thermal analyzer (Perkin Elmer Instruments, Pyris Diamond DMA), with a frequency of 1 Hz, in sinusoidal tension mode, and a heating rate of 3° C/min over a range of 50 to 200° C. N₂ flow rate set to 40 psi was circulated in the DMA furnace during the measurements. The gap distance was set at 2 mm for rectangular test specimens (length 15 mm, width 8-10 mm and thickness 0.05-0.08 mm). The maximum of the tan delta was used to determine the glass transition temperature, while the crosslink density was determined by utilizing the minimum storage modulus in the rubbery plateau.

[0030] An Instron universal electromechanical tester 5567 was used to conduct tensile testing of specimens for all the formulations. During the test, the rectangular test specimen (length 35 mm, width 6 mm and thickness 0.05-0.08 mm) was placed in the grips of the testing machine, carefully making sure the grips were tightened evenly and firmly, to prevent the slippage of the specimen while testing. The crosshead speed of the machine was set at the rate of 1 mm/min, which was calculated considering the specimen gauge length of 25 mm and strain rate of 0.04 mm/min. The specimen was pulled at the constant rate of extension. 10 specimens were tested for each formulation and those with the closest values were selected to obtain mean values. Standard deviations were indicated as error bars.

[0031] Oxygen permeability of crosslinked films was measured using an 8001 Model oxygen permeation analyzer (Illinois Instruments, Inc.). Each film sample with a 0.05-0.08 mm thickness was sandwiched between two steel masking plates, containing a circular hole centered in, smaller than the film sample size. Later, the plates were placed in the test chamber using a silicon-free film sealant. Pure oxygen gas (99.9%) at 40 psi was sent into the upper half of the chamber at a flow rate of 20 cm³/min while an oxygen-free (99.999% zero grade nitrogen) carrier gas at 40 psi was introduced through the lower half with 10 cm³/min flow rate. Oxygen molecules diffusing through the film into the lower chamber were carried to the sensor by nitrogen gas. This allowed a direct measurement of the oxygen transmission rate (OTR) through the films. The tests were conducted at 0% relative humidity under dry conditions and OTR units of measure were reported as (cm⁻³ O₂·m⁻²·day) and Barrer (10⁻¹⁰·(cm⁻³·O₂·cm⁻²·s⁻¹·mmHg⁻¹)). The 'cm⁻³' represents the thickness of the film. The 'cm⁻²' and 'mmHg⁻¹' are the reciprocals of the surface area of the film and the pressure of the oxygen gas, respectively.

[0032] The nD values of copolymers were measured at ambient temperature with an Abbe refractometer, model 60/HR (Epic, Inc.). The light source of the refractometer was sodium D1 (yellow) lamp. The refractive index of the prism, nDpervent, is 1.91617 at the used wavelength (λ) of 589.6 nm at 20° C. The copolymer solutions were discharged a few drops from the pipette directly onto the prism surface and the hinged prism box was closed over the sample. For the cured films, proper wetting liquids (nDpervent−nDsample/ nDpervent) with a known refractive index were used to coat the surfaces of the upper and lower prism, as well as the sample. The scale reading was performed at the field telescope, turning the control knob to a position where the observed field is divided into light and dark portions, the dark area below. The refractive index of the sample, nDsample, was derived directly from the scale reading using the following expression:

\[ n_{\text{sample}} = \sin(\alpha) \left/ \sqrt{(n_{\text{prism}})^2 \sin^2(\phi) + \cos^2(\alpha) \sin^2(\phi)} \right. \]

Where φ is the scale reading in degrees, α is 60.000°, β is 29.500°, and nDpervent is the index of the prism glass (1.91617).

[0033] The main objective of the current study was to synthesize acrylate-based copolymers with unique properties imparted by the presence of fluoroalkyl containing monomer, and the accurate balance among other nonfluorinated reactants. In addition, this study was carried out to investigate the effect of copolymer molecular weight, along with the effect of hydroxyl-functional chain transfer agent on the high-solids fluoroacrylates. Accordingly, a systematic characterization was conducted to acquire more detailed information about the fluorine inclusion into high solids acrylic coatings.

Preparation and Depiction of Copolymers

[0034] Low, medium, and high molecular weight acrylates were all synthesized in a semibatch system under monomer-starved conditions. The fluoroalkyl methacrylate monomer was added to the mixture of monomers along with initiator, solvent, and chain transfer agent, and added to the reaction over the entire course of the polymerization. The 2,2'-azobis (2-methylpropionitrile) was selected as an initiator due to the poor hydrogen-abstraining ability of its radicals [38]. Solution polymerization required that both the monomers and the resulting copolymer should be soluble under the reaction conditions in order to avoid precipitation, which would result in a decreased degree of polymerization and reaction rate. Methyl ethyl ketone was the preferred reaction solvent for the synthesis of the copolymers, due to the solubility of reactants and products. The number-average (Mn) and weight-average molecular weights (Mw), and the polydispersity index of copolymers were determined by GPC as shown in Table 4. It is observed that the PDI of the low molecular weight copolymers are close to 1.5, whereas the PDI of the higher molecular weight counterparts are closer to 2.0. The theoretical values of PDI for copolymers via radical recombination and disproportionation are 1.5-2.0, respectively [39, 40]. This suggests that the low molecular weight copolymers were produced mainly via termination of growing chain by radical recombination, and higher molecular weight copolymers terminated by disproportionation.
TABLE 4

<table>
<thead>
<tr>
<th>Copolymer Feed Ratio (vol. %)</th>
<th>MMA/BMA/HEMA (mol. %)</th>
<th>M_n (M/M)</th>
<th>Number-Average Molecular Weight (M_n)</th>
<th>Hydroxyl Equivalent Weight (M/M)</th>
<th>Viscosity (mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0-CTA5</td>
<td>MMA/BMA/HEMA</td>
<td>1873</td>
<td>1.55</td>
<td>5.7</td>
<td>327.6</td>
</tr>
<tr>
<td>Low M_n</td>
<td>35:15:30</td>
<td></td>
<td></td>
<td></td>
<td>74.4 ± 5.1</td>
</tr>
<tr>
<td>F0-CTA2.5</td>
<td>MMA/BMA/HEMA</td>
<td>6325</td>
<td>1.89</td>
<td>17.8</td>
<td>355.7</td>
</tr>
<tr>
<td>Medium M_n</td>
<td>35:15:30</td>
<td></td>
<td></td>
<td></td>
<td>355.1 ± 4.3</td>
</tr>
<tr>
<td>High M_n</td>
<td>35:15:30</td>
<td>11177</td>
<td>2.19</td>
<td>29.2</td>
<td>383.1</td>
</tr>
<tr>
<td>F5-CTA5</td>
<td>MMA/BMA/HEMA</td>
<td>1995</td>
<td>1.59</td>
<td>6.1</td>
<td>330.2</td>
</tr>
<tr>
<td>Low M_n</td>
<td>25:40:30</td>
<td>6699</td>
<td>1.74</td>
<td>18.7</td>
<td>358.9</td>
</tr>
<tr>
<td>F5-CTA2.5</td>
<td>MMA/BMA/HEMA</td>
<td>11823</td>
<td>2.21</td>
<td>30.6</td>
<td>386.9</td>
</tr>
<tr>
<td>Medium M_n</td>
<td>25:40:30</td>
<td>1937</td>
<td>1.52</td>
<td>5.9</td>
<td>333.9</td>
</tr>
<tr>
<td>High M_n</td>
<td>25:30:10</td>
<td>6143</td>
<td>1.97</td>
<td>16.9</td>
<td>353.5</td>
</tr>
<tr>
<td>F10-CTA5</td>
<td>MMA/BMA/HEMA</td>
<td>10987</td>
<td>2.02</td>
<td>28.0</td>
<td>392.3</td>
</tr>
<tr>
<td>Low M_n</td>
<td>25:30:10</td>
<td>6143</td>
<td>1.97</td>
<td>16.9</td>
<td>353.5</td>
</tr>
</tbody>
</table>

*10-%CTA0.5 = 10 vol. % TEMA (2,2,2-trifluoroethyl methacrylate); 0.5 wt. % CTA (chain transfer agent); based on total amount of the reaction monomers and the initiator.

*Number-average functionality = Number-average molecular weight (M_n)/hydroxyl equivalent weight.

*Hydroxyl equivalent weight = 100/(% TEMA, M_n of TEMA) * (% CTA/M_n of CTA) * %hydroxy-functional reactive group (HEMA or CTA)

*Viscosity (mPa·s) = (g of HEMA or CTA) / (100 g resin) ° 100.

A highly effective mercapta having hydroxyl functionality was used in order to reduce the molecular weight and to incorporate additional hydroxyl functionality into a significant number of oligomer molecules. Average functionalities were calculated by dividing the number-average molecular weight to the equivalent weight of copolymers. In addition, the effect of copolymer molecular weight on the viscosity of acrylic solutions (the copolymer content was 60% by weight) was also evaluated and all were summarized in Table 4.

Proposed structures of fluorinated acrylic copolymers and their non-fluorinated analogs are shown in FIG. 1.

Structural Characterization of Copolymers

The FTIR spectrum (FIG. 2) confirms the structure of the copolymer (F10-CTA5) in all aspects. From a comparison of the spectrum of poly(HEMA) with that of the copolymer, the broad absorption peak in the range 3300-6000 cm⁻¹ is attributed to O — H stretching in the 2-hydroxyethyl methacrylate (HEMA) moiety of the copolymer. Two distinct bands occurring at 2958 and 2877 cm⁻¹ are due to C — H stretching mode of methyl (CH₃) and methylene (CH₂) groups. In the copolymer, a strong C — O stretching vibration is observed at 1712 cm⁻¹. The carbonyl stretching vibration is due to the ester group. On the other hand, the ester group is observed at 2958 and 2877 cm⁻¹. The absorptions at 1452 and 1412 cm⁻¹ can be attributed to in-plane bending vibrations of C — H bonds in CH₃ groups [41]. The absorption band at 1365 cm⁻¹ is attributed to C — H bending vibration of CH₂ groups.

The characteristic absorption of C — C bond at 1640 cm⁻¹ disappears for all the copolymers. The absence of the peak in the copolymer is indicative of the participation of vinyl group in the copolymerization. Due to C — F stretching [42], F10-CTA5 shows a vibration in the range 1100-1300 cm⁻¹. Whereas, no characteristic band related to C — F bonds is observed in the FTIR spectra of fluorine-free copolymers. Two distinct bands occurring at 935 and 836 cm⁻¹ are due to out-of-plane C — H bending (twisting) vibrations of methyl and methylene groups. A strong band appears at 746 cm⁻¹ resulting from the in-plane rocking vibration of the methylene groups in the copolymer structure.

¹³C NMR shows a singlet in a region from 70 to 74 ppm, assigned to fluorine in —CF₂ group. The H NMR spectra of copolymers confirm the presence of C — CH₂ — CF₃ protons from 2,2,2-trifluoroethyl methacrylate (singlet around 4.4-5.3 ppm). The ¹³C NMR spectra of copolymers confirm the presence of C — CH₂ — CF₃ carbons from 2,2,2-trifluoroethyl methacrylate (singlet around 122 ppm). The other chemical shifts in the H and ¹³C NMR spectra are summarized in the experimental section (See Table 3).

The structure of acrylic copolymers has been characterized by MALDI-TOF mass spectrometry. MALDI-TOF was used for evidence of the anticipated end groups during the free-radical polymerization. All the low and medium molecular weight acrylic copolymers provided comparatively clearer mass spectra than high molecular weight (F0CTA0.5, F5CTA0.5, and F10CTA0.5) copolymers (M_n > 10 000). The shortcoming with M_n higher than 10 000 derives from the fact that the mass spectrometer used in the analysis has a limited resolution, much lower than needed for high molecular weight copolymers. This problem can be overcome by subjecting the copolymer to partial degradation to reduce the molar mass of the copolymer. As the degradation goes on, the length of the chain decreases and new end-groups are generated. However, the sequence of the partially degraded copolymer will be identical to the initial copolymer [43].

The enlarged mass spectrum of F10CTA5 (M_n = 1970) in the ion mass region of 1000-1500 was selected for a detailed analysis of copolymer composition and end groups (See FIG. 3). The analysis was applied directly to the unfractiomed sample. Three major series (A, B, and C) and four minor series (D, E, F, and G) were observed in the MALDI mass spectrum of F10-CTA5. The growing copolymer may terminate by the transfer of hydrogen or the other species from the initiator, solvent, or chain transfer agent present in the system. Therefore, each polymer chain might end with different species such as H/(Hydrogen)+; H+1 (Initiator); H+CTA (Chain Transfer Agent); 1+1; 1+CTA; CTA+CTA; H+S(Solvent); 1+S; S+S, and CTA+S.
Table 5 also presents the observed (experimental) ion mass value of the strongest signal (highest intensity) among the respective peaks in each peak cluster. Herein, random structure stoichiometry has been predicted based on the several end group possibilities. Calculated ion masses were compared with the experimental ones, and the m/z values are in agreement with an error less than or equal to 0.01%. As an example, ion mass of A series observed in the mass region of 1000-1200 (m/z = 1125.58 Da) almost agreed with the calculated mass values of the five possible copolymer chains with anticipated end groups as shown below.

$$\text{Ion Mass (m/z)}_{\text{calc}} = [\text{MMA}]_{\text{mon}} + [\text{BA}]_{\text{mon}} + [\text{HEMA}]_{\text{mon}} + [\text{TFEMA}]_{\text{mon}} + [\text{R}_1 \text{ and R}_2 \text{ terminal groups}] + [\text{Na}^+]$$

Among the respective peaks in each peak clusters, herein, random structure stoichiometry has been predicted based on the several end group possibilities. Calculated ion masses were compared with the experimental ones, and the m/z values are in agreement with an error less than or equal to 0.01%. As an example, ion mass of A series observed in the mass region of 1000-1200 (m/z = 1125.58 Da) almost agreed with the calculated mass values of the five possible copolymer chains with anticipated end groups as shown below.

$$\text{Ion Mass (m/z)}_{\text{calc}} = [\text{MMA}]_{\text{mon}} + [\text{BA}]_{\text{mon}} + [\text{HEMA}]_{\text{mon}} + [\text{TFEMA}]_{\text{mon}} + [\text{R}_1 \text{ and R}_2 \text{ terminal groups}] + [\text{Na}^+]$$

(ion Mass (m/z)$_{\text{calc}}$), the calculated mass of the copolymer, $\Delta[MMA]$ or $\Delta[BA]$ or $\Delta[HEMA]$ or $\Delta[TFEMA]$; the monoisotopic mass of the corresponding monomer unit, [Na$^+$]; the mass of the sodium ion.)
As shown in Table 5, the peak at about 1481 Da may be attributed to [(MMA)₆-(BA)₉-(HEMA)₉-(TFEMA)] Na⁺ chain with the end groups of S(Solvent) and CTA (Chain Transfer Agent) or it may correspond to [(MMA)₆-(BA)₉-(HEMA)₉-(TFEMA)] Na⁺, having H (Hydrogen) and CTA (Chain Transfer Agent) as end groups. The peaks corresponding to each series are interrelated with each other by the addition or subtraction of one butyl acrylate unit (128 Daltons), shown in FIG. 3. For example, [A+Na⁺] losses up to 3 butyl acrylate units from m/z=1509 to m/z=1125. Likewise, in [B+Na⁺] series, the difference between the peaks is also 128 Daltons (Da), which corresponds to the mass of butyl acrylate unit. The same interrelation is observed between the peaks of each series. In addition, [A+Na⁺] series is interrelated with [B+Na⁺] series at 1225 Da, loses one methyl methacrylate unit (100 Da) and shows a peak of [A+Na⁺] series at 1125 Da. Accordingly, [B+Na⁺] to [C+Na⁺]; [C+Na⁺] to [D+Na⁺]; [D+Na⁺] to [E+Na⁺]; [E+Na⁺] to [F+Na⁺]; and [F+Na⁺] series to [G+Na⁺] series, are all interrelated with each other by one methyl methacrylate unit (100 Da). Similar results for the other random copolymers (low and medium molecular weight series) with different monomer ratios in the feed were also confirmed by MALDI-TOF mass spectrometry (data not shown).

Surface Properties

Thin films were prepared by spin coating to investigate the wetting behavior of the copolymers. The wetting behavior was examined by contact angle measurements using two probe liquids. The largest possible angle, advancing angle, and the smallest possible contact angle, receding angle, for all the formulations were measured and tabulated in Table 4. The surface tensions of acrylic films were calculated from the average of advancing (θₐ) and receding (θₑ) contact angles. Owens-Wendt geometric mean with the two-liquid method [44] was applied. The equilibrium contact angle for a liquid drop on a solid surface is usually discussed in terms of Young’s Equation (3) and Fowke’s Equation (4).

\[
\gamma_s - \gamma_{sl} \cos \theta = \gamma_v \sin \theta
\]  
(3)

\[
\gamma_v = \gamma_s - \gamma_{sl}
\]  
(4)

where \(\gamma_s\), \(\gamma_{sl}\), \(\gamma_v\), \(\theta\), \(\gamma_p\), and \(\gamma_d\) are surface tension of solid, surface tension between solid and liquid, surface tension of liquid, contact angle, total surface tension, dispersion component, and polar component, respectively. The surface tension of solid surface and liquid, and their relationships are given by

\[
\gamma = \gamma_p + \gamma_d
\]  
(5)

\[
\gamma = \gamma_p + \gamma_d
\]  
(6)

\[
\gamma = \gamma_p + \gamma_d
\]  
(7)

where \(\gamma_p\), \(\gamma_d\), \(\gamma_p\), and \(\gamma_d\) represent the polar component, and dispersion component from the liquid and the solid, respectively. The surface tension of acrylic film was obtained from the contact angles and the surface tensions of two different probe liquids, deionized water (\(\gamma_w = 22.0 \text{ mJ/m}^2\), \(\gamma_d = 50.2 \text{ mJ/m}^2\), \(\gamma_p = 72.2 \text{ mJ/m}^2\)) and ethylene glycol (\(\gamma_w = 29.3 \text{ mJ/m}^2\), \(\gamma_d = 19.0 \text{ mJ/m}^2\), \(\gamma_p = 48.3 \text{ mJ/m}^2\)) by using the following expression driven from Equations (3) and (7).

\[
(1 + \cos \theta) = 2(\gamma_p \gamma_d)^{1/2} + 2(\gamma_p \gamma_d)^{1/2}
\]  
(8)

<table>
<thead>
<tr>
<th>Copolymers</th>
<th>Surface Tension (mJ/m²)</th>
<th>Contact angle (°)</th>
<th>Deionized Water</th>
<th>Ethylene Glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\gamma_p)</td>
<td>(\gamma_d)</td>
<td>(\theta_{adv})</td>
<td>(\theta_{rec})</td>
</tr>
<tr>
<td>F₀-CTA5</td>
<td>7.3</td>
<td>41.0</td>
<td>48.3</td>
<td>68.1 ± 1.8</td>
</tr>
<tr>
<td>Low M₅</td>
<td>10.5</td>
<td>34.6</td>
<td>45.1</td>
<td>70.9 ± 3.1</td>
</tr>
<tr>
<td>F₀-CTA2.5</td>
<td>8.6</td>
<td>36.7</td>
<td>45.3</td>
<td>74.4 ± 1.5</td>
</tr>
<tr>
<td>Medium M₅</td>
<td>28.4</td>
<td>7.6</td>
<td>36.0</td>
<td>93.8 ± 3.4</td>
</tr>
<tr>
<td>F₅-CTA5</td>
<td>25.6</td>
<td>10.2</td>
<td>35.8</td>
<td>96.2 ± 1.6</td>
</tr>
<tr>
<td>Low M₅</td>
<td>25.7</td>
<td>8.4</td>
<td>34.2</td>
<td>100.4 ± 2.0</td>
</tr>
<tr>
<td>F₅-CTA2.5</td>
<td>19.6</td>
<td>8.2</td>
<td>27.8</td>
<td>120.9 ± 3.5</td>
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<tr>
<td>Medium M₅</td>
<td>24.6</td>
<td>2.2</td>
<td>26.8</td>
<td>128.0 ± 2.2</td>
</tr>
<tr>
<td>F₁₀-CTA5</td>
<td>25.8</td>
<td>1.9</td>
<td>27.7</td>
<td>125.7 ± 0.9</td>
</tr>
</tbody>
</table>
The difference between the advancing and receding angles is referred to as the contact angle hysteresis, an important diagnostic tool of surface studies [45]. As summarized in Table 6, small amounts of fluorine on the surface report a fairly high advancing contact angle, since the liquid is reluctant to advance and to wet the surface. However, fluorine had relatively little effect on the receding contact angle. The advancing values for deionized water were quite high, whereas, receding values were lower. As a consequence, large values of hysteresis were found. Contact angle hysteresis was most likely caused by chemical heterogeneity of the topmost layer, and surface reconstruction of the polymer film after contact with the deionized water [46].

Contact angle measurements indicate that the surface of fluorinated acrylic copolymers has more hydrophobic character as compared to fluorine-free acrylates, and contact angle elevates when the amount of fluorine is increased in the copolymer composition. In addition, the surface energies of the P(MMA-ran-BA-ran-HEMA-ran-TFEEMA) are consistently lower than their P(MMA-ran-BA-ran-HEMA) fluorine free analogues, at equivalent percentages of chain transfer agent (CTA) incorporation. The lowest surface energies (around 27 mJ/m²) are reported for F10 series, which may be explained on the basis of the difference in the electromotive activity between fluorine and hydrogen, the higher carbon-fluorine bond strength, and the small bond polarization of carbon-fluorine bond [47].

Preparation and Coating Properties of Thermosetting Acrylics

The major crosslinking reaction between copolymer and melamine formaldehyde resin is depicted in FIG. 4. Bauer et al. [48] reported that the hydroxyl groups tend to be more reactive with fully alkylated melamines, via strong acid catalysis. Therefore, in our study, a commercial methylated MF Class 1 resin was used with a strong acid catalyst, p-toluenesulfonic acid monohydrate. After the acrylic copolymers were crosslinked with the MF resin; general coatings tests, as well as tensile, dynamic mechanical, barrier, and optical properties were evaluated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness</th>
<th>Adhesion</th>
<th>@20°</th>
<th>@60°</th>
<th>@90°</th>
<th>(B/in²)</th>
<th>(500 cycles)</th>
<th>Robs</th>
<th>Direct</th>
<th>Reverse</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>Low</td>
<td>5H</td>
<td>5B</td>
<td>78</td>
<td>108</td>
<td>93 ± 6</td>
<td>40</td>
<td>&gt;200</td>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td>Med</td>
<td>5B</td>
<td>75</td>
<td>104</td>
<td>134</td>
<td>15</td>
<td>25</td>
<td>&gt;200</td>
<td>3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>High</td>
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<td>101</td>
<td>147</td>
<td>6</td>
<td>20</td>
<td>&gt;200</td>
<td>3.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>F5</td>
<td>Low</td>
<td>5H</td>
<td>5B</td>
<td>88</td>
<td>126</td>
<td>110 ± 10</td>
<td>40</td>
<td>&gt;200</td>
<td>3.5</td>
<td>1</td>
</tr>
<tr>
<td>Med</td>
<td>5H</td>
<td>83</td>
<td>123</td>
<td>150</td>
<td>5</td>
<td>25</td>
<td>&gt;200</td>
<td>3.5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>5B</td>
<td>81</td>
<td>120</td>
<td>162</td>
<td>3</td>
<td>25</td>
<td>&gt;200</td>
<td>4</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>F10</td>
<td>Low</td>
<td>5B</td>
<td>95</td>
<td>139</td>
<td>128 ± 8</td>
<td>40</td>
<td>&gt;200</td>
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<tr>
<td>Med</td>
<td>5H</td>
<td>91</td>
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<td>178</td>
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<td>2</td>
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<tr>
<td>High</td>
<td>5B</td>
<td>90</td>
<td>132</td>
<td>186</td>
<td>5</td>
<td>20</td>
<td>&gt;200</td>
<td>4</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

The error is ±2 gloss units.

Table 7 presents coatings properties for cured films obtained from mixtures of copolymer series and melamine formaldehyde resin (films were cast and kept under ambient conditions for 12 h followed by thermal curing at 120° C. for 1 h). High hardness and high solvent resistance were observed for all of the films. Gray [32] previously evaluated the thermoset coatings of the acrylic oligomers which were prepared by using different hydroxy-functional and nonhydroxy-functional chain transfer agents. His results indicated that hydroxy-functional mercaptans gave better hardness and solvent resistance to the coating than nonhydroxy-functional mercaptans. Therefore, it is postulated that the hydroxy-functional chain transfer agent, 2-hydroxyethyl mercaptan, in the formulations boosted the hardness, as well as positively altered the overall performance of the films.

As observed in Table 7, pencil hardness, crosshatch adhesion, and appearance of the films are almost identical with those of the non-fluorinated control. However, a higher degree of gloss was observed with an increase in the fluorine content and with a lower molecular weight. Gloss measurements with an incident light at 20° and 60° were performed on the acrylic films cured on the steel substrates, in order to quantify the amount of light reflected at the specular angle from the surface. Since the readings obtained at 60° were over 70, the readings at 20° were also made to obtain higher precision. For example, gloss at 20° for F0 (low Mₙ) was measured as 78 but reached to a value of 95 for F10 (low Mₙ). On the other hand, abrasion resistance and adhesion to the substrate enhanced for higher molecular weight copolymers. After 500 cycles on the Taber abraser, less weight loss was detected for acrylic coatings prepared with high molecular weight copolymers. These coatings also showed better adhesion (186 lb/in.²) in the pull-off adhesion test.

Tensile properties of copolymers are summarized in FIG. 5(a) and 5(b). FIG. 5 clearly shows that tensile strength and tensile modulus values uniformly increased upon introduction of increasing levels of TFEEMA for films cast from acrylic copolymers with the MF resin. When crosslinking agent was introduced, tensile strength and modulus improved significantly as expected with respect to films without crosslinker [49].

Both tensile modulus and tensile strength are greatly influenced by the molecular weight of the copolymers, and crosslink density of the films prepared with the corresponding copolymers. This results in an increase of tensile modulus and...
their nonfluorinated counterparts. While the highest modulus (3000 MPa) was revealed at 10% TFEMA for a high molecular weight copolymer, the lowest value observed (1000 MPa) was at 0% TFEMA content for a low molecular weight copolymer. Likewise, the tensile strength increased up to 35 MPa, resulting from 10% TFEMA content at the high molecular weight copolymer, whereas the lowest value of the tensile strength was reported as 15 MPa at the fluorine-free low molecular weight copolymer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C) by DSC</th>
<th>Storage Modulus (N/m²)</th>
<th>Crosslink Density (mol/m³)</th>
<th>Tg (°C) by DMA</th>
<th>Max. tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>12</td>
<td>7.3E+06</td>
<td>666</td>
<td>117</td>
<td>0.65</td>
</tr>
<tr>
<td>Med</td>
<td>29</td>
<td>11.0E+06</td>
<td>1073</td>
<td>125</td>
<td>0.37</td>
</tr>
<tr>
<td>High</td>
<td>42</td>
<td>26.5E+06</td>
<td>2278</td>
<td>128</td>
<td>0.26</td>
</tr>
<tr>
<td>F5</td>
<td>8</td>
<td>7.6E+06</td>
<td>723</td>
<td>121</td>
<td>0.52</td>
</tr>
<tr>
<td>Low</td>
<td>26</td>
<td>18.3E+06</td>
<td>1729</td>
<td>128</td>
<td>0.26</td>
</tr>
<tr>
<td>High</td>
<td>41</td>
<td>25.3E+06</td>
<td>2209</td>
<td>135</td>
<td>0.18</td>
</tr>
<tr>
<td>F10</td>
<td>14</td>
<td>9.8E+06</td>
<td>863</td>
<td>118</td>
<td>0.29</td>
</tr>
<tr>
<td>Low</td>
<td>30</td>
<td>22.8E+06</td>
<td>2163</td>
<td>120</td>
<td>0.27</td>
</tr>
<tr>
<td>High</td>
<td>44</td>
<td>26.9E+06</td>
<td>2444</td>
<td>130</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Glass transition temperatures of the copolymers are shown in Table 8. Lower glass transition temperatures are observed for F5 series copolymers in comparison to their F0 and F10 counterparts. The higher amount of n-butyl acrylate (Tg of the high molecular weight homopolymer: ~54°C) in the F5 formulations causes a slight decrease in the Tg values. Alternately, the increase of MMA to TFEMA ratio in the composition does not affect the Tg drastically, although the glass transition temperature of poly(MMA) is always lower than that of poly(MMA). For all the low molecular weight copolymers, Tg values are below the room temperature. As the molecular weight of copolymers increases, higher Tg values are observed. The dependence of glass transition temperature on molecular weight was previously reported by Gibbs and DiMarzio [50]. They made quantitative predictions concerning the variations of glass transition temperature with molecular weight and concluded that for amorphous polymers, Tg increased with molecular weight toward asymptotic limits, which were reached at a number average molecular weight of about 10,000 [51, 52]. Mazzola et al. [12] also reported the increase of Tg with the increase in molecular weight of partially fluorinated acrylic copolymers based on ammonium 2-fluoroacrylate and acrylic acid.

The crosslink densities of the cured films were calculated using viscoelastic measurements from dynamic mechanical analysis. The crosslink density of the film has been defined as the moles of effectively elastic network chains per cubic meter of sample [53, 54]. The storage modulus (E’ values) at temperatures well above the Tg of the cured material is an indication of crosslink density [55]. The crosslink density can be calculated by using the following expression derived from the theory of rubber elasticity [56], where R is the gas constant (8.3145 N·m·molecule·K), T is the absolute temperature in Kelvin, and $E'_{min}$ is the minimum value of elastic modulus in the rubbery plateau:

$$n_c = \frac{E'_{min}}{3RT} \quad (9)$$

The Tg, E’min, crosslink density, and the maximum tan δ for the nine coating films are also summarized in Table 8. The Tg of the crosslinked films was obtained from the maximum of the α-transition. For F0 series, Tg increased from 117 to 128°C with the increase in copolymer molecular weight, while the crosslink density increased from 660 to 2278 mol/m³. For F5 series, Tg increased from 121 to 135°C when the molecular weight of the copolymer was increased, likewise the crosslink density increased from 723 to 2209 mol/m³. Even the higher fluorine percentage (10%) did not change this trend (low molecular weight F10 had a Tg of 118°C with a crosslink density of 863 mol/m³ and the Tg increased up to 130°C and the crosslink density reached a value of 2444 mol/m³). A result, the findings were as crosslinking proceeds, Tg increases, and the height of the tan δ peak decreases as extent of cure increases (See Table 8). Glass transition temperatures of the final reacted coatings were higher than those of uncured copolymer counterparts. Readily crosslinked films formed strong networks and gave high crosslink density, measured at temperatures around 50°C above the glass transition temperature of the cured films.

Barrier and Optical Properties

Oxygen permeability values at 25°C are reported as cc/m²/day in Table 9. The oxygen transmission rate (OTR) of each film is presented as the average value of the last 20 data points observed in the plateau region of OTR versus time graph, and the standard deviation is reported as less than 3%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>nD (copolymer)</th>
<th>nD (film)</th>
<th>Oxygen Permeability (cc/m²/day)</th>
<th>Oxygen Permeability (Barrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>1.46557</td>
<td>1.53068</td>
<td>600 ± 7</td>
<td>0.235 ± 0.003</td>
</tr>
<tr>
<td>Med</td>
<td>1.46643</td>
<td>1.53212</td>
<td>420 ± 5</td>
<td>0.165 ± 0.002</td>
</tr>
<tr>
<td>High</td>
<td>1.46782</td>
<td>1.53857</td>
<td>356 ± 10</td>
<td>0.120 ± 0.003</td>
</tr>
<tr>
<td>F5</td>
<td>1.45543</td>
<td>1.50017</td>
<td>960 ± 20</td>
<td>0.376 ± 0.007</td>
</tr>
<tr>
<td>Low</td>
<td>1.45716</td>
<td>1.50857</td>
<td>560 ± 8</td>
<td>0.219 ± 0.003</td>
</tr>
<tr>
<td>High</td>
<td>1.45813</td>
<td>1.51879</td>
<td>430 ± 5</td>
<td>0.168 ± 0.002</td>
</tr>
<tr>
<td>F10</td>
<td>1.43479</td>
<td>1.49045</td>
<td>1670 ± 50</td>
<td>0.653 ± 0.020</td>
</tr>
<tr>
<td>Low</td>
<td>1.43577</td>
<td>1.49066</td>
<td>916 ± 35</td>
<td>0.359 ± 0.013</td>
</tr>
<tr>
<td>High</td>
<td>1.43883</td>
<td>1.49130</td>
<td>907 ± 20</td>
<td>0.254 ± 0.007</td>
</tr>
</tbody>
</table>

The mean value of 3 refractive index measurements is reported. The standard deviation is less than or equal to 0.0001.

In F0 series, a significant decrease of OTR from 0.235 to 0.120 Barrer (48%) is observed with the increase of the number average molecular weight of the copolymer from $M_n=1873$ to $M_n=1177$. As for F10 series, the oxygen transmission rate seems to be more noteworthy with 61% reduction from low molecular weight (F10-CTA5, $M_n=1790$) to high molecular weight (F10-CTA5.5, $M_n=10987$). On the contrary, the inclusion of fluorinated monomer leads to poorer barrier properties. The OTR value increases by a factor of 2.1 for low $M_n$ copolymers (from F0CTA5, $M_n=1873$ to F10CTA5, $M_n=1790$) and 2.8 for high $M_n$ counterparts (from
while the TFEMA concentration goes from 0 to 10 vol. %.

[0058] The refractive indices of the copolymers before and after curing were also compared (see Table 9). Fluorine-substituted monofunctional methacrylate monomer has been demonstrated to have significant effects on the optical properties. Liu et al. [57] studied the copolymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) with methyl methacrylate (MMA) in fluoroalkanol to obtain a good cladding material for an optical fiber based on poly(methyl methacrylate) (PMMA). They compared the refractive index of the PMMA film with that of the copolymer and related the lower refractive index of the copolymer to the presence of fluorinated units. In our study, for low molecular weight copolymer solutions, refractive index value decreased from 1.46557 to 1.43479; and for cured films, refractive index value decreased from 1.53068 to 1.49045, while 2,2,2-trifluoroethyl methacrylate increased from 0 to 10% in the composition. The inclusion of fluorinated monomer in the standard formulation also resulted in improved refractive index, by lowering the value 2.1% and 3% for medium and high molecular weight copolymers respectively.

[0059] Acrylate-based copolymers were successfully synthesized with different acrylate monomers to obtain new high-solids surface active acrylics with potential uses for the automotive industry. Surface properties initially motivated this study of adding fluorine to the coating. Obviously, there are a range of properties that fluoropolymers bring to the final film, including chemical inertness, thermal resistance, low friction, and water repellence. For dielectric properties and thermal resistance, the use of large quantities of fluorine throughout the coating may be necessary. However, the incorporation of small amounts of fluoroalkyl monomers (5-10 wt. %) to copolymerization was anticipated as adequate to obtain the desired surface properties, thus there is no need of large amounts of fluorinated groups throughout the bulk of the film.

[0060] As for the general coating properties, Malshe et al. [11] previously studied the coating properties of fluorinated acrylic copolymers based on methyl methacrylate (MMA), butyl acrylate (BA), and 2-hydroxy ethyl methacrylate (HEMA). They partially esterified the hydroxyl functionality of HEMA with tetrafluoro propionic acid and cured the polymer with butylated melamine formaldehyde resin. In their study, fluorine incorporation extended the protective ability of coating against corrosion; however, coating properties (i.e. pencil hardness, gloss, impact resistance, solvent resistance) were not noticeably improved. The low levels of fluorine used in the top coat copolymer did not change the coating properties of the film drastically, but acrylic films with higher solvent resistance, pencil hardness, and gloss were obtained as compared to the study reported by Malshe and coworkers [11]. Not being bound by theory, it may be due to the fact that the copolymers with higher hydroxyl functionality caused films to become stronger and more solvent resistant due to the crosslinking reactions, and the less tendency of uncrosslinked copolymers to act as plasticizers [58].

[0061] It is well known that fluoroalkyl containing monomers are used in contact lenses to improve oxygen permeability [59]. Poly(methyl methacrylate) (PMMA) was previously reported as a barrier to oxygen with a transmission rate of 0.5 Barrer, which was not suitable for extended wear, thus new fluoroacrylate-based contact lens materials with improved levels of oxygen permeability were introduced later. In the instant invention, the increase in fluorine concentration also caused a higher oxygen transmission rate. However, the values were found to be still considerably low as compared to the ones in polymeric contact lens materials [60].

[0062] Higher molecular weight acrylates respond with a high modulus and crosslink density (see FIG. 5 and Table 8); consequently, causing a significant increase in the effective diffusion path length of gas molecules, leading to appreciable reductions in oxygen permeability. As expected, O2 permeability was confirmed to be inversely related to the crosslink density and the molecular weight. The higher crosslink density (the lower free volume) in organic domains associated with the higher molecular weight (higher number-average functionality) resulted in decrease of oxygen transmission rate (see Table 9). Permeability to small molecules; particularly water and oxygen, contributes to corrosion. Therefore, it is very satisfactory that low oxygen transmission rates were obtained for the protective coatings.

[0063] The acrylic resins described in this paper also satisfy the environmental regulations with a higher solids content. The surface active, high barrier acrylic coatings were formulated with reduced solvent levels, which can still be applied using conventional equipment. The usage of lower molecular weight acrylic copolymers resulted in reducing the viscosity (see Table 4). In addition, the oxygenated solvent, methyl ethyl ketone (MEK), had also a favorable viscosity reduction profile for these acrylic copolymers. Even though MEK has still been labeled as a volatile organic compound (VOC), the removal of MEK from hazardous air pollutants (HAPs) list occurred at the end of 2005 [61]. As a result, the aforementioned acrylic resins with a solids content of 60% by weight are suitable for use in high-solids clearcoats for automotive original equipment manufacturer (OEM) coating systems, which are still mostly solventborne.

[0064] In view of the teaching presented herein, it is to be understood that numerous modifications and variations of the present invention will be readily apparent to those of skill in the art. For example, while the invention has primarily been described with reference to methyl methacrylate, n-butyl acrylate, 2-hydroxyethyl methacrylate, and 2,2,2-trifluoroethyl methacrylate, other acrylic copolymers containing fluoroalkyl containing monomers are included within the scope of the present invention. As such, the foregoing is illustrative of specific embodiments of the invention but is not meant to be a limitation upon the practice thereof. It is the following claims, including all equivalents, which define the scope of the invention.

[0065] We claim:

REFERENCES

[0121] [56] Pascual, J. P.; Sautereau, H.; Verdu, J.; Williams, R. J., Thermosetting Polymers, Marcel Dekker, NY, 2002.
1. A top coat composition comprising:
   at least one of an acrylate and methacrylate selected from a
   group consisting of a fluorinated acrylate, a fluorinated
   methacrylate, a fluorinated hydrocarbon copolymerized
   with an acrylate, a fluorinated hydrocarbon copolymer-
   ized with a methacrylate and combinations thereof; and
   a crosslinking agent.
2. The top coat composition of claim 1, wherein said acry-
   late is a plurality of acrylates.
3. The top coat composition of claim 2, wherein said plu-
   rality of acrylates are selected from a group consisting of
   methyl methacrylate, n-butyl acrylate and 2-hydroxyethyl
   methacrylate.
4. The top coat composition of claim 1, wherein said flui-
   orinated methacrylate is 2,2,2-trifluoromethyl methacrylate.
5. The top coat composition of claim 1, wherein said at
   least one of said acrylate and said methacrylate is between
   1 and 25 wt % of said top coat composition.
6. The top coat composition of claim 1, wherein the at
   least one of said acrylate and said methacrylate is between
   2.5 and 15 wt % of said top coat composition.
7. The top coat composition of claim 1, wherein said
   crosslinking agent is methylated melamine formaldehyde
   resin.
8. The top coat composition of claim 1, wherein said
crosslinking agent is an ethylene glycol acrylate.
9. The top coat composition of claim 1, wherein said
crosslinking agent is a methylenebisacrylamide.
10. The top coat composition of claim 1, wherein said
crosslinking agent is a methylenebisacrylamide.
11. A process for making a top coat composition compris-
    ing providing a solvent;
    contacting the solvent with at least one of an acrylate and a
    methacrylate selected from a group consisting of a flu-
    orinated acrylate, a fluorinated methacrylate, a fluori-
    nated hydrocarbon copolymerized with an acrylate, a
    fluorinated hydrocarbon copolymerized with a meth-
    acrylate and combinations thereof;
    adding a chain transfer agent and an initiator to form a
    copolymer; and
    contacting the copolymer with a crosslinking agent.
12. The process of claim 11, wherein the acrylate is a
    plurality of acrylates.
13. The process of claim 12, wherein the plurality of acry-
   lates are selected from a group consisting of methyl
    methacrylate, n-butyl acrylate and 2-hydroxyethyl
    methacrylate.
14. The process of claim 11, wherein the fluorinated meth-
    acrylate is 2,2,2-trifluoromethyl methacrylate.
15. The process of claim 11, wherein the at least one of the
    acrylate and the methacrylate is between 1 and 25 wt % of
    the top coat composition.
16. The process of claim 11, wherein the at least one of the
    acrylate and the methacrylate is between 2.5 and 15 wt % of
    the top coat composition.

* * * * *