UV-Curable PFPE-(Meth)acrylates: a new class of UV-Curable Resins

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SPECIALTY POLYMERS

PFPE-(Meth)acrylates - Portfolio

Product	Functionality	Fluorine content (% by wt.)	Chemical-physical properties
Fluorolink MD700	Bifunctional Urethane Methacrylate	52	Appearance = clear R.I. = 1.342 Viscosity (25°C) = 430 cP
Fluorolink AD1700	Tetrafunctional Urethane Acrylate	24	70% w/w dry content in Butyl Acetate / Ethyl Acetate [Acrylics] = 2.67 Eq/kg
Fomblin MD40	Bifunctional Urethane Methacrylate	58	Appearance = clear R.I. = 1.313 Viscosity (25°C) = 695 cP

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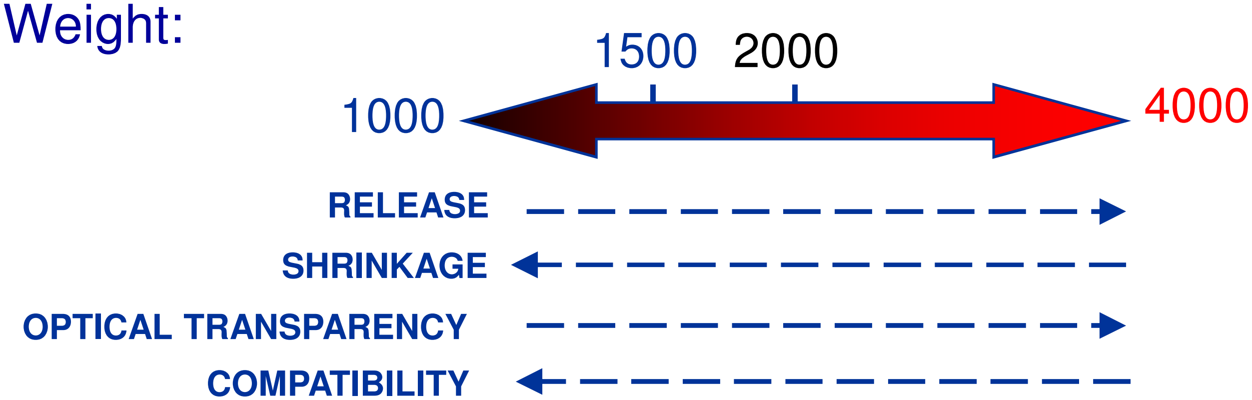
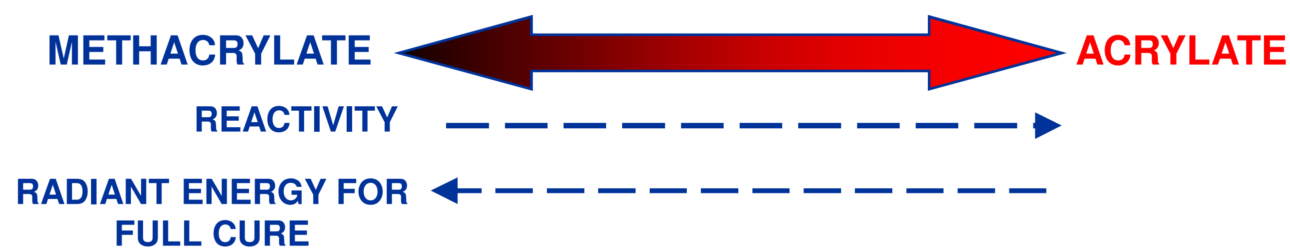
PFPE-(meth)acrylates: structure – property relationship

- PFPE Molecular Weight:



- Type of End-group:



UV- curable Perfluoropolyethers

Bifunctional

PFPE-urethane (meth)acrylates

Fluorolink MD700: chemical-physical properties

$CH_2=C(CH_3)-\underset{\underset{O}{||}}{C}-O$ $CH_2CF_2O-[-(CF_2CF_2O)_m-(CF_2O)_n-]-CF_2CH_2$ $O-\underset{\underset{O}{||}}{C}-C(CH_3)=CH_2$

PFPE backbone
MW_n = 1800 AMU

Short linear aliphatic
urethane block

- R.I. (25°C) = 1.342, [F] = 52% (w/w), η (25°C) = 430 cP
- Miscible with conventional acrylic monomers, but only in a well defined window
- Blooms very effectively to the surface of the coating, imparting low surface energy, water/oil repellence, antisticking properties

Fomblin MD40: chemical-physical properties

$CH_2=C(CH_3)-C(=O)-O$ ~ $CH_2CF_2O-[-(CF_2CF_2O)_m-(CF_2O)_n-]-CF_2CH_2$ ~ $O-C(=O)-C(CH_3)=CH_2$

PFPE backbone
MWn = 4000 AMU

Urethane block

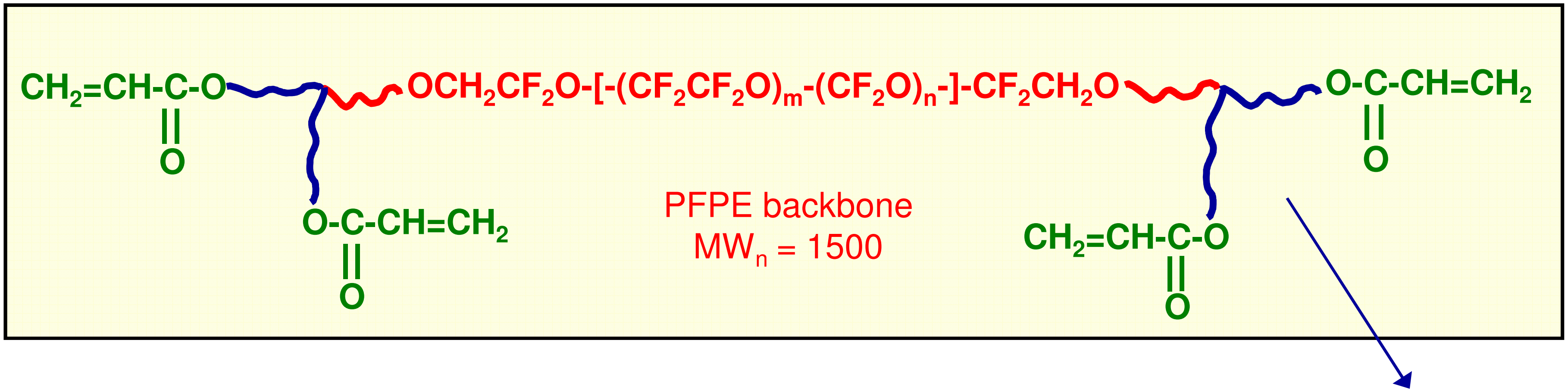
- R.I. (25° C) = 1.313, [F] = 58% (w/w), η (25° C) = 695 cPoise
- Soluble only in fluorinated solvents (Galden from Solvay Specialty Polymers)
- Compatible with: Darocur 1173 (≤ 1% w/w), Irgacure 184 (≤ 0.5% w/w)
- The homopolymer is an elastomer with outstanding chemical resistance, low surface energy and exceptional antisticking properties, low elastic modulus

UV- curable Perfluoropolyethers

Tetrafunctional

PFPE-urethane (meth)acrylates

Fluorolink AD1700: chemical-physical properties



Long cyclo-aliphatic
Urethane block

- Tetrafunctional derivative
- [F] = 24 % (w/w)
- Soluble in AcOEt, MEK, BuOAc
- Good compatibility with commercial UV-curable paints
- Suggested use: low surface energy additive for UV-curable paints, effective in providing easy removal of fingerprints

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UV-curing conditions: remarks

- PFPE-(meth)acrylates are strongly affected by oxygen inhibition.

- Curing under nitrogen is recommended for all the formulations with a high PFPE content; PFPE-acrylates (Fluorolink AD1700) can be cured in the air by choosing the proper package of reactive diluents and photoinitiators.

- Standard curing in the air can be applied when using PFPE-(meth)acrylates at additive levels

- Among the many possible combinations of photoinitiators, Darocur® 1173 (optionally in combination with Irgacure® 127) gives the best performance.

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UV- curable Perfluoropolyethers

Materials Characterization

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Shrinkage upon curing

Material	Molecular Weight (AMU)	Shrinkage upon curing
FLK MD700	1800	6.0%
Fomblin MD40	4000	1.7%

The shrinkage is inversely proportional to the Molecular Weight of the oligomer (distance between two crosslinking sites)

Surface Properties Characterization

Cured Material	SYLGARD 184	FLK MD700	Fomblin MD40
S.C.A. vs. H_2O	101°	113° ± 2°	113° ± 2°
S.C.A. vs. *n*-C_{16}	—	58°± 2°	52° ± 2°

γ ~ 25 mN/m

γ ~ 12 mN/m

- PFPE-based elastomeric materials show an outstanding W/O Repellency.
- Silicones display a higher surface energy than PFPEs and are not oil repellant.

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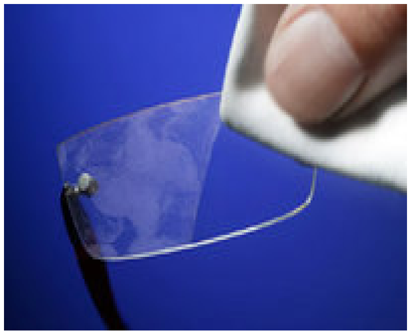
Chemical Resistance (Swelling)

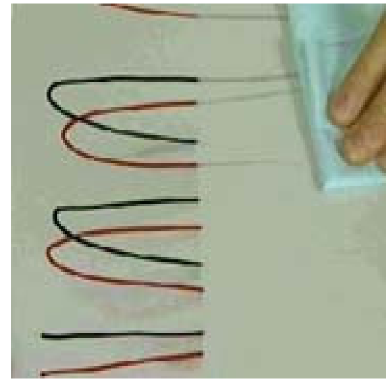
Material	Swelling into MIBK (% w/w)	Swelling into CH_2Cl_2 (% w/w)	Swelling into MEK (% w/w)
SYLGARD 184	72	133	57
FLK MD700	11	13	13
Fomblin MD40	**4**	**7**	**0**

All the measurements were performed at the equilibrium

- PFPE-based elastomers are not swollen by hydrogenated organic solvents
- Cured Fomblin MD40 shows the best chemical resistance
- Only fluorinated solvents are able to swell the cured PFPE elastomers

UV-curable PFPEs: markets and applications





PFPE-(METH)ACRYLATES

> 60% (w/w)
PFPE content

< 5.0% (w/w)
PFPE content

Optics/Photonics

Anti Reflective/Antismudge Top Coats

Polymeric Waveguides, Cladding of Optical Fibers

Additives for UV-curable paints

Surface energy reduction, Water/Oil Repellency, Antigraffiti, Easy Removal of Fingerprints

High PFPE content: formulation for aluminum

Composition (parts by weight)	Chemical-physical properties	Substrate	Pencil Hardness	MEK d.r.	Cross Cut Test
- Fluorolink AD1700 50.0 - HDDA 15.0 - THFFA 50.0 - Darocur 1173 4.0 - Sartomer CN386 1.0 - Benzophenone 1.0	Thickness = 60 µm Visc.(25°C) = 65 cP % PFPE = 13.3 γ_c = 19.9 ± 0.2 mN/m	Aluminum Q-panels	H	> 200	100%

Curing conditions (air): 6x10 m/min, H bulb 13 mm, UV power System VPS 1600 (240 W/cm)

- Formulation which combines low surface energy, outstanding chemical resistance and flexibility.
- Self-Healing effect: once the coating is scratched, it flows back into the scratch, returning the surface to its original smooth state (effect of the low T_g of the PFPE chain)

Formulation for aluminum: FLK AD1700 vs. silicone acrylate

Composition (parts by weight)	Static Contact Angle vs. H_2O (°)	Static Contact Angle vs. *n*-hexadecane (°)	Surface Energy (mN/m)
FLK AD1700 - HDDA - THFFA 35(dry content):15:50	**109±1**	**63±1**	**15.0**
Silicone acrylate-HDDA-THFFA 35:15:50	**99±3**	**28 ± 1**	**25.0**

Curing conditions (air): 6x10 m/min, H bulb 13 mm, UV power System VPS 1600 (240 W/cm)

Fluorolink AD1700 outperforms silicone-acrylates in terms of surface energy reduction

Fluorolink AD1700 as a coating surface modifier

Commercial UV-curable formulations loaded with 1%, 2%, and 5% w/w of Fluorolink AD1700 (thickness = 15 µm, Substrate = PMMA):

Test	Blank	1% w/w FLK AD1700	2% w/w FLK AD1700	5% w/w FLK AD1700
Static Contact Angle vs. H_2O (°)	82 ± 5	103 ± 3	109 ± 3	113 ± 1

- **Fluorolink AD1700 improves the water repellency at a low dosage.**
- **Excellent compatibility with the hydrogenated formulations.**

PFPE-(meth)acrylates: conclusions

PFPE-(meth)acrylates are liquid oligomers characterized by unique properties:

- Very low R.I., high thermo-optic coefficient
- Low Surface Energy
- Ability to migrate to the surface of the coating
- Do not contain any PFOS and PFOA

which make them ideal raw materials for manufacturing:

- Coatings having outstanding water/oil repellency, antigraffiti properties, easy cleanability of stains and fingerprints

- Optical coatings for lenses, displays, photonic devices, etc..

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