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Fluorinated polymeric materials for the protection of monumental buildings

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SUMMARY: A study was performed based on the preparation of fluorinated polymers, where several H-atom in different positions were replaced with F-atom by selecting different fluoro containing acrylic monomers and by copolymerization with nonfluorinated acrylates or vinylethers. The structure design was aimed to optimize (e.g. minimize) the fluorine content of the final material while obtaining improved chemical and photochemical stability, good filmability and impermeability against condensed water as possible carrier of aggressive chemicals.

The suitability of these new materials for protective coating of stones is tested by evaluating their stability to UV-Vis irradiation and their selective permeability to water vapour vs. condensed water.

Introduction

Free radical copolymerization, which can also be convenient for developing water emulsions or suspensions, is used with selected fluorinated acrylic or acrylic-like derivatives and with non-fluorinated analogs to produce various structurally different materials having a given average fluorine content.

The replacement of hydrogen with fluorine atoms improves chemical, thermal and photochemical stability of polymeric materials 1), while the consequent reduction of surface energy produces a high repellency for condensed water 2). On the other hand the presence of fluorine can dramatically affect the chemical reactivity and the most common fluorinated

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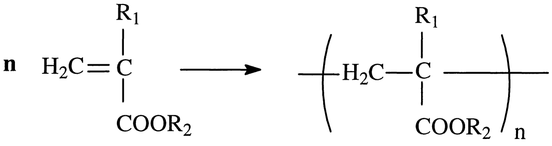
monomers, such as tetrafluoroethylene, vinylidene fluoride and vinyl fluoride, need complex procedures for their conversion into macromolecular compounds3), whereas fluoroalkyl-acrylic monomers can be easily homo- and copolymerized by free radical mechanism to yield side chain fluorinated polymers.

Partially fluorinated acrylic polymers have been studied in the last years in order to assess their suitability to be employed as coating materials for outdoor protection of different type of lythotypes4-6).

Starting with acrylate monomers having the general structure (**I**)



$$n\ H_2C{=}\underset{COOR_2}{\overset{R_1}{C}} \longrightarrow \left(H_2C-\underset{COOR_2}{\overset{R_1}{C}} \right)_n$$

I

various modifications were introduced by replacing hydrogen with fluorine atoms or fluoroalkyl groups in the backbone (R1) 7), or in the side chain (R2) 8).

The structure design was aimed at obtaining improved chemical and photochemical stability, good filmability and impermeability against condensed water while optimizing (e.g. minimizing, for obvious economical reasons) the fluorine content of the final material. Fluorine content and distribution in the macromolecules is modulated through selection of different monomers with high (e.g. 1H,1H,2H,2H-perfluorodecylmethacrylate, XFDM) and low (e.g. 2,2,2-trifluoroethylmethacrylate, TFEM) fluorine content, and their copolymerization with not fluorinated acrylates or methacrylates with either linear or branched alkoxy chains.

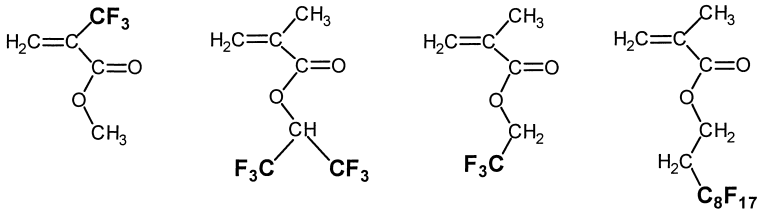
Accelerated photooxidation treatments to evaluate the photostability of these new materials are carried out by irradiation of thin polymer films with a Xenon lamp which simulates the spectrum of solar light.

Finally two different carbonatic lithotypes widely used in Italian historical monuments and characterized by different porosity, namely Noto Stone (Sicily) and Candoglia Marble (north Italy), are employed to evaluate the performance of these polymeric materials as protective coatings.

Preparation of partially fluorinated acrylic copolymers

The fluorinated monomers used for the preparation of the polymers described in this paper are reported in the scheme 1.

Homopolymers of the three side-chain fluorinated monomers were easily obtained in good yield with α,α-azobisisobutyronitrile (AIBN) as the initiator, their polymerization following the conventional mechanism and kinetics of free radical polymerization of acrylates with the possibility of regulating molecular weight by proper chain transfer agents 9) and of carrying out emulsion polymerization10). In order to obtain polymers with variable content of fluorine and modulated properties, random copolymerization11) with several nonfluorinated acrylates was also attempted (Table 1).



MTFMA **HFIM** **TFEM** **XFDM**

Scheme 1. Fluorinated monomers employed: methyl-α-trifluoromethylacrylate (MTFMA), 1,1,1,3,3,3-hexafluoro-2-propylmethacrylate (HFIM), 2,2,2-trifluoroethylmethacrylate (TFEM), and 1H,1H,2H,2H-perfluorodecylmethacrylate (XFDM)

Methyl-α-(trifluoromethyl)acrylate (MTFMA) and 1,1,1,3,3,3-hexafluoro-2-propylmethacrylate (HFIM) are characterized by an electron-poor double bond and are expected to give easy, mainly alternating copolymerization with comonomers having an electron-rich double bond12) such as vinyl ethers (Table 2).

Tab. 1. Side chain fluorinated acrylic copolymers (MA=methylacrylate, EHA=2ethylhexylacrylate, MM=methyl-, BM=butyl-, OM=octyl-, LM=lauryl-, and EHM=2ethylhexylmethacrylate)

Copolymer	Molar composition	F, wt %	T_g, °C
XFDM/MA	1/16	17	15
XFDM/MM	1/1	51	46
	1/20	13	110
XFDM/BM	3/2	52	45
	1/6.5	22	29
XFDM/OM	1/3.8	21	-6
	1/5.2	2	-2
XFDM/LM	1/1.2	38	27
	1/5.4	17	-9
XFDM/EHM	1/4	24	20
	1/8	15	13
XFDM/EHA	1/5	22	-52
	1/14	10	-63
TFEM/MA	2/1	27	43
TFEM/BM	1.5/1	22	69
	1/1.7	14	57
TFEM/OM	1.8/1	21	43
	1/1.4	13	27
TFEM/LM	2.3/1	20	38
	1/2.6	7	1

With both MTFMA and HFIM the copolymers were mainly alternating, with the fluoromethacrylate units in slight excess (Table 2). The degree of alternation, evaluated by ^{1}H-NMR analysis, is somewhat higher in case of the bulkier t-BVE vinyl ether$^{7)}$. More structurally disordered copolymers with vinyl ethers were obtained when using TFEM (0.77 mole fraction when starting from equimolar feed with BVE) and XFDM (giving a XFDM/EHVE 86/14 mole ratio copolymer, i.e. with a composition very close to the 89/11 mole ratio of a MM/BVE copolymer). The trend towards alternation, at least with EHVE, is thus in the order:

MTFMA ÷ HFIM > TFEM > XFDM ≥ MM

All side chain fluorinated copolymers are amorphous and their T_g can be modulated over a broad interval (Tables 1 and 2), by varying composition and/or monomers structure.

Tab. 2. "Quasi" alternating copolymers obtained from bulk polymerizations: equimolar feed ratio. BVE=n-butyl-, i-BVE=i-butyl-, t-BVE=t-butyl-, EHVE=2-ethylhexyl-, CHVE=cyclohexyl- and MVE=methylvinylether

Polymer	Molar composition	F, wt %	T_g ,°C
PMTFMA	—	31.6	89
MTFMA/BVE	62/38	23.6	46
MTFMA/EHVE	60/40	20.0	43
MTFMA/MVE	55/45	15.5	117
MTFMA/t-BVE	50/50	20.3	110
PHFIM	—	48.3	81
HFIM/BVE	61/39	38.0	32
HFIM/EHVE	61/39	33.9	8
HFIM/i-BVE	62/38	38.3	45
HFIM/CHVE	57/43	31.0	77
HFIM/t-BVE	58/42	36.9	77

The behaviour of these polymers at the water/air interface was investigated, by preparing thin films on gold coated glass substrates via LB deposition and by spin coating(13) from XFDM/EHM copolymers of various compositions. These films were characterized by contact angle measurements and with the ATR technique.

The kinetics of the drying process was used as an indicator of the wetting behaviour by monitoring the variations in thickness and refractive index for films which had been kept in deionized water for 12 hours, until thickness and refractive index of the initial state were reached. As expected, the possibility of water swelling is higher with a lower fluorine content. The surface pressure/surface area isotherms of the monolayer show a plateau, which might be ascribed to a double layer formation. The monolayer of the materials with a content of perfluorinated monomers up to 20 % are stable enough to be transferred using the LB technique. The two copolymers studied (XFDM/EHM 1:4 and 1:15, respectively) showed a slightly different transfer behaviour, which resulted in a more hydrophobic surface in the case of the copolymer with a lower content of perfluorinated side chains (1:15).

In contrast to the spin coated films, the LB films presented an anisotropic structure, that is the alternated presence of layers of more hydrophilic main chains and more hydrophobic side chains. No order has been detected in the side chain region. However, the water uptake was unexpectedly faster for the fluorine rich 1:4 copolymer. This is due to its higher hydrophilicity, arising from a transfer mechanism (deposition only on dipping) opposite with respect to that of the 1:15 copolymer; as the consequence of this different behaviour the LB film of the 1:4 copolymer presented the polar acrylic backbone at the polymer-air interface.

Advancing contact angle values of the spin coated films are higher for the copolymer with high F content and in this case increase with time, thus suggesting the migration of fluorinated chain to the surface.

Photostability

Weight loss, gel formation, changes in MWD and molecular structure of the partially fluorinated copolymers were investigated in order to test the effect of UV irradiation on films stability14). Molecular weight distribution changes were followed by Size Exclusion Chromatography (SEC) of the soluble fractions of the various samples.The main data obtained are summarized in Table 3.

XFDM/EHM copolymers show a substantial photochemical degradation after irradiation with simulated solar light at controlled temperature (44°C). Under the same conditions TFEM homopolymer showed no crosslinking and negligible weight loss (Table 3).

The photostabilization effect by the fluorine substitution is confirmed for other homopolymers and in particular for the homopolymer of MTFMA, which shows a fair photostability, at least within the first 100 hours of irradiation, when its FTIR spectrum did not show any appreciable change with respect to the unaged material.

Tab. 3. Weight loss and gel formation during accelerated photooxidation of fluorinated polymethacrylates

Polymer	Irradiation time, hrs	Weight loss, %	Gel formation, wt %	Molecular weight modification
Poly-TFEM	200	1	0	Moderate degradation
	400	2	0	
	900	2	0	
XFDM/EHM (1/4)	200	2	0	Broader MWD and higher M_n
	400	8	28	
	900	17	61	
XFDM/EHM (1/7)	200	2	0	Broader MWD
	400	9	34	Broader MWD
	900	18	72	Gel formation

The two fluorinated XFDM copolymers behave similarly as to weight loss. Volatilization of low molecular weight compounds, or of short fragments, formed during the degradation process, goes up to ca. 20 % of the initial weight during 900 hrs of irradiation, when the amount of insoluble polymer (gel fraction) becomes very large. The crosslinked structures, responsible for the presence of the insoluble fractions, grow at a higher rate in the copolymer containing more EHM units. The formation of high molecular weight fractions from the XFDM/EHM copolymer is already evident after 200 hrs irradiation (expecially for the low F-containing 1/7 copolymer), when insoluble crosslinked polymer is not present yet. On the contrary the two homopolymers PTFEM and poly(ethyl methacrylate) (PEM), with short unbranched side chains, undergo very small weight changes and remain completely soluble, irrespective of the presence or absence of F atoms15).

The fluorinated PTFEM endures better than PEM prolonged photooxidative conditions, since the latter undergoes a marked broadening of molecular weight distribution.

These results seem to suggest that the photostability of these copolymers of fluorinated methacrylates decreases with the presence of hydrogenated methacrylate comonomers in the order :

short n-alkyl- > long n-alkyl- > branched alkyl-

the crosslinking reaction being the dominant pathway in the complex photodegradative process.

When acrylate instead of methacrylate comonomers are involved, the prevailing outcome of the photodegradation process is chain fragmentation, as observed in the case of PMA homopolymer and of the XFDM/MA copolymer.

The occurrence of a photodegradation process involving almost exclusively the main chain is supported by the observation of the SEC plot of photooxidized XFDM/MA, showing that the weight loss is not, or not only, due to rupture of the ester linkage but also to a depolymerization process.

Large effects on the chemical structures of the XFDM/EHM polymers were also determined by FT-IR analysis. The major spectral changes, consisting in the appearance of O-H stretching absorption in the 3600-3100 cm^{-1} region together with lowering of C-H and C-O stretching absorption and broadening of C=O stretching bands, showed that extensive photooxidation occurs in the structure, being also responsible of chain scissions and crosslinking reactions. On the contrary relatively small changes were observed in the C-F absorption bands, occurring in the 1150-1220 cm^{-1} range.

In agreement with the previously discussed data on molecular weight degradation of the copolymers of XFDM with either linear (MA, BM, LM) or branched (EHM) acrylic monomers and on the basis of the FT-IR analysis, the MA and EHM units of the copolymers, containing a reactive hydrogen atom on the tertiary carbon atom either in the main chain or in the branched alkyl side chain, appear to be responsible of a steep increase of the photoinstability of the polymeric structure, while the XFDM structure seems to possess higher stability even in the presence of free radicals created in the system by the degradation of the non-fluorinated acrylic units.

Stone surface protective behaviour

Previous preliminary work concerning the evolution of protection efficiency on stones of these partially fluorinated materials gave promising results[16)], but also evidenced the difficulty of obtaining reliable quantitative data on polymer structure/protective properties relations. Indeed the dishomogeneity of the applied thin polymer films, deriving from both the method of application and the roughness and irregularity of the stone surface, sometime overwhelms other effects. A systematic study was carried out with two different carbonatic lithotypes, namely Candoglia marble (porosity lower than 1 %) and Noto stone (30÷40 % porosity).

Insights about the effect of fluorine content and distribution on the coating performance were obtained by examining copolymers of XFDM with MM and EHM with 24.0 wt % fluorine (XFDM/MM 1/7 and XFDM/EHM 1/4) and 16.7 wt % fluorine (XFDM/MM 1/14 and XFDM/EHM 1/7).

The coatings were applied either by brush or by capillary absorption from polymeric solutions in the appropriate solvent (ethylacetate) on one side of previously conditioned 5x5x1 and 5x5x2 cm stone specimens. After complete solvent evaporation (several days at room temperature, with final vacuum pumping) the amount of deposited polymer was carefully weighed and the contact angle against water was determined according to the Normal Recommendation 33/89 [17)].

Contact angles of both treated lithotypes were rather large, indicating a good water repellency (Table 4). The higher values for the more porous Noto stone can be tentatively related to better penetration of the polymer with formation of a thicker, and then more uniform, protective film. In any case the water vapour permeability is reduced.

No significant difference in the surface properties (contact angle) could ever be observed as the consequence of the increase in the concentration of the polymer solution, which however determined a much more effective impermeabilization of the stone.

Tab. 4. Protective properties of XFDM copolymers on stone [a]

Stone	Protective copolymer	Contact angle	Water capillary absorption, mg/cm^2		Water vapour permeability, g/m^2	
			Untreated	Treated	Untreated	Treated
Candoglia	XFDM/MM 1/7	113-128	0.36-1.59	0.25-0.51	n.d.	n.d.
	XFDM/EHM 1/4	131-136	1.03-1.06	0.72-0.77	12-15	7.8-10
	XFDM/MM 1/14	113-118	0.96-1.07	0.34-0.54	9.3-14.2	7.2-8.5
	XFDM/EHM 1/7	127-129	0.84-1.18	0.42-0.77	8.5-12	6.3-7.7
Noto	XFDM/MM 1/7	143-146	229-257	2.3-16.7	n.d.	n.d.
	XFDM/EHM 1/4	132-145	223-247	5.2-15.3	313-357	329-355
	XFDM/MM 1/14	136-140	218-247	2.5-3.0	299-348	268-328
	XFDM/EHM 1/7	139-142	226-241	2.9-8.3	326-330	301-310

[a] Ranges of values refer to 4 different study concentrations of treating polymer solutions (from 0.5 to 4 wt% in ethyl acetate), leading to different thickness and homogeneity of the obtained coating films.

Even more striking is the improvement, when comparing the capillarity water absorption of polymer-coated stone surfaces, deriving from partial fluorination of long side chains as opposed to short ones. In fact[18)], when the behavior of two fluorinated copolymers, TFEM/ethyl methacrylate and XFDM/LM, was compared with that of their unfluorinated analogs poly(lauryl methacrylate) (PLM) and Paraloid B72™ (Rohm and Haas), the observed reduction in the capillarity water absorption of the fluorinated copolymers was clearly related to the difference in the measured contact angles (larger in the case of the long side chain polymers) when comparing these “polymer couples”. Such effect was particularly clear in the case of the porous Noto stone where, again, the stone morphology led to increased polymer uptake as compared to the Candoglia marble.

Conclusions

Even if the long term goal of this research, namely the identification of one or more polymeric structures that can be advantageously employed in the protection of valuable stone surfaces, is still to be reached$^{11)}$, the resuts so far obtained allow to focus more precisely future investigations and provide already information to design polymeric coating structures allowing a more efficient preservation of monumental stones in a aggressive polluted environment.

Although side chain fluorination of acrylic copolymers has always some effect on their thin film hydrophobicity, its intrinsic photostabilizing action is only partial; in addition, it is known that not only the average chemical composition, but also the structural and morphological order can affect the water permeability and wettability of these copolymers. Future efforts will therefore be focussed on improving photochemical stability in order to maintain the protection behavior provided by the partially fluorinated coating materials examined in this study for longer time periods.

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