

AN INTEGRATED APPROACH TO DESIGN FLUORO SUBSTITUTED “SMART” POLYMERS FOR PROTECTION OF MONUMENTAL BUILDINGS

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Abstract

Introduction of fluorinated groups in the structure of either fully acrylic or acrylic - vinyl ether copolymers, is achieved through the use of commercially available or specifically synthesized fluorinated acrylic comonomers. If suitably selected, these fluoroacrylates can allow both control on the macromolecular structure and tailoring of material properties that are relevant for coating applications, such as film-forming behavior, adhesion, water repellency and intrinsic photostability. Several copolymers of fluorinated acrylates and methacrylates with not-fluorinated methacrylates and vinyl ethers have been evaluated in terms of chemical stability under accelerated photoaging conditions, and their behavior as protective coating materials has been studied after application to various stone substrates that are commonly found in ancient buildings and objects of cultural significance.

Key words: fluorinated acrylic monomers and polymers, stone protection, alternating copolymers, photostability, durability, water repellency, vapour permeability, ageing.

1. Introduction

The requirements for a coating material to be employed in the protection of valuable stone surfaces are i) Barrier properties (condensed water and oil repellency, water vapor permeability, good film forming and adhesion properties); ii) Weatherability (chemical and photochemical stability, thermal stability, no yellowing, reversible adhesion and solubility); iii) Optical properties (transparency, no influence on the chromaticity of the treated stone surface) (Botteghi 1992).

Such modulated multiresponse behaviour can only be attempted with materials based on multifunctional macromolecules. Indeed macromolecules were selected also by nature as building blocks for materials capable of playing the many roles necessary for the development of life. In this significance, properly designed multifunctional macromolecules can keep information provided by the designer and finally behave in a smart way, that is, adapt their response to the external conditions or stimuli.

This fascinating idea was used as guideline in the present work that describes the preparation and characterization of the stability and the protective properties of coating

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materials based on partially fluorinated acrylic polymers. These materials were selected as they can present the following characteristics, which can be controlled by altering the synthetic process and/or the polymer composition:

- a. the presence of fluorine-carbon bonds improves chemical and photo-stability;
- b. the introduction of different units by copolymerization allows to modulate the thermal properties (glass transition temperature, T_g), and than the mechanical response, within a broad range;
- c. adhesion to the stone, film homogeneity and stability can be varied by introducing moderate amounts of functional groups in terpolymers;
- d. the content and spatial distribution of F (fluorine), varied in different ways, allows to selectively control short and long term water repellency and vapour permeability.

All the above characteristics can be varied according to the need, i.e. depending on the type of outdoor exposition and on the nature of the stone, by a simple synthetic process which does not require too complex techniques and does not produce polluting species (Ciardelli 1996 and 1997). Also, acrylic-based polymeric materials can be prepared as dispersions in aqueous media, either by direct synthesis through emulsion polymerization or by appropriate formulation of water-based suspensions. In this latter case additional problems and opportunities arise from a) latex penetration in porous matrix and film formation; b) water repellency in the presence of hydrophilic groups; c) environmental issues.

2. Experimental methods

The materials prepared in the course of this work belong to two main structural classes, and these were related with: a) the random copolymerization of different fluorinated methacrylates with unfluorinated ones; b) the more or less alternating copolymerization of fluorinated acrylates or methacrylates with unfluorinated vinyl ethers.

Approach (a) was mainly followed with acrylates having a perfluorinated alkoxy chain spaced apart from the ester group by one or two unfluorinated carbons. In this way conventional copolymerization of the F-containing monomers with unfluorinated ones yields substantially random copolymers, which can present minor chemical variability (e.g. tapered structure, enrichment in fluorinated co-units at either the low or the high molecular weight end of the MWD curve), depending on the synthetic conditions adopted (batch, one-shot feed, sequential or continuous monomer addition, etc.). The distribution and overall content of F in the macromolecules was controlled by simply varying comonomers structure and content in the feed. Polymerizations were carried out either in homogeneous (solution or bulk) or heterogeneous (emulsion) phase, and MW controlled by usual transfer agents such as thiols.

3. Results and Discussion

3.1 Copolymers and terpolymers of fluorinated acrylic monomers with unfluorinated acrylic esters and/or vinyl ethers

Structure of the aliphatic comonomer and its composition was varied to obtain materials with a given T_g ; slight positive deviations from the Fox equation were usually observed, indicating not purely random distribution of sequences and/or occurrence of intermolecular

interactions or microheterogeneity involving the fluorinated moieties. The main structures investigated and the range of basic properties are summarized in tab. 1.

Table 1: Copolymers of fluorinated and unfluorinated acrylic esters

polymer ^a	composition (molar range)	F (range, wt %)	T _g ^b (range, °C)
XFDM / MA	100/0 - 6/94	61 - 17	47 - 15
XFDM / MM	50/50 - 5/95	51 - 13	46 - 110
XFDM / BM	60/40 - 14/86	52 - 23	45 - 29
XFDM / OM	21/79 - 16/84	26 - 21	-6 - -2
XFDM / LM	45/55 - 15/85	38 - 16	27 - -9
XFDM / EHM	20/80 - 11/89	24 - 15	20 - 13
XFDM / EHA	17/83 - 7/93	23 - 11	-52 - -63
TFEM / MA	100/0 - 66/34	34 - 27	63 - 43
TFEM / BM	60/40 - 37/63	22 - 14	69 - 57
TFEM / OM	64/66 - 42/58	16 - 13	43 - 27
TFEM / LM	70/30 - 28/62	21 - 8	38 - 1

- a) MA = methyl acrylate; MM = methyl methacrylate; BM = butyl methacrylate; OM = octyl methacrylate; LM = lauryl methacrylate; EHM = 2-ethylhexyl methacrylate; EHA = 2-ethylhexyl acrylate; XFDM = perfluorooctylethyl methacrylate; TFEM = 2.2.2-trifluoroethyl methacrylate.
- b) T_g = glass transition temperature.

When fluorine substitution in the acrylic esters occurs very close to the main chain as in α -CF₃, α -F and β , β' -F₂ acrylic esters, the reactivity is very different. The high positive charge density on the double bond in addition to allowing conventional semi-random copolymerization with unfluorinated acrylates, opens new possibilities in terms of introduction of different units and, particularly, of such electron-rich monomers as vinyl ethers (VE) and α -olefins. Good conversion with these fluorinated acrylates was indeed obtained by using vinyl ethers. These latter are incapable of polymerizing under free radical conditions but, thanks to the high electron density on their double bond, can form charge transfer complexes with the fluorinated monomers to which the method b) can be conveniently applied.

By changing the distance of fluorine substitution from the acrylic double bond this tendency to alternation with vinyl ethers could also be varied. Thus copolymers with isolated VE units, quasi-alternating distribution and strictly alternating distribution were obtained. The mainly alternating distribution of these last copolymers does not allow to predict T_g on the basis of the Fox equation. Moreover T_g was also modulated to a significant extent by the comonomers structure (tab. 2).

Table 2: Copolymers of VE's with variously fluorinated acrylic monomers

polymer ^a	composition (molar range)	F (range, wt %)	Tg ^b (range, °C)
TFEM / BVE	76/24 - 63/37	28 - 25	47 - 36
HFIM / BVE	100/0 - 51/49	48 - 34	81 - 17
HFIFA / BVE	100/0 - 50/50	55 - 39	108 - 35
HFIFA / tBVE	50/50	39	82
HFIFA / iBVE	50/50	39	48
HFIFA / EHVE	50/50	33	9
HFIFA / CHVE	50/50	36	73
MTFMA / BVE	100/0 - 62/38	37 - 26	89 - 46
MFPE / BVE	52/48	16	21

- a) BVE = butyl vinyl ether; tBVE = *tert*-butyl vinyl ether; iBVE = *iso*-butyl vinyl ether; EHVE = 2-ethylhexyl vinyl ether; CHVE = cyclohexyl vinyl ether; HFIFA = 1,1,1,3,3,3-hexafluoro-2-propyl α -fluoro-acrylate; MFPE = ethyl 3,3-difluoro-2-methyl-propenoate; MTFMA = methyl α -trifluoromethyl acrylate.
- b) Tg = glass transition temperature.

3.2 Photochemical stability

The photodegradation processes were studied by means of accelerated photoaging under strictly controlled conditions, using a fluorescent Xenon lamp to mimic solar irradiation. Chromatographic and spectroscopic techniques were used during up to 2000 hs to monitor the behaviour of selected fluorinated copolymers and of a few representative unfluorinated analogs [Chiantore 2000]. This has allowed to identify the points of weakness in the macromolecular structure and to design new macromolecules with improved photostability, by appropriate selection of the fluorinated comonomer and of its distribution along the chain with respect to the unfluorinated one(s).

3.3 Protective evaluation

As indicated at the beginning, adhesion to the stone is an important requisite for a durable protection. The multiple (cooperative) weak polar interactions of the ester groups with the stone surface provides already a fair adhesion.

Comparative evaluation of the performances of the fluorinated coating materials with respect to their unfluorinated analogs and to other commonly employed coating materials, such as reactive silicones, have shown fair to excellent increase in protection efficiency when H were replaced by F atoms [Alessandrini 2000]. Such improvement was particularly good when small amounts of reactive alkoxy silane groups were present in the side chains, as in the terpolymer shown in fig. 1.

Yet it can be improved by introducing in the copolymer a modest amount of functional groups capable to link more or less strongly with stone surface itself. In particular, co-units with alkoxy silane group in the side chain can covalently (and, under appropriate conditions, reversibly) bond with the silanol groups of the stone. Therefore the consequent terpolymer can combine the already mentioned useful structural properties with good wetting of the

inorganic surface and convenient adhesion to the same, therefore improving the homogeneity of the final film and the extent of surface covering, both at the outer surface and within the pores of the stone itself.

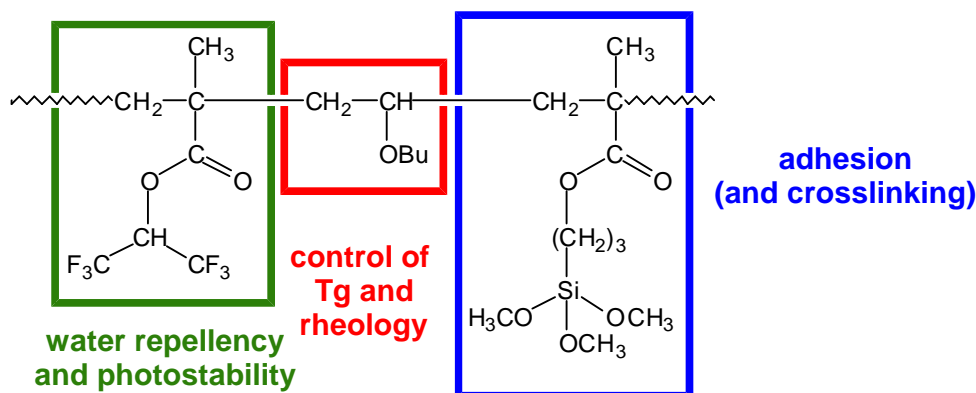


Figure 1

The film resulting from application of the above polymer is dependent on the solution rheology (viscosity). Indeed, when the film-forming material is a reactive low molecular weight compound, such as a silane derivative, viscosity can be too low for appropriate film formation; in addition, these products may form films with modest mechanical properties. On the contrary, the use of high molecular weight macromolecules, which can be more convenient for modulating the many necessary properties, commands application from solution.

In order to overcome the problem of solvent emission a more complex quaterpolymer was designed where, to the basic structure of a functional (reactive), fluorinated terpolymer, a fourth monomer with water compatible side chain was added to allow formation of a stable water dispersion (latex) by emulsion polymerization process (fig. 2).

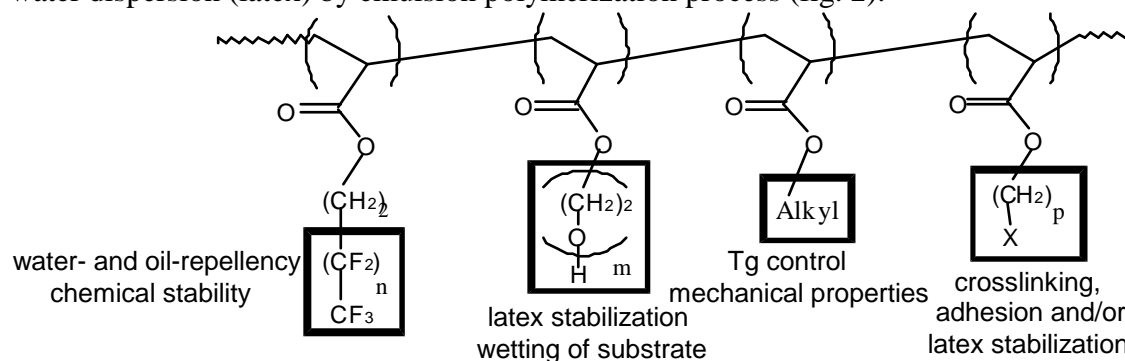


Figure 2

This general structure is widely used in formulations of waterborne stain- and water repellent coating products in the textile, leather and electrographic industries among others.

4. Conclusions

Even if the amount of collected data is not yet exhaustive, the present study provides for the first time a broad indication about the potentiality of polymer synthesis to help solving the complex problems related to monumental stone preservation and protection.

This preliminar but, in our opinion, very significant achievement was possible thanks to the integrated work of research groups with complementary expertise. Indeed, such approach allowed to go all the way from detailed molecular synthesis to application on stones, through characterization of both protective polymer and stone properties.

The focus on fluorinated polymers appears to be substantiated by the obtained results; in particular the possibility of varying, in addition to thermal, mechanical and chemical properties, also fluorine content and distribution provides materials for a broad range of applications in the specific field.

To test this final point the future work will be mainly devoted to optimize a limited number of substances in order to produce sufficient quantity for applications to monuments.

Aknowledgment

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5. References

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