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Original article

Acrylic copolymer coatings for protection against UV rays

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ABSTRACT

This paper summarizes the basic properties of new acrylic copolymers with UV-absorbing groups (derivates of benzotriazole) bonded in macromolecular chains. These polymers are highly suitable as a material for UV protective coating of artifacts sensitive to natural and/or artificial UV light. Diane type epoxy resin was used as a test organic material with very low resistance to UV radiation. The behavior of new copolymers was compared with the UV protecting ability of Paraloid B72. Based on obtained results, we have chosen the copolymer whose properties were most similar to those of Paraloid B72, but whose protective ability is superior. This copolymer is now commercially available.

1. Research aim

The purpose of our research was to prepare a special type of acrylic copolymer with a UV-absorbing group bonded in polymer chains. Such transparent polymer coatings have a considerable ability to protect different types of organic material against UV light without any risk of migration of the UV-absorbing component through the protecting film. The basic properties and UV preservation potential of these copolymers were studied and the behavior of the new material was compared with Paraloid B72.

2. Introduction

As it has been well known for a long time, UV radiation is among the most severe factors causing damage to organic materials of which objects of cultural heritage are typically made [1]. This energy-rich radiation promotes chemical change in natural organic substances, such as wood, paper, fibres, vegetable oils and resins, as well as in synthetic polymers such as epoxy resins unsaturated polyester resins, polystyrene and polyethylene. Radiation energy absorbed by such substances induces photo-oxidative destruction, degrading the material's physico-mechanical, optical and other properties. This is why protection against UV radiation (along with provisions to prevent ambient temperature and humidity changes) is one of the most important steps in the conservation of historical artifacts made of such materials. The effect of UV radiation can be best reduced by complete elimination of light from the environment in which the artifact is stored. However, this is only practicable in depositories. Artifacts in expositions cannot be fully shielded from light and protection against UV rays depends largely on the choice of light sources, e.g., where UV light constitutes only a minor fraction. Further mitigation against the effect of UV damage involves coating the artifact with a suitable polymeric film containing substances that shield UV rays or absorb and convert them into harmless radiation at lower energy levels, thereby, reducing the damaging effect. Where the surface of the object (fabrics, archived documents, etc.) cannot be protected with a film, artifacts on display can be placed in showcases with windows fitted with a suitable UV filter, typically a sheet of material, which absorbs the UV component, thus, reducing the amount of UV radiation hitting the artifact. However, for artifacts located outdoors, a suitable UV-absorbing coating often remains the only feasible option [2].

From among the range of protective coatings, transparent paints pose a major problem. Not only should the coating absorb a major fraction of the incident UV radiation; the coating itself should be resistant to UV and its own optical or mechanical properties should remain unaffected by UV. The coating should not lose its solubility (reversibility) and, naturally, should not cause damage to the material to which it has been applied (e.g. due to the solvents used for its application). The requirements for good UV resistance and for an inert substance, which leaves the materials treated intact, are usually well met by acrylic copolymers, such as the well-known Paraloid B 72 (ethyl methacrylate/methyl acrylate copolymer) [3]. However, the polymer on its own is not very efficient in absorbing

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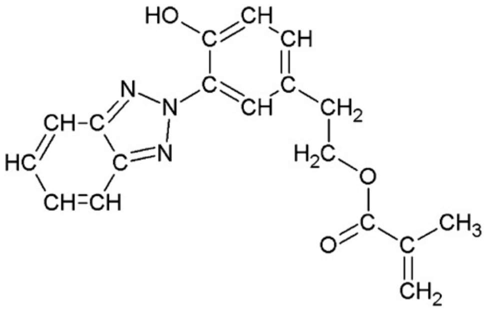

Fig. 1. Structure of UV-absorbing component of acrylic copolymer chain.

UV radiation and consequently it fails to fully protect the artifact. This drawback is sometimes eliminated by adding a suitable UV-absorbing or shielding ingredient. Such ingredients can include inorganic nanoparticles (e.g. oxides such as TiO_2, ZnO or CeO_2) [4–7] or organic substances (e.g. benzophenone derivatives, such as o-hydroxybenzophenones with various substituents or benzotriazoles, such as 2-hydroxyphenylbenzotriazoles) [4,7]. Inorganic additives are very stable and do not migrate through the polymer film but for transparent coatings, the size of inorganic particles has to be considerably smaller than the wavelengths of visible light (400–800 nm).

The disadvantage of organic low-molecular-weight ingredients not bonded (fixed) in the polymer is that they can migrate through the film in certain circumstances. As a result, the protective effect can vary appreciably or vanish altogether at some spots [4,7,8]. As another drawback, such systems are often prepared by the restorers themselves without any precise evaluation of the protective effect. It is much more effective if the UV-absorbing organic protective system (or a fraction of it at least) is immediately embedded in the polymeric chain. The amount of such bonded UV-absorbing groups is, thus, determined by the manufacturing process; the efficiency remains constant in the long run and can be measured in advance.

Polymers modified in such a way can be used as a protective varnish for transparent and colorless coating of both synthetic and natural organic materials in applications where (e.g.) Paraloid B72 with a UV-absorbing additive is usually used.

The feasibility of embedding a derivative of the alcohol 2-(2-*H*-benzotriazol-2-yl)-4-(2-hydroxyethyl) phenol esterified with methacrylic acid (sample seen on Fig. 1) in the chains of an acrylic copolymer has been demonstrated previously [9]. Testing the efficiency of copolymers containing the above UV-absorbing component for the protection of some organic materials is the subject of this paper.

3. Materials and methods

3.1. Materials, preparation of the copolymers

Monomers, provided by Momentive Speciality Polymers, Sokolov, Czech Republic, were used for experiments. The choice of monomers was made in order to use generally available types in such a ratio that the glass transition temperature (Tg) of the final copolymer was close to 40 °C (Tg of Paraloid B72). For these reasons, the mixture of methyl methacrylate (usual acrylate monomer) and ethyl acrylate (much less toxic than methyl acrylate contained in Paraloid B72) with a small addition of acrylic acid was used. Observed samples of copolymers differed by the precise content of initial monomers and by the degree of polymerization (Table 1). Polymerizations took place in methyl ethyl ketone (MEK) solution. The mixture containing UV-absorber 2-(2′Hydroxy-5′-methacryloxyethylphenyl)-2H-benzotriazole, with a molecular weight of 292 g/mol referred to herein as Soltex EE, product of VUOS Rybitví, Czech Republic (27 parts by weight) dissolved in a mixture of monomers (427.5 parts by weight of methyl methacrylate, 441.0 parts by weight of ethyl acrylate and 4.5 parts by weight of acrylic acid) with 9 parts by weight of azobisisobutyronitrile as radical polymerization initiator (AIBN, molecular weight 146.21 g/mol produced as VAZO 67 by DuPont, USA) were added during 3 hours into the glass reactor with MEK under argon atmosphere, tempered under reflux to 80 °C. After 1 hour, the second part of initiator AIBN (13.5 parts by weight) dissolved in MEK was added. After stirring for 3 hours at 80 °C, the mixture was cooled to 60 °C and a UV stabilizer of HALS type–Tinuvin 292 (Ciba, USA) was added. After dissolving the Tinuvin, the mixtures of random acrylic copolymer and UV stabilizer were cooled to room temperature.

The purpose of adding Tinuvin is to enhance the resistance of the acrylic copolymer to UV rays and to suppress the formation of any micro cracks, which can reduce the protective function of the polymeric film. The combination of Tinuvin 292 and a suitable UV-absorber is also recommended by the manufacturer [12]. This UV stabilizer type is frequently used by restorers with a view to enhancing the UV resistance of natural resins (such as dammar) as well as synthetic polymers [6,13–18]. An overview of the copolymer samples and their basic properties is included in Table 1.

3.2. Measuring methods

Molecular weight distribution of the acrylic copolymers was determined by gel permeation chromatography (GPC) on a waters liquid chromatograph using PLgel Mixed-C columns, 300 × 7.5 mm, calibrated with polystyrene standards (Polymer Laboratories).

Table 1
List of acrylic copolymers examined and their basic properties.

Sample	Composition of monomer mixture [% w/w]				Content of Tinuvin 292 [% w/w]	Tg theor. [°C]	Solid [% w/w]	Mn [g/mol]	PDI
	EA	MMA	KA	Soltex EE					
PAR 10/1	47.0	49.5	0.5	3.0	0.1	45.0	48.1	10,984	2.71
PAR 10/2	49.0	47.5	0.5	3.0	0.1	42.3	48.1	11,192	2.68
PAR 10/3	50.5	46.0	0.5	3.0	0.1	40.3	47.9	10,627	2.83
PAR 10/6	47.0	49.5	0.5	3.0	0.1	45.0	47.5	12,616	2.58
PAR 10/7	49.0	47.5	0.5	3.0	0.1	42.3	47.9	14,743	2.80
PAR 10/8	50.5	46.0	0.5	3.0	0.1	40.3	47.3	14,214	2.97
B 72[d]	70.0[a]	30.0[a]	–	–	–	40.0[b]	40.0	18,500[c]	–

EA: ethyl acrylate; MMA: methyl methacrylate; KA: acrylic acid; EMA: ethyl methacrylate; MA: methyl acrylate; Soltex EE: radically polymerized UV filter (benzotriazole type R); Tinuvin 292: antioxidant HALS (Ciba USA); B72: Paraloid B72 (Rohm & Haas, USA); Tg: glass transition temperature; Mn: number-average molar mass; PDI: polydispersity index.

[a] Literature data from [3].

[b] Literature data from [3,10].

[c] Literature data from [11].

[d] Composition of Paraloid B72 is EMA/MA (70/30).

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