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PARALOID B72 NANODISPERSION PREPARATION TECHNOLOGY AND ITS POSSIBILITIES FOR USE IN THE MONUMENT CARE

David Škoda[1], Renata Pučalíková[1], Ivo Kuřitka[1] and Klára Kroftová[2]

1. *Centre of Polymer Systems, Tomas Bata University in Zlin, Tr. Tomase Bati 5678, Zlin, CZ-76001, Czech Republic; dskoda@utb.cz*
2. *Czech Technical University in Prague, Faculty of Civil Engineering, Department of Architecture, Thákurova 7, Prague 6, CZ-162 00, Czech Republic; Klara.Kroftova@seznam.cz*

ABSTRACT

The paper summarizes the results of laboratory research on acrylate polymer Paraloid B72, the use of which is widespread in the consolidation and protection of historical materials. The aim of laboratory research was primarily to analyze the possibilities of modifying particle sizes, given that this material characteristic plays an important role in the penetration process and hence the effectiveness of the consolidator. The contribution shows and compares the basic properties of the tested dispersions of Paraloid B72. The tested polymer system has a smaller particle size and it is possible to assume the possibility of proper use in monument care.

KEYWORDS

Paraloid B72, nanodispersion, ethanol, cultural heritage, consolidation

INTRODUCTION

Many materials used for plastering reinforcement have been based on acrylic copolymer dispersion in recent decades [1]. Acrylic polymers are macromolecular reinforcing agents derived from acrylic acid, methacrylic acid and their esters (e.g. Paraloid B72, Primal AC33, Hydro-Grund 750, Veropal UV40 and others). Acrylates are applied in the form of dispersions in organic solvents and are currently used in the consolidation of plasters, wall paintings and sgraffitts or to protect the substrate against UV radiation (e.g. Paraloid B72, Veropal UV40, Solakryl BMT, Disapol M 1-40 and others). In general, the main advantages of these devices include high efficiency and variability, i.e. usability in many phases of technology, low cost, easy accessibility and user experience. The acrylates can also be characterized by their high bonding ability, high photooxidation and hydrolytic stability and, in particular, sufficient penetration capacity. Among the disadvantages of the application of acrylates can be the introduction of foreign material into historical matters and especially irreversibility (especially in penetration), high diffusion resistance, surface film formation and last but not least negative impact on the optical properties of the treated material (especially when massive use) [2].

Paraloid B72 Acrylic Resin is one of the most widely used means used since the 1960s to strengthen natural stone, plaster, wood, etc. [3]. Paraloid B72 is especially known as consolidation and impregnation agent of mural paintings and oil paintings, as a picture varnish or as a fixative for charcoal and chalk drawings, pastels, as well as for the consolidation of wood. It is also recommended as an adhesive for glass and ceramics. Its positive features include easy processing, UV resistance, non-stickiness and resistance to acid rains and biological attack. The matured material is transparent and has good optical properties.

For the purpose of restoration and conservation practice, Paraloid B72 granules are dissolved in organic solvents, the choice of which affects the properties and the way of use. Since Paraloid B72 is widely used in restoration praxis as mentioned, its particle size plays important role in a penetration process and final consolidation [4, 5]. In the case of use of a too concentrated solution, the risk of over-absorbing surface of the treated material, the formation of a sealable film and the appearance of shine may occur. Particle size study can be realized in case of Paraloid B72 dispersions. These studies involve a use of good and bad solvents which enable to tune the size of particles and dispersion characteristics. Moreover, the use of various surfactants within these experiments was found beneficial as well [6].

METHODS

In this work we studied dispersions of Paraloid B72 by means of its particle size. We have chosen different solvents system based on good solvents such as ethanol and acetone. Contrary, water was used as a bad solvent to achieve precipitation of Paraloid B72 particles [7]. The aim of this work is to find an optimal solvent combination to achieve different particle size of Paraloid B72.

Chemicals

Paraloid B72 was supplied from Krusta shop. Ethanol (technical) and acetone (p.a.) were purchased from Mikrochem (Slovakia). Tween 20 sufractant was supplied from Sigma-Aldrich.

Instrumentation

Particle size distributions were analyzed on a Malvern Zetasizer ZS instrument by dynamic light scattering technique (DLS) [8]. Refractive index of Paraloid B72 was set to 1.48. The samples for DLS measurement were used as prepared.

Experimental part

10 wt% dispersion of Paraloid B72 was prepared as follows: Paraloid B72 (4.0 g) was dissolved in ethanol (44.0 ml) to produce clear dispersion. The second dispersion was obtained by the addition of 10 ml of acetone into the first dispersion of EtOH and Paraloid B72. The concentration of Paraloid B72 in ethanol + acetone is 8.6 wt%. Then, 10 ml of each dispersion was used for water addition. To modify the particle size, the aliquots of water was added into 10 ml of both dispersions.

Tab. 1 - Prepared dispersions of Paraloid B72

Paraloid B72 [g]	Solvent 1	[ml]	Solvent 2	[ml]	Wt %
4.0	EtOH	44.0			10.0
4.0	EtOH	44.0	Acetone	10.0	8.6

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RESULTS

Paraloid B72 is copolymer consisted from ethyl methacrylate (EMA) and methyl methacrylate (MA) with weight average molecular weight 65128 M_w. This number represents the total weight of polymer divided by the number of polymer molecules. The weight fractions of EMA and MA are 70 % and 30 %, respectively. A number average molecular weight is 11397 M_n. This value is determined by measuring the molecular mass of n polymer molecules, summing the masses, and dividing by n (Figure 1).

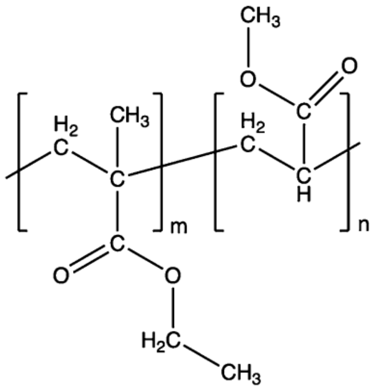

Fig. 1 - Structure of Paraloid B72 (m = 70, n = 30).

Based on the knowledge of Paraloid B72 structure, the gyration radius of Paraloid B72 polymer chain can be derived. This number give us an information about the size of polymer particle in dispersion.

Polymer chain length (L) can be calculated from Equation1.

$$L = \sin\alpha * d * P, \quad (1)$$

Where α is bond angle in polymer chain, d is C-C bond length and P is degree of polymerization. Then, the gyration radius is calculated from Equation 2.

$$S = \sqrt{\left(\frac{M_O * 2\left(\frac{L}{2}\right)^2}{M_O}\right)}, \quad (2)$$

Where M_o is molecular weight of monomer unit formed by 0.7 EMA and 0.3 MA. The gyration radius calculated from presented equations (Equations 1 and 2) is ca. 7.6 nm. From this we can conclude that the diameter of Paraloid polymer particle is ca. 15.2 nm.

We have studied two model systems of Paraloid B72 in different solvents. As a good solvents, ethanol and acetone were chosen. It was found that these solvents dissolve Paraloid B72 resulting in clear dispersions. In case of EtOH and EtOH + acetone solvents, the concentration of Paraloid B72 was 10 and 8.6 wt%, respectively. The volumes of studied samples were 10 ml. To evaluate the size of Paraloid B72 particles in prepared solvents, a dynamic light scattering (DLS) method was employed. This method provides the information about hydrodynamic diameter of analyzed particles. The values of particle sizes and PdI indexes are given in Table 1. As illustrated, particle size is changing with the addition of water.

Dispersion of Paraloid B72 in ethanol was clear and according to DLS measurement the particle size of Paraloid is 26 nm (Fig. 2). After addition of 1 ml of water the size remained the same. However, after addition of 2 ml of water the size was increased to 58 nm while the dispersion was still clear. Addition of 4 ml resulted in color change and milky dispersion was observed. According to DLS analysis the size of Paraloid B72 is about 797 nm. With the addition of 6 and 8 ml of water the precipitation of bigger white bulky solid was observed. This behavior is connected to shift of equilibrium to precipitation of Paraloid B72. The dispersion above the precipitate was analyzed by DLS and the sizes were about 683 and 416 nm. This decrease is caused by the precipitation of bigger particles of Paraloid B72 after water addition whereas smaller particles were preserved in the suspension.

In the case of dispersions based on ethanol and acetone, smaller size of Paraloid B72 was evidenced (Fig. 3). This observation can be assigned to supporting effect of acetone. Acetone works as a good solvent for Paraloid B72 and we assume that its presence allows for better solubility of Paraloid in this system of solvents. The size of 11 nm is smaller than the gyration diameter calculated above (15 nm). This difference can be caused by specific orientation of polymer in this solvent system. DLS measurements of dispersions exhibit big increase of size when 4 ml of water were added. In this case the precipitation of Paraloid was evidenced and milky color of dispersion was observed as well as in the previous case. The size after addition of 4 ml is about 383 nm. However, after the addition of 6 and 8 ml of water, the particle size is almost similar. From this we can conclude that the particles in residual dispersion are stable with the sizes about 360 nm.

DLS distribution curves of Paraloid B72 in EtOH and EtOH with acetone are displayed in Figures 2 and 3, respectively. Fig. 2 illustrates Paraloid B72 in EtOH solvent with water additions. Distribution peaks revealed almost monomodal distribution except the sample with the addition of 6 ml of water. In this case the peak is very broad indicating wide particle size distribution. As mentioned above, this behavior is attributed to precipitation of Paraloid in the dispersion. Fig. 3 shows DLS curves of Paraloid B72 in EtOH and acetone solvents. Similarly to previous dispersion, broad size distribution is observed after addition of 6 ml of water.

Polydispersity index values (PdI) of prepared dispersions are between 0.14 and 0.36 indicating moderately polydisperse distribution type (Table 2).

Tab. 2 - DLS results of Paraloid B72 dispersions.

Solvent	**DLS results**	**Water addition**					
		0 ml	**1 ml**	**2 ml***	**4 ml**	**6 ml**	**8 ml**
EtOH	Z-Ave [nm]	26	25	58	797	683	416
	Main peak [nm]	29	23	74	964	686	519
	PdI	0.25	0.34	0.23	0.17	0.36	0.19
EtOH+Acetone	Z-Ave [nm]	11	14	48	383	365	359
	Main peak [nm]	12	14	61	418	641	417
	PdI	0.20	0.33	0.20	0.22	0.29	0.14

**dispersion used for Tween 20 addition*

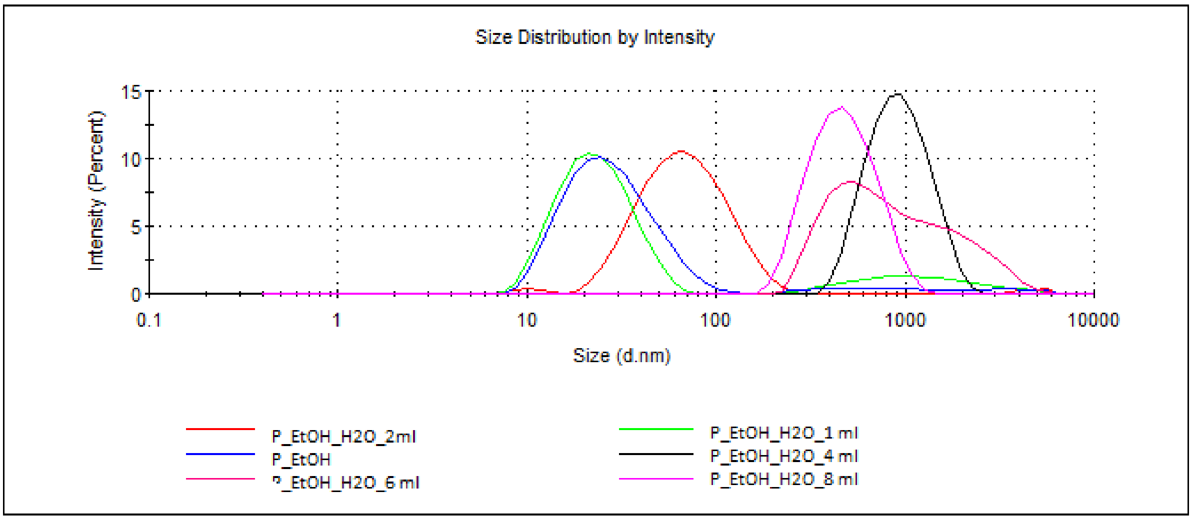

Fig. 2 - DLS size distribution curves of Paraloid B72 dispersion in EtOH with water additions.

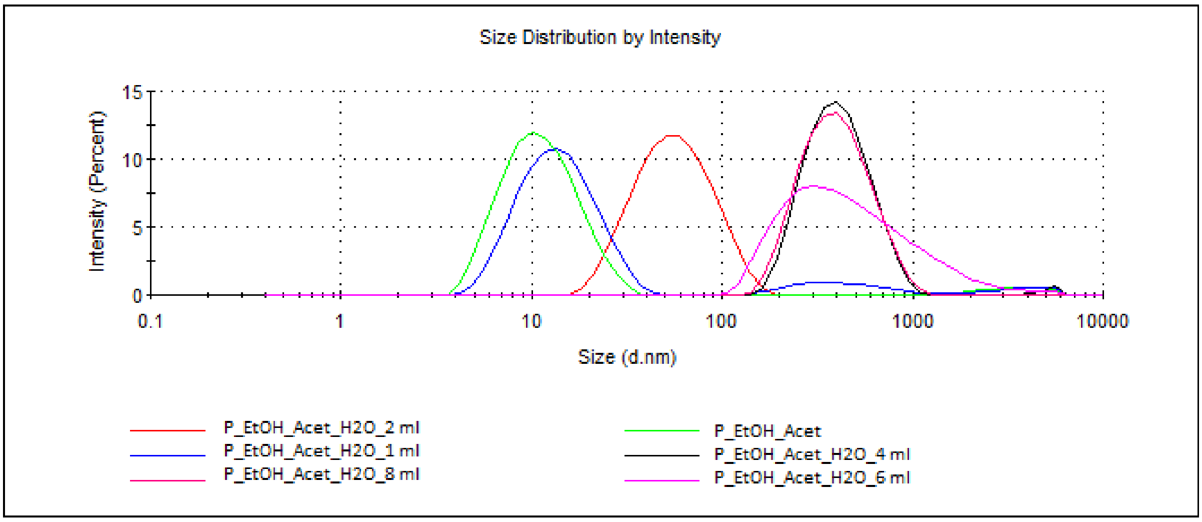

Fig. 3 - DLS size distribution curves of Paraloid B72 dispersion in EtOH + acetone solvents mixture with water additions.

From the obtained data we can conclude, that EtOH and EtOH + acetone solvent systems can be used for dispersions of Paraloid B72. Moreover, the additions of water portions modified particle size of polymer.

Effect of Tween 20 surfactant addition on the size of Paraloid B72 particles was studied in case of dispersions in EtOH solvent with 2 ml of water addition. As displayed in Table 3, the addition of 0.3 ml of Tween 20 led to particle size increase up to 97 nm. This change is caused most probably due to agglomeration of Paraloid particles and their coating with the Tween 20 surfactant.

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Tab. 3 - DLS results of Paraloid B72 dispersion after Tween 20 addition.

solvent	DLS results	without Tween 20	Tween 20 (0.3 ml)
EtOH + 2 ml water addition	Z-Ave [nm]	58	97
	Main peak [nm]	74	121
	PdI	0.23	0.26

CONCLUSION

In this work particle size distribution of Paraloid B72 copolymer was studied. Paraloid B72 was dispersed in ethanol and ethanol + aceton solvent mixture and its size was about 26 and 11 nm, respectively. After water addition, the particle size was significantly increased due to precipitation of Paraloid B72 particles. With the use of acetone as a co-solvent we achieved smaller particles of Paraloid B72. Based on the obtained data we can conclude, that the system of ethanol and acetone with 2 ml water addition can be found as an optimal mixture for following applications in restoration. Moreover, the tuning of particle size is beneficial for utilization of Paraloid in different morphologies of consolidated materials. In other words, different porosity of consolidated materials require different particles of consolidant. From this point of view, the particle size modification brings important data for further use of Paraloid B72. We believe that these data can be useful for application of Paraloid B72 in restoration praxis.

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