

**INFLUENCE OF PARTICLE SIZE AND PHASE DISTRIBUTION ON
ADHESION OF ADHESIVE DISPERSIONS BASED ON
POLYCHLOROPRENE GRAFTED WITH MMA**

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Besides optimum rheological properties and adhesion, adhesives must meet other conditions: not toxic, flammable and does not pollute the environment. Classical adhesives based on volatile organic compounds; do not fully meet these requirements, for which aqueous dispersion adhesives environment have become increasingly used, tending to replace almost completely organic solvent-based adhesives. Through grafting operation of elastomeric chains with methyl methacrylate, of dispersion of their solution in the aqueous environment and the use in the composition of the sodium montmorillonite, was obtained adhesive "water-based" with the characteristics of high initial and final adhesion, comparable with the organic solvents, and low toxicity or even absent. Particle size provides important information on the optical properties, stability, and viscosity of the system. At the same time, can elucidate the kinetic aspects of both during the emulsion the synthesis when obtain composite materials. Particle size distribution of adhesives solutions was determined with equipment Mastersizer 2000 (Malvern Instruments, UK) laser light, the range from 0.02 to 2000 nm, with precision of $\pm 1\%$. By measuring the particle size and phase distribution on micron-scale or nanometer, it has been shown that the smaller the particles the better penetrate porous media substrates, and on the other hand, the dispersions can have a high dry matter content, which may lead to an optimum combination of rough media. This class represents the most innovative volatile organic replacement based adhesives products.

Keywords: adhesive dispersions, particle size, phase distribution.

INTRODUCTION

Due to the considerable expansion of the fields it is used in, adhesive production has extended and diversified in the last years. At the same time, adhesives with optimal pre-established properties, both regarding the way they are obtained and the types of blends, have been developed. But aside from the optimal values of the rheological and adherence properties, adhesives must meet other conditions as well: not to be toxic, inflammable and not to pollute the environment. Classical adhesives, based on volatile organic compounds, do not meet these conditions entirely. For reasons such as pollution, fire hazard and economical ones, adhesives with aqueous dispersion medium have become more and more used and they are not far from practically replacing adhesives with organic solvents for good, but they need to have comparable properties in order for this to happen. Adhesive dispersions are emulsions or latex consisting of a stable continuous liquid phase in which a second phase, discontinuous, immiscible with the first one, is present (US Patent 5407993, 1995). Broadly, these can be classified as macro- and micro-dispersions. The classification is based on the size of the dispersed particles: macro-dispersions have dimensions in the range 0.2-50 μm and micro- and nano-dispersions between 10 and 200 nm (Alexandrescu *et al.*, 2013). Systems having particles with diameters between 10 and 1000 nm are usually called colloidal systems (Knecht *et al.*, 2008). The properties of polymers can be modified to correspond to the

desired applications. Three possibilities to modify the properties of polymers are known: blending, grafting and hardening (Alexandrescu *et al.*, 2011).

Grafting is the method by which macromolecular chains of identical or different monomers are covalently bonded to the backbones of the polymer that must be modified (Zhang *et al.*, 2012). Grafting is controlled by the following factors: nature of polymer, monomer, solvent, nature of initiator, the used additives and the temperature.

EXPERIMENTAL PROCEDURE

Materials

Polychloroprene NEOPRENE AD 20, (DuPont) as polymer, methyl methacrylate (Merck, Germany) as monomer; benzoyl peroxide as initiator, dodecylmercaptan as inhibitor (both Sigma-Aldrich Chemie, Germany), ZnO and MgO (active substance 95%) as cross-linking agent and to consume the hydrochloric acid eliminated during reaction and natural resin colophony (Caroco) as adherence improver were used.

Procedure

The natural clays with modified surface are layered silicates used successfully to obtain nano-composite materials and adhesives due to the properties they impart. The modified sodium montmorillonite have the following characteristics: the chemistry of advanced intercalation, which facilitates the exfoliation of layered structures into nanometric layers, which maximizes the interfacial contact and the capacity to modify the chemistry of the surface by organic and inorganic ionic exchange reactions.

Two types of polychloroprene composites were prepared: with 2, 4 and 7% montmorillonite reported to polychloroprene, as well as containing 4% montmorillonite, which were subjected to grafting on roller with different amounts of methyl methacrylate. The amount of 4% was selected because a higher quantity has as effect the strengthening of mixtures. The producers recommend using of 2-5%.

The technology involves three steps: compounding the polychloroprene rubber or the ones grafted with methyl methacrylate with montmorillonite and ingredients specific to adhesive compounds from Table 1, dissolution of products obtained in the same mixture of solvents and dispersion of solutions obtained following the formulation from Table 2. To increase the grafting efficiency and reduce the formation of block copolymers, benzoyl peroxide was introduced in compositions subjected to grafting.

The dispersion was done into the installation consists of a three-necked thermo-resistant glass flask, 2 L capacity, to which a stirrer and a thermometer were attached, the third one being for introducing the components. A VELP rod stirrer was used, recommended for mixing of materials with a wide variety of viscosities. For an efficient stirring the rod for medium viscous dispersions, with an elongated agitator, two arms and a stationary blade was used, the blades' inclination and the rotation direction being important for the movement of the liquid into the flask.

The compounds were swollen for ½ h in the same solvent mixture, introduced into the dissolution container under stirring (400 rpm) until full homogenized (about 30 min), then the 10% poly(vinyl alcohol) aqueous solution, triethanolamine and demineralized water were added. The components were added drop by drop into the rubber solution for 1 h. The obtained adhesive dispersions were first characterized physico-chemical, according to current standards.

Table 1. Formulations for obtaining of polychloroprene compounds non-grafted and grafted with methyl methacrylate containing montmorillonite (parts by weight)

Composite, g/dispersion	C1	C2	C3	C4	C5	C6
Polychloroprene Denka AD 20	200	200	200	200	200	200
Methyl methacrylate	-	-	-	10	20	30
Na montmorillonite	4	8	14	8	8	8
Benzoyl peroxide	-	-	-	1	1	1
Dodecylmercaptan	-	-	-	2	2	2
MgO	8	8	8	8	8	8
ZnO	10	10	10	10	10	10
Natural resin colophony	4	4	4	4	4	4
Total	226	230	236	243	253	263

Table 2. Formulations to prepare dispersions from compounds C1-C6

Composites, g	C1	C2	C3	C4	C5	C6
Compound	47.03	47.87	49.12	50.58	52.63	54.77
Solvents	32.97	32.13	30.88	29.42	27.37	25.23
Polyvinyl alcohol, liquid solution 10%	50	50	50	50	50	50
Triethanolamine	15	15	15	15	15	15
De-mineralized water	80	80	80	80	80	80
KOH, 10% solution, ml	1	1	1	1	1	1
Total	226	226	226	226	226	226

Testing Methods

Particle size distribution was determined by laser light scattering using the Mastersizer Hydro 2000S Particle Size Analyzer, Malvern Instruments Ltd., equipped with Malvern soft, which controls the system during the measurements and processes the information based on standard operation procedure (SOP). The three standard points to read the distribution characteristics are $D(v, 0.1)$, $D(v, 0.5)$ and $D(v, 0.9)$, which represent the fractions from the total particle volume having the size higher than a given value (Ma *et al.*, 2001; Mu and Seow, 2006).

The adherence was measured according to SR EN 1392:2006 standard, test known as “peeling test at $(23 \pm 2)^\circ\text{C}$ ”. The following supports were used: (a) mixture of standard rubber, hardness 85°Sh A; (b) leather; (c) split leather; (d) linen; (e) cotton cloth; (f) synthetic leather. The steps followed were: preparing of support by polishing to increase its roughness when standard/standard samples were jointed, application of the adhesive dispersion, drying, jointing of test samples, conditioning and peeling measurements (Zheleva, 2012). The adhesives were applied by brushing as monolayers on rubber and as bilayers on textiles, split and synthetic leather. The drying was done in separated rooms, equipped with devices for vapor absorption. The open time ranged between 15 min and 1-2 h, depending on the absorptive properties of supports. The drying time was reduced by preheating the supports at 70°C (Busato, 2002).

After drying the supports were jointed and pressed down for 30 s at 3.5-4.0 atm, then conditioned according to the European standard EN 1391 (24 and 72 h at the standard temperature of $23 \pm 2^\circ\text{C}$; samples conditioned for 72 h heated for 3 h at 50°C or 168 h at 70°C to accelerate the aging, but only for St/St joints). The peeling test was done using a TEBA dynamometer (Timisoara, Romania) after 24 and 72 h for the samples

conditioned at room temperature, immediately for those heated at 50°C and after 24 h for those heated at 70°C using a speed of 100 mm/min.

RESULTS AND DISCUSSION

Particle sizes provide important information on optical properties, stability or viscosity of a system. At the same time they are able to elucidate kinetic aspects taking place during emulsion polymerization or obtaining of some composite materials.

Dynamic light scattering (DLS), also known as photon correlation spectroscopy (PCS), measures the fluctuations of intensity of scattered light which occur due to the Brownian movement of particles and is time-dependent.

To establish the influence of montmorillonite on particle size distribution, C1-C3 samples, containing various amounts of montmorillonite. To have a general view on sizes and particle size distribution of dispersions containing montmorillonite, non-grafted or grafted with MMA, the curves are represented superposed in Figure 1.

For the sample containing the lowest amount of montmorillonite the distribution is bimodal. This is due, in addition to the method of obtaining the dispersion – mechanical dispersion, to the presence of montmorillonite, with particles ranging between 13 and 16 μm . Increasing the amount of montmorillonite the peaks of fractions with small and medium sizes increases also (it appears as a shoulder at 7-8 μm for sample C1), and the one at larger sizes becomes a shoulder peak. The highest montmorillonite amount used – 7 parts to 100 parts rubber – gives completely different sizes and distribution: peaks at small and medium values disappear practically and very large size particles appear and prevail, ranging from approx. 100 to 700 μm . This is explained by the agglomeration of latex particles produced by the high amount of montmorillonite, exceeding the recommended one.

Grafting with methyl methacrylate was done only for polychloroprene rubber having the composition C2, from which compounds C4-C6 were obtained.

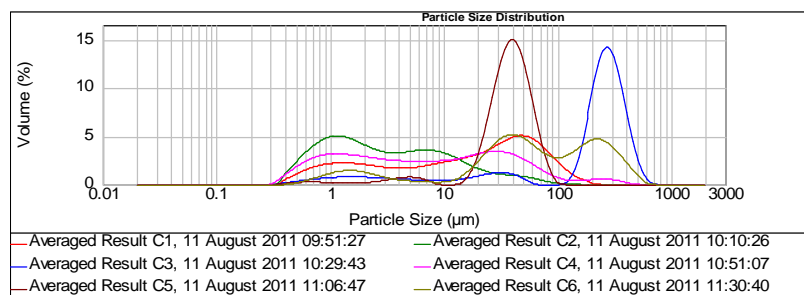


Figure 1. Superposed distribution curves for samples C1-C6

Dispersion C4, with the same amount of montmorillonite as sample C2 and the lowest amount of grafted MMA has a completely different particle size distribution from that presented by C2: particles size range between 0.12 and about 600 μm , the particles with average diameters of about 1.02 and 12 μm respectively prevailing. The weight of large particles, with average diameters of about 260 μm , is very small.

Increasing the amount of MMA, dispersions have different size distribution, very similar in shape but not in size to dispersion C3. Thus, the most particles range between 15 and 100 μm , the fractions ranging between 0.3 and 1.0 μm and between 2 and 10 μm being negligible.

The maximum amount of MMA grafted on polychloroprene has as result again a broad distribution, close to that of dispersion C4, but the fractions of particles have reversed predominant size: the preponderant fraction is the one with large size, ranging between 10 and 100 μm (peak at about 40 μm), followed by the one between 100 and 700 μm and the peak at ca 240 μm , while the one with the smallest size, between 0.4 and 9 μm , is much lower. The values of standard points for samples C1-C6 are given in Table 3.

Table 3. Standard points for reading distribution characteristics for dispersions C1-C6

Sample	D(v, 0.1), μm	D(v, 0.5), μm	D(v, 0.9), μm
C1	1.039	18.351	76.753
C2	0.694	2.703	18.866
C3	4.206	244.891	399.907
C4	0.773	6.892	56.523
C5	20.245	38.204	61.837
C6	2.145	57.269	293.842

It is found that both control chloroprene rubber dispersions containing different amounts of montmorillonite, and those modified by chemical grafting with increasing amounts of MMA have polymodal particle size distribution. Analyzing the size distribution for sample C3, containing 7 parts montmorillonite/100 parts rubber, it can be seen that the largest particle population has sizes larger than 200 μm , while populations with sizes smaller than 100 μm are reduced, so that the distribution curve can be practically assimilated with the unimodal type. The same aspect is found for sample C5, which contains 4 parts montmorillonite and 15 parts MMA reported to rubber, except that the largest particle population has sizes smaller than 100 μm .

The dispersions obtained by chemical grafting of polychloroprene latex are stable for 30 to 40 days but the technology is time and money consuming.

Bonding capacities were determined for the dispersions C1-C6. The peeling resistances for the initial and modified dispersions are given in Table 4.

Table 4. Peeling resistance, N/mm, for C1 - C6 dispersion with additives

Dispersion/ support	24h					72 h			168 h	72h/3h at 50°C, immediate peeling	72h/168h 70°C, peeling after 24h
	St/ St	St/ L	St/ SL	St/ Le	St/ C	St/ SyL	St/ St	St/ St	St/ St	St/St	St/St
C1	3.1	0.2	2.4	1.5	2.8	0	3.9	5.1	2.7	5.6	
C2	3.6	0.8	2.8	5.2	3.7	0	5.5	7.2	3.5	6.1	
C3	2.6	0.5	1.9	2.6	2.7	0.3	3.1	3.9	2.5	5.5	
C4	5.9	0.9	3.4	7.3	5.3	1.0	4.3	6.0	3.9	8.0	
C5	6.8	2.1	3.9	8.7	6.4	1.8	5.5	7.4	5.2	9.2	
C6	8.1	4.2	4.8	9.1	8.2	2.3	6.1	7.5*	7.1	12*	

St – standard rubber; L – leather; SL – split leather; Le – linen; C – cotton; SyL – synthetic leather; * - tear rubber

Table 4 emphasizes the following influences of grafting and of additives:

- grafting of methyl methacrylate onto polychloroprene chains increases the adherence with 15-40%, depending on support and monomer amount, their peeling

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resistance being very close or even higher than those of the solvent-based adhesives on support as leather, split leather, linen and cotton cloth (higher than 3 N/mm);

- high values of the adherence were obtained at 50 and 70°C, which suggests that the dispersions in which the polychloroprene is grafted with methyl methacrylate give very resistant binding at higher temperature.

- It has been shown that the smaller the particles and have a broader distribution, better penetrate porous media substrates, and on the other hand, the dispersions can have a high dry matter content, which may lead to an optimal combination rough media.

CONCLUSIONS

High performance environmentally friendly aqueous adhesive nanodispersions for shoe manufacture were obtained by mechano-chemical grafting of polychloroprene using benzoyl peroxide as initiator and colophony resin and MMT as adhesion improvers.

Particle size and particle size distribution increase when the polychloropren is grafted, both increasing with the amount of methyl methacrylate introduced.

Peeling resistance is higher for dispersions containing grafted polychloroprene with, it increases with monomer amount and depends on the nature of substrate to which the standard rubber is bonded.

Aging for 168 h at 70°C increases the adherence in all the cases between about 2,7 and 12 times, depending on the degree of polychloropren grafting and the nature of the adhesion improver used.

The obtained adhesives dispersions, and especially C6, are very adequate for manufacturing of footwear resistant to high temperatures.

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