UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
DOCTORAL SCHOOL IN CHEMISTRY

ABSRTACT

PhD THESIS

AQUEOUS ADHESIVE DISPERSION S BASED ON ELASTOMERS

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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.

In 2004, through the Governmental Decree no. 254, the Romanian Government adopted the European Directive to ecologically label clothing and leather articles, which specify the total quantity of volatile organic compounds (VOC) allowed for use during the final assemblage (adhesive bonding) of footwear articles, namely 25 mg VOC/pair for adult footwear and 20 mg VOC/pair for children's footwear. 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.

The doctoral thesis is structured in two parts:

Bibliographical research, which contains 4 chapters:

Chapter 1, in which literature data concerning the general notions of adhesive and adhesion is presented.

Chapter 2, which contains the ways in which the aqueous medium dispersion systems and adhesives with such a medium are obtained, the requirements being related to performances and factors that ensure the success of application.

Chapter 3, which contains literature data regarding the rubber grafting.

Chapter 4, containing data regarding the use of adhesives in the footwear industry.

Experimental research, which includes 5 chapters and ends with general conclusions.

Chapter 5 presents reagents, the materials used, the preparation of samples and equipment used to obtain the prepared adhesive dispersions.

Chapter 6 includes the main technologies used to obtain methyl methacrylate grafted polychloroprene adhesive dispersions, in order to improve the adherence of pairs to different or identical supports, which have also led to a patent application regarding their development.

Chapter 7 contains the characterization of adhesive dispersion from the point of view of dimensions and distributions of particles' dimensions, as well as stationary and dynamic rheological behaviors.

Chapter 8 deals with the characterization of films obtained from dispersions prepared by the controlled removal of the dispersion medium by optical and electron microscopy, x-ray diffraction and FT-IR spectroscopy.

Chapter 9 presents the results obtained for the bonding capacities of the prepared adhesive dispersions for various pairs of supports.

Chapter 10 presents general conclusions.

1. GENERALITIES ON ADHESIVES AND ADHESION

Currently, adhesives are practically used in the manufacturing of all finished products and, in most cases, are the safest and most convenient joining procedure.

1.1. Short history on adhesives and their uses

Glues are well known and have been used for a long time. Ancient Egyptians would use them to plate Tutankhamen's treasures and the old Greek word for glue, ***κολλα***, was turned into colloid. Plant or animal based glues were used until the 20th century. In the 20th century, synthetic products were developed and the notion of adhesive was introduced.

1.2. Adhesives and adhesion

Adhesives are defined as ***materials that, when applied on the surfaces of objects, can join them and make them resist to separation.***

The terms ***adherent*** and ***substrate*** are used to describe a body or material that is about to be joined with an adhesive. Other basic terms are: ***shelf-life*** – the period during which an adhesive can be stocked before being used – and ***pot-life*** – the maximum time between the last stirring and application.

Basically, an adhesive must have the capacity to: [10,12]

(i) *Wet the surfaces*, namely *the angle of contact with the surfaces* on which the adhesive is applied *has to be close to zero* (has to spread), which requires, an intimate contact between adhesive and surface.

(ii) *Harden*, to become a strong cohesive solid; this can be done by chemical crosslinking, removing of solvent/dispersion medium, or cooling for thermal adhesives.

The reasons for the development of adhesives are:

- in an adhesive bonding the forces are distributed on much larger surfaces than when they are bonded with screws or rivets;
- the lack of dimensional stability for anisotropic materials can be corrected;
- materials of various types can be assembled: paper with wood or metal, rubbers or plastomers with wood or metal, various metals, etc.;
- allow the bonding of materials that cannot be joined by other means (powders, fabrics, paper, abrasive cloths, non-woven fibres, foil, thin layers of paper or plastic materials etc.).

A *disadvantage* of adhesives as a means of bonding is the considerable reduction of resistance produced by water and its vapors. Additionally, exploitation temperatures are lower that those for mechanically bonding agents, being limited by the glass transition temperature of the polymer and its chemical degradation. [13, 14]

The *advantages* include the capacity of adhesives to joint different materials, the possibility to be spread on large surfaces, the aesthetic and aero-dynamic exterior aspect of the bonding and the use of machines or robots to apply them.

1.3. Classification of adhesives

The variety of raw materials, the possibilities to combine various compositions, the physical state of each adhesive, the application method, the structuring procedure, the final properties and multiple uses, along with the diversity of materials to be joined, make impossible the existence of a unique classification criterion. [15, 16] The criteria for classification, the class to which the adhesive belongs to and examples are shown in Table 1.1.

Table 1.1. Classification of adhesives

Classification criterion	Class	Examples
Origin	Natural Synthetic	Plant glues, starch Animal glues Synthetic resins Phenolic resins Epoxy resins
Chemical type	Inorganic Organic	Cement Acetate, rubber resins Polyester resins
Temperature range	For low temperatures	Phenolic resins
	For medium temperatures	Epoxy resins
	For high temperatures	Quinolinic resins
Adherent type	For gluing	Metal-metal (loctite) Metal-glass Metal-plastic material Plastic-glass material Plastic-wood material

1.4. Forces of attraction involved in the adhesion process

The adherent must be compatible with the adhesive. The interactions between them can be either primary bonds or secondary ones. Primary bonds (ionic, covalent and metallic) rarely are encountered in the adhesion processes, while secondary ones, such as Van der Waals, are prevailing. [17, 18]

1.5. General properties of adhesives

To evaluate an adhesive, a series of general properties that describe its behavior, starting from its preparation for use until the joining it was used for was destroyed, must be taken into consideration. The general characteristics of adhesives actually include working properties and consist mainly in: viscosity, conservation time, working time, penetration capacity, adhesiveness, processing velocity, etc. [23, 24]

1.6. Adherence theories

There are six theories on adherence: physical absorption, chemical bonding, diffusion, electrostatics, mechanical blockage, and of the weak limiting separation layer.

1.7. Adhesive bonding

When evaluating the quality of a bonding obtained with adhesives, the joining of materials with different mechanical properties generally must be considered. [57] Moreover, the bonding can be subjected or not to mechanical stress and the materials can be deformable or not.

1.7.1. Types of stresses

Bonding by overlapping produces a homogenous distribution of stresses in the gluing layer if it is not subjected to another mechanical stress, as shown in Figure 1.4.

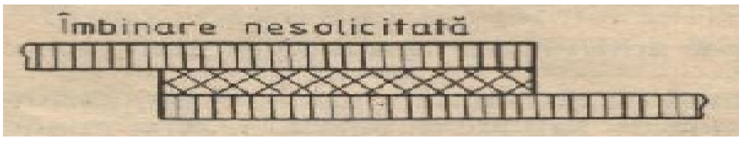


Figure 1.4. Bonding without mechanical stress

When the materials to be bonded together cannot be deformed by stresses parallel to the bonding direction, figure 1.5, an even distribution occurs in the bonding layer.

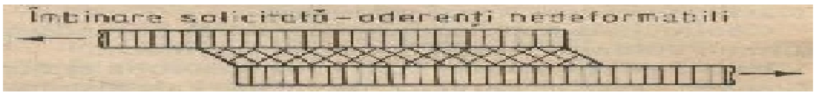


Figure 1.5. Bonding of materials that cannot be deformed with mechanical stress

However, if materials can be deformed, such as in Figure 1.6, a more pronounced deformation of the adhesive occurs at both ends of bonding area (closer horizontal lines), in comparison with the center of the overlapping area.

Figure 1.7. Bonding of materials that can be deformed with mechanical stress

Types of mechanical stresses encountered in the case of adhesive bonding:

1. pull or tearing – the force is perpendicular to the bonding area;

2. shearing and compression – the force that acts on the adhesive layer, along the two bonded surfaces, tends to move them in opposite directions;

3. pilling – it is determined when one or both adherents are flexible;

4. shock – the energy absorbed by a standard sample when it is suddenly hit by the hammer of a testing apparatus;

5. ***bending*** – the force acts on the rigid parallelepipedic samples supported at both ends, glued precisely in the middle;

6. ***splitting*** – the forces is applied in opposite directions at one of the ends of the bonding plane between two rigid adherents.

For maximum efficiency in choosing the type of bonding, the following general principles must be taken into account: [58, 59]

1. the adhesive must be applied in the direction of maximum loading;
2. it must cover as much as possible of the contact surface;
3. the application must be made as a uniform layer;
4. a continuous and thin adhesive film must be maintained;
5. the concentration of bonding stresses must be prevented.

1.7.2. Types of bonding

In Figures 1.14-1.18, the types of bonding most encountered in practice are presented.

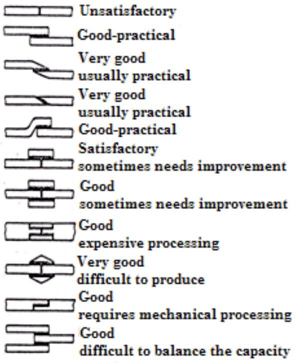


Figure 1.14. Types of linear adhesive bondings

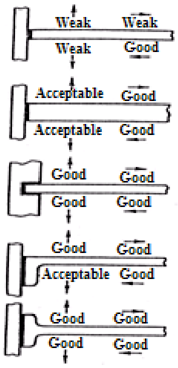


Figure 1.15. Angular bondings

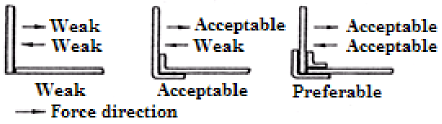
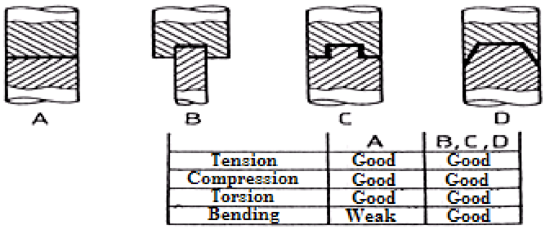
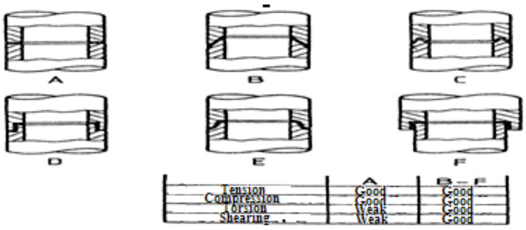


Figure 1.16. Corner bondings



	A	B, C, D
Tension	Good	Good
Compression	Good	Good
Torsion	Good	Good
Bending	Weak	Good

Figure 1.17. Rod bondings



	A	B – F
Tension	Good	Good
Compression	Good	Good
Torsion	Weak	Good
Shearing	Weak	Good

Figure 1.18. Cylindrical bondings

Generally, the elements presented in Figure 1.9 are found in an adhesive bonding:

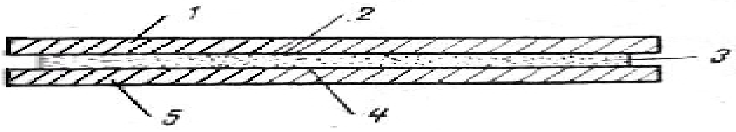


Figure 1.19. Structure of an adhesive bonding: 1 – first substrate; 2 –first interface; 3 –adhesive film; 4 – second interface; 5 – second substrate

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2. DISPERSE SYSTEMS WITH AQUEOUS MEDIUM

Systems consisting of particles of different size dispersed in a homogenous medium are called **disperse systems**. **Colloidal** systems belong also to this category.

A disperse system is a polyphasic system with at least two components: **a dispersion medium** or **a continuous phase** – which is a low molecular weight compound – and a **dispersed** or **discontinuous phase** – constituting the kinetic units of the system and having larger sizes than the molecules of the medium. The term "colloidal" defines the states with dispersed poly-molecular particles having at least one dimension in the range 1-1000 nm. [1]

2.1. Classification of disperse systems

Given the way the kinetic units (particles) of disperse systems are formed and their interaction with the dispersion medium (water), disperse systems are often divided in three distinct categories: [4, 5]

- Lyophobic systems, made of micro- or macro-molecules, characterized by a weak interaction between disperse phase and dispersion medium. Lyophobic sols, suspensions, emulsions and lattices are included in this category.
- Micellar association systems, where the interaction of the dispersed phase with the dispersion medium is strong, property which gave them the name of "lyophilic systems".
- Solutions of macromolecular compounds, non-ionic or ionic, or molecular colloids, with properties identical to micellar ones from the points of view of interaction and stability.

2.2. Methods of obtaining aqueous polymer dispersions

Aqueous polymer dispersions can be obtained by three methods: *emulsion polymerization, dispersion of water-insoluble polymer solutions* dissolved in coupling solvents in the presence of sufficient surfactant amounts or *dispersion of concentrated hydrophilic polymer solutions.*

2.3. Classification of adhesive dispersions

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. 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 ion the range 0.2-50 μm and micro- or nano-dispersions between 10 and 200 nm. [15] Systems having particles with diameters between 10 and 1000 nm are usually called **colloidal systems**. [16]

According to their diameter, colloidal particles are divided as ***fine*** – with diameters between 100 and 2500 nm and ***ultra-fine*** – with diameters between 1 and 100 nm.

2.4. Adhesives with aqueous dispersion medium

Water-based adhesives are known since 1970. The dispersed phase is made of rubber and contains certain additives such as synthetic resins, in order to increase adhesion. [18] They have a lower viscosity so that they can be applied on different substrates in various thicknesses. But not all of them are ecological or solvent-free; some contain volatile organic compounds, with direct consequences on the viscosity.

Water-based adhesives are divided into dissolved and dispersed in water. The soluble ones include animal and plant glues and the dispersed ones contain natural or synthetic polymers.

Synthetic latices are aqueous polymer dispersions obtained by emulsion polymerization. Such polymers are of chloroprene, styrene-butadiene, vinyl acetate, acrylates, vinyl chloride, etc. type. [19] They are used for labels, packing, bonding of wood products, compacting of prefabricated products, panel lamination, high pressure lamination, buildings, joining of tiles, masonry etc.

Water is a high surface tension liquid, which makes water-based adhesives good for binding high surface tension materials such as paper. They are used for long production because the spreading time on substrate is long.

However, water-based adhesives have some limitations: they are not suitable for low surface tension substrates, such as films from plastics, metal sheets, poly(vinyl chloride) and spongious materials. Also, their performances are lower than those of solvent-based ones regarding: [20]

- resistance to pilling at room temperature;
- resistance to shearing at high temperatures;
- flexibility of jointed materials;
- resistance to humidity.

The most important requirements impose to water-based adhesives are:

1) performance, including the resistance of bonding, durability and adaptability to the process;
2) ease of application;
3) technology of crosslinking;
4) blending options.

It must be mentioned that application on substrate and blending techniques involve manufacturing problems such as arranging of equipment in the production process compared with that used for classical solvent-based adhesives.

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3. ELASTOMER GRAFTING

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.* [1]

The physical *blending* of two or more polymers is made to combine their properties and obtain the desired characteristics.

Grafting is the method by which macromolecular chains of identical or different monomers are covalently bonded to the backbons of the polymer that must be modified.

Hardening consists in the polymerization of a mixture of oligomers with formation of a layer that adheres to substrate by physical forces. This gives a smooth finish due to the covering of the surface roughness and is different from the curing or vulcanization of rubber, which produces the chemical crosslinking of polymeric chains.

Only polymer modification by grafting is discussed further on, with emphasizing of free-radical chemical grafting used in the experimental part, but excluding the enzymatic one.

3.1. Grafting techniques

Grafting of polymers can be made by the following techniques: chemical, with radiations, photo-chemical, enzymatic and by plasma.

3.2. Factors controlling grafting

Grafting is controlled by the following factors: nature of polymer, monomer, solvent (if it is done in solution), nature of initiator, the used additives and the temperature.

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4. THE USE OF ADHESIVES IN THE FOOTWEAR INDUSTRY

Beside the basic materials, some other auxiliaries such as adhesives are used for manufacturing of footwear.

4.1. Classification of adhesives used in the footwear industry

The classification criteria for adhesives used in the footwear industry are: [1, 2]

a) chemical nature of the basic polymer;
b) physical nature of the basic polymer;
c) destination;
d) the way the adhesive transforms from a liquid state to a solid one.

4.2. Applications of adhesives in the footwear industry

The purposes for which adhesives are used in the footwear industry are synthesized in Table 4. The table also presents their origin.

Table 4.1. Adhesives for footwear manufacturing: use, types and origin

Use	**Types of adhesives**	
	Internal production	**Import**
Bending upper margins	Natural rubber solution	Polyamide thermal cement
Application of linings	Natural rubber solution	Natural rubber solution/latex
Insole	Natural rubber solution; solvent-based polychloroprene adhesives	Natural rubber solution; polychloroprene adhesives based on organic solvents
Application of toe caps	Polychloroprene adhesives based on organic solvents	Polyamide-based thermo-adhesive toe cap

Table 4.1 (continuing)

Application of heel counters	Polyvinyl alcohol (vinyl acetate-based latex)	Vinyl acetate- and acrylate-based latex
Bonding uppers to insole	Solvent-based polychloroprene adhesives	Solvent-based polychloroprene adhesives. Latex based on natural rubber. Polyamide thermal cement
Heel dressing	Solvent-based polychloroprene adhesives	Solvent-based polychloroprene adhesives
Gluing the sole	Polychloroprene/Polyurethane adhesives based on mono- and bi-component organic solvents	A variety of polychloroprene and polyurethane adhesives based on mono- and bi- component organic solvents
Injection of the sole	Polyurethane adhesives/ Polyurethane adhesives based on organic solvents	Polyurethane adhesives based on organic solvents; TR rubber and organic solvent-based adhesives; Solvent-based polychloroprene adhesives
Gluing the insole cover	Natural rubber solution	Natural rubber solution/Latex based on synthetic resins
Other operations: dressing insole margins, gluing rands and filling	Polychloroprene or polyurethane adhesives based on organic solvents	Polychloroprene or polyurethane adhesives based on organic solvents.

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5. MATERIALS AND CHARACTERIZATION METHODS

5.1. Materials

a) Polychloroprene - NEOPRENE AD 20, DuPont product.

b) Polychloroprene latex DISPERCOLL C 84, containing: chloroprene rubber, water, 1% potassium hydroxide and sodium salt of some acid resins.

c) Methyl methacrylate – monomer.

d) Initiator – benzoyl peroxide, melting point – 108°C.

e) Inhibitor – dodecyl-mercaptan,

f) Zinc oxide:

- **Active –** white-light yellowish powder, active substance - 99,2%, humidity – 0,15%, impurities – max. 0,6%.
- **aqueous dispersion** (Borchers VP 9802), active substance – 93-95%, water-soluble substances 1%.

g) Magnesium oxide (calcined magnesite) – white powder, active substance – 98,5%, humidity - 0,2%, impurities – max. 0,8%, density – 3,2 g/cm^3.

h) Silicon dioxide - DISPERCOLL S 3030 – aqueous silicon acid colloidal solution.

i) Aqueous emulsion of a diphenylamine derivative 50% – RHENOFIT DDA-50 EM.

j) Mixture of styrenated phenols (Vulcanox SP).

k) Poly (vinyl alcohol) with a high hydrolysis degree, white powder or light yellowish powder with the density of 1,21-1,31 g/cm^3.

l) Triethanolamine – colorless liquid, melting point – 20-21^{0}C, boiling point – 277-279^{0}C, density – 1,124 g/cm^3, refractive index – 1,4852.

m) Methylene chloride – clear liquid with the density of 1,323 g/cm^3, concentration – 99,5%, distillation range (min. 95%) – 39-41°C.

n) Ethyl acetate – clear liquid with the density of 0,903 g/cm^3, boiling point – 77^{0}C, concentration – 99,95%.

o) Natural resin, **colophony.**

p) Crosslinking agent to optimize peel resistance – **Desmodur RE** – 27% triphenylmethane triisocyanate solution in ethyl acetate [5], Bayer, Germany. Technical characteristics: white liquid that changes its consistency and color in open spaces, density –0,99g/cm^3, stored in aluminum containers that are kept closed.

r) Thickening agent – **LAVIOTIX P 1,** natural refined clay used for the rheological control of water dispersions

s) pH regulator – aqueous solution 10% of **KOH**.

5.2. Characterization methods

1. Characterization of the dispersed phase by amount of *dry substance, relative viscosity, free monomer and poly(methyl methacrylate) concentrations, pH, particle size and their distribution.*

2. Characterization of films obtained from adhesive dispersions by *optical and scanning electron microscopy, Fourier transform IR absorption spectroscopy (FT-IR), X-ray diffraction, differential calorimetry – DSC for determining the glass transition temperature.*

3. Determinatio of bonding capacity.

6. TECHNOLOGIES FOR OBTAINING ADHESIVE DISPERSIONS

6.1. Technology of obtaining adhesive dispersions by chemical grafting in aqueous dispersion

Into the polychloroprene latex DISPERCOLL C 84 methyl methacrylate was added under stirring, which – in time and by heating – produces the swelling of rubber’s particles.

The initiation period starts after the induction one, in which the potential inhibitors accidentally present are consumed. The initiator decompose into free radicals by heating. They initiate on one hand the polymerization of the methyl methacrylate and on the other hand extract hydrogen or chlorine atoms off polymer’s chains, thus creating free radicals on the macromolecular chain. The last initiate the polymerization of the monomer and thus the grafted polymer is obtained. Dodecylmercaptan stops the increasing of chains by releasing a hydrogen atom. This, at its turn, transforms into free radical, but it is inactive due to stabilization by conjugation.

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 viscoous dispersions, with an elongated agitator, two arms and a stationary blade was used, the bladers’ inclination and the rotation direction being important for the movement of the liquid into the flask.

During the grafting operation a low pressure was ensured inside the flask by adapting a laboratory vacuum pump with a 5 m^3/h flow to the reaction flask.

The receipts from Table 6.1 were used and the control dispersion (A0), as well as those chemically grafted with methyl methacrylate (A1-A3) resulted.

Table 6.1. Technological receipts used for obtaining adhesive dispersions by chemical grafting of polychloroprene from latex (parts by weight)

Composites, g	**A0**	**A1**	**A2**	**A3**
Polychloroprene latex	442,48	442,48	442,48	442,48
Methyl methacrylate	-	8,22	14,03	18,15
Triethanolamine	-	4,11	4,91	6,05
Benzoyl peroxide	-	0,82	0,70	0,61
Dodecylmercaptan	-	1,64	1,40	1,22
Borchers VP9802	17,70	13,15	11,22	9,69
Rhenifit DDA50	11,06	8,22	7,02	6,05
Dispercoll S3030	11,96	8,22	7,02	6,05
De-mineralized water	17,70	13,15	11,22	9,69
TOTAL	**500**	**500**	**500**	**500**

The components introduced function as: pH stabilizer – triethanolamine, thickening agent – Dispercoll S 3030, antioxidant – Rhenofit DDA 50, stabilizer and crosslinking agent – Borchers VP9802 as well as de-mineralized water to obtain the desired concentrations.

The polychloroprene latex was introduced into the flask and the stirrer, vacuum pump and the cooler were adapted. The water flow was adjusted into the cooler, the stirring and the heating started and the monomer added during ½ h.

The initiator was introduced at 80^0C and the stirring maintained for 5 h while the temperature was kept constant. Then, the polymerization inhibitor was added, maintaining the heating and stirring for 1 h. After cooling at room temperature, the rest of the ingredients were added during ½ h, the product removed from the flask and characterized using the methods described in subchapter 5.2. The pressure into the reaction vessel was 5 mm Hg.

The four adhesive dispersions obtained were first characterized physico-chemical by: dry substance, free monomer and poly (methyl methacrylate) concentrations, flowing time using a Ford viscosity cup and pH (Table 6.2).

Table 6.2. – Physico-chemical characteristics of adhesive obtained by chemical grafting of polychloroprene latex

Physical-chemical characteristic/dispersion	**A0**	**A1**	**A2**	**A3**
Dry substance, %	51,98	61,06	58,28	57,84
Free monomer concentration, %	0,00	0,01	0,03	0,05
Poly (methyl methacrylate) concentration, %	0,00	0,00	0,00	0,00
Flowing time through the Ford viscosity cup, s	22	34	28	24
pH	10	13	13	13

6.2. Technology of obtaining adhesive dispersions by roller grafting

The technology involves three steps: chemical grafting of rubber on roller with methyl methacrylate, using the receipts presented in Table 6.3, followed by the dissolution of the obtained compositions into a convenient solvent and the dispersion of solutions in water containing steric and electrostatic stabilization agents as well as for pH adjustment.

*Table 6.3. Receipts used for obtaining compounds based on reference polychloroprene and grafted with methyl methacrylate (*parts by weight*)*

Composites, g	**B0**	**B1**	**B2**	**B3**
Polychloroprene rubber	200	200	200	200
Benzoyl peroxide	-	1	1	1
Methyl methacrylate	-	20	30	40
Zinc oxide	10	10	10	10
Magnesium oxide	8	8	8	8
Styrenated phenol	4	4	4	4
Dodecylmercaptan	-	2	2	2
Total	**222**	**245**	**255**	**265**

To increase the grafting efficiency and reduce the formation of block copolymers, benzoyl peroxide was introduced in compositions subjected to grafting.

The roller blending regime was the following:

- elastomer plasticization -	4 min;
- adding the benzoyl peroxide and the grafting agent -	30 min;
- adding ZnO, MgO and styrenated phenol -	10 min;
- cooling and adding the dodecylmercaptan -	10 min;
- homogenization and removal of the mixture out of roller -	5 min;
Total:	***59 min;***

The B0-B3 compositions obtained by processing on roller were dissolved in a mixture of methylene chloride/ethyl acetate 30/70 and the obtained solutions dispersed into aqueous medium. The dissolution was made in a glass flask: the sample was introduced, the solvent mixture added and the stirrer adapted to the reaction vessel. The stirring (300 rpm) was maintained for 1,5-2,0 h, until homogenization produced.

The dispersions were prepared using the receipts from Table 6.4. [18, 19]

Table 6.4. Receipts used to obtain adhesive dispersions by dispersing solutions of compoundings B0-B3

Composites, g	**B0**	**B1**	**B2**	**B3**
Compound	46,25	50,99	53,07	55,17
Solvent mixture	33,75	29,01	26,93	24,83
Polyvinyl alcohol, liquid solution 10%	50	50	50	50
Triethanolamine	15	15	15	15
De-mineralized water	80	80	80	80
KOH, 10% solution	1	1	1	1
Total	**226**	**226**	**226**	**226**

The components were added drop by drop into the rubber solution for 1 h. [20, 21]

The obtained adhesive dispersions were first characterized physico-chemical, according to current standards. The results are presented in Table 6.5.

Table 6.5. – Physico-chemical characteristics of adhesive dispersions obtained by grafting on roller

Physico-chemical characteristic/dispersion	**B0**	**B1**	**B2**	**B3**
Solid substance concentration	48,58	52,06	53,64	57,59
Free monomer concentration, %	0,00	0,03	0,06	0,1
Methyl poly-methacrylate, %	0,00	0,10	0,14	0.2
flow time through the Ford viscosity cup, s	18	17	19	20
pH	13	13	13	13

6.3. Technology of obtaining of adhesive dispersions with sodium montmorillonite by grafting on roller

The natural clays with modified surface are ***layered silicates*** used successfully to obtain nano-composite polymeric 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 individual nanometric layers, which maximizes the interfacial contact;
- *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 stenghtening 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 6.6, dissolution of products obtained in the same mixture of solvents and dispersion of solutions obtained following the formulation from Table 6.7.

Compounds in Table 6.6 were subjected to roller grafting in the same way as polychloroprene ones (B series). Differences occur only for the time zinc oxide and magnesium oxide, styrenated phenol and montmorillonite were introduced, the total time increasing from 10 to 15-20 minutes.

*Table 6.6. 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
Styrenated phenol	4	4	4	4	4	4
Total	**226**	**230**	**236**	**243**	**253**	**263**

The dispersion was done into the installation presented in subchapter 6.2. 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 de-mineralized water were added.

Table 6.7. 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

The adhesive dispersions obtained were physicao-chemical characterized, similarly to those belonging to B series. The results are presented in Table 6.8.

Table 6.8. Physico-chemical characteristics of adhesive dispersions obtained by grafting on roller in the presence of sodium montmorillonite

Characteristic/dispersion	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
Solid compounds concentration	48,58	52,06	53,64	57,59	58,02	56,14
Free monomer concentration, %	0,00	0,00	0,00	0,10	0,16	0,22
Poly(methyl methacrylate) concentration,%	0,00	0,00	0,00	0,10	0,23	0,57
pH	13	13	13	13	13	13
Flowing time through Ford viscosity cup, s	18	17	19	20	21	20

6.4. Conclusions

Three types of adhesive dispersions based on polychloroprene rubber modified by chemical grafting with methyl methacrylate were prepared using two different technologies: grafting in dispersion (latex) and in the polymer bulk using the roller technique.

If the first method gives directly dispersions of polychloroprene rubber grafted with methyl methacrylate, the second one requires the obtaining of grafted rubbers, dissolving into a mixture of solvents and dispersion of solutions under mechanical stirring in the water containing agents of dispersion, stabilization and pH adjustment.

The second method is more time-consuming and the obtained dispersions are coarser, mechanical dispersing not allowing obtaining of fine dispersions, especially for viscous polymer solutions and the dispersion medium is introduced into the polymer solution.

14 of the adhesive dispersions were selected and tested from the following points of view: rheological, structural, dimensions of particles, microscopical, glass transition temperature and adherence on different substrates.

7. CHARACTERIZATION OF ADHESIVE DISPERSIONS

Lattices, dispersions or polymeric colloids with aqueous dispersion medium are used especially as film-forming agents for various coatings. [1-3]

Formation of polymeric film from latex depends on its characteristics (nature of polymer, particle shape, sizes and particle size distribution, etc.) and on the experimental conditions during drying (rate of water evaporation, temperature, humidity).

On one hand the selected adhesive dispersions were characterized, and on the other one the films resulted by the controlled removal of dispersion medium, using specific methods.

7.1. Particle sizes and size distribution

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. [5, 6]

Dynamic light scattering (DLS), also known as photon correlation spectroscopy (PCS), measures the fluctuations of intensity of scattered lightwhich occur due to the Brownian movement of particles and is time-dependent. [7]

Particle size distribution of the initial polychloroprene latex and of aqueous dispersions of rubber modified by grafting with MMA, processed or not with auxiliary compouns to provide them some characteristics required by application were determined using Mastersizer 2000 equipment (Malvern Instruments, UK) using laser light, which allows the determination of a wide range of particle size, [8, 9] between 0,02 and 2000 µm, with an accuracy of ± 1%. The result of analysis is the distribution of particle volumes, expressing, for each class of sizes, the percentage of particles having a volume higher than a given value. This can be converted into numerical or gravimetric distribution, distribution of surfaces or diameters. All parameters are automatically recorded and can be subsequently examined, processed or compared. [10, 11]

The standard points for reading the distribution characteristics are: **D(v, 0.5), D(v, 0.1) and D(v, 0.9**), which have the following meanings:

- **D(v, 0.5)** – value of abscissa, in microns, for which 50% of the sample volume has particles with diameter higher than a given value, also known as Mass Median Diameter.
- **D(v, 0.1)** – value of abscissa for which 10% of the sample volume has a higher diameter than a given value.
- **D(v, 0.9)** – value of abscissa for which 90% of the sample volume has a higher diameter than a given value.

7.1.1. Particle size distribution of dispersions obtained by chemical grafting of latex particles

Figure 7.5 presents, superposed, the distribution curves for dispersions A0-A3.

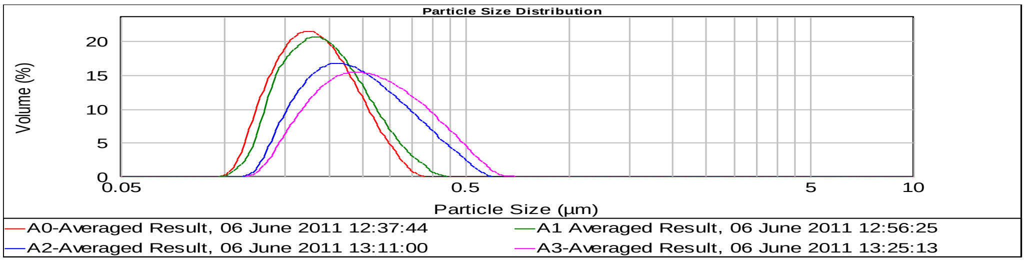


Figure 7.5. Superposed curves of particle size distribution for samples A0 – A3.

The control polychroloroprene dispersion, as well as those obtained by grafting in latex state exhibit unimodal distributions. Particle sizes and distribution range increase with the amount of MMA used for grafting compared with the non-modified sample. Thus, the lower limit of size increass from 0.105 to 0.120 µm, while the maximum limit reaches ca. 0.700 µm, compared to approximately 0.32 µm for the non-modified one.

The values of standard points are presented in Table 7.1. Their values also increase with grafting degree.

Table 7.1. Values of standar points for reading distribution for dispersions A0-A3

Sample	D(v, 0.1), µm	D(v, 0.5), µm	D(v, 0.9), µm
A0	0,132	0,181	0,259
A1	0,139	0,191	0,282
A2	0,158	0,235	0,383
A3	0,168	0,260	0,426

7.1.2. Particle size distribution for aqueous dispersions obtained from polychloroprene modified by roll grafting

Figure 7.10 presents superposed distribution curves for samples B0-B3

The figure shows that particle size descrease and particle size distribution become narrower with increasing of amount of grafted.

Table 7.2 presents the values of the three standard points of reading distribution characteristics for dispersions B0-B3.

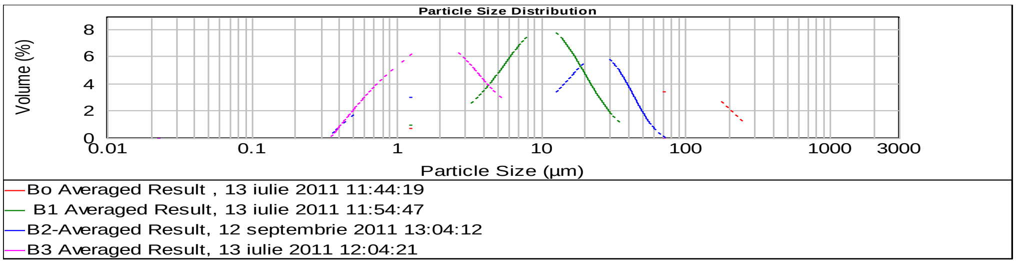


Figure 7.10. Superposed distribution curves for samples B0 – B3

Table 7.2. Standard points for reading distribution characteristics for dispersions B0-B3

Sample	D(v, 0.1), µm	D(v, 0.5), µm	D(v, 0.9), µm
B0	2,256	24,588	143,293
B1	1,846	8,799	21,168
B2	0,815	9,637	35,430
B3	0,738	2,107	10,104

Modifying of polychloroprene by graftin on roll with MMA has the following effects on particle size distribution of dispersions obtained by mechanical dispersion of solutions:

- maintaining the type of polymodal distribution;
- decreasing of particle sizes with the increase of MMA amount used in grafting, from 10 to 20 parts raported to the rubber amount, compared with the control sample, except for sample B2 containing 15 parts MMA, for which D(v, 0.5) and D(v, 0.9) values are higher.

7.1.3. Particle size distribution for aqueous dispersions obtained from polychloroprene rubber modified on roll in the presence of montmorillonite

To establish the influence of montmorillonite on particle size distribution, C1-C3 samples from Table 6.6 were prepared, containing various amounts of montmorillonite. To have a heneral view on sizes and particle size distribution of dispersions containing montmorillonite, non-grafted or grafted with MMA, the curves are represented superposed in Figure 7.17.

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. Tis is explained by the agglomeration of latex particles produced by the high amount of montmorillonite, exceeding the recommanded one.

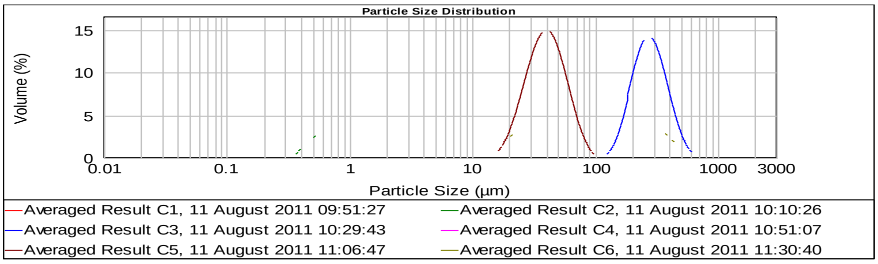


Figure 7.17. Superposed distribution curves for samples C1-C6

Grafting with methyl methacrylate was done only for polychloroprene rubber having the composition C2, from which compounds C4-C6 in Table 6.6 were obtained.

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, prevaling the particles with average diameters of about 1.02 and 12 µm respectively. 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 7.3.

Table 7.3. 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 raported to rubber, except that the largest particle population has sizes smaller than 100 µm.

In conclusion, the dispersions obtained by mechanical dispersion of solutions of samples obtained by grafting on roller have larger particle sizes and much wider size distributions, determined by the method of obtaining, mechanical dispersion having as main disadvantages obtaining of large particles, with wider distribution, and lack of reproducibility. In addition, due to high viscosities of solutions required to minimize the amount of solvents, dispersion was done by introducing the dispersion medium under stirring into solutions but not by introducing small amounts of solution into medium. The reverse operation could lead to a smaller particle size.

7.2. Rheological behaviour

Rheology, defined as the science of deformation and flow, studies the response of bodies under external mechanical loadings and establishes the mathematical models that describe their response to such actions.

Rheological characteristics of disperse systems affect the storage stability and final use properties of a wide variety of industrial products, [12, 13] provide information on microstructure [14] and, allowing the assessment of consistency and apparent plasticity, [15] are important for predicting their behavior when are applyed.

The rheology under the action of **shear forces** divided in ***stationary*** and ***dynamic*** (***oscillatory***).

In ***stationary rheological*** experiments, shear deformation (γ) is applied with a given speed ($\dot{\gamma}$) and the resulting shear stress is measured (τ). Thus information on consistency (viscosity) of the system and its dependence on stationary shear rate can be obtained.

Dynamic rheological experiments involve small amplitude measurements and provide information on the microstructure of systems. Unlike stationary shear tests, the dynamic ones are non-destructive and can be performed without affecting the sample microstructure.

7.2.1. Rheological behaviour of dispersions obtained by modification of polychloroprene rubber from latex

7.2.1.1. Stationary rheological behaviour

Rheograms obtained for adhesive dispersion A0 when increasing and decreasing shear rates are presented in Figure 7.18.

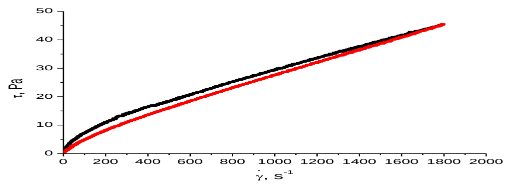
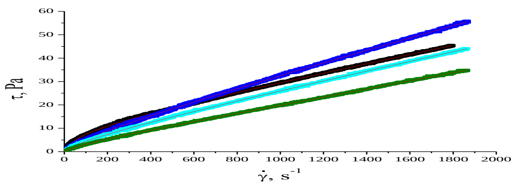
	

Figure 7.18. Rheogram of dispersion A0 with: ■ – increasing; ■ – decreasing shear rates	Figure 7.19. Rheograms of samples A0-A3 with increasing shear rates: ▪ – A0, ▪ – A1, ▪ – A2, ▪ – A3; red curves – fitting with Cross equation

The rheogram obtained with increasing shear rates shows that: dispersion starts to flow at about 2 Pa, present an ideally plastic behavior at speeds below 40 s^{-1}, becomes pseudoplastic up to about 400 s^{-1} and above 400 s^{-1} is again ideally plastic. At a shear rate of about 40 s^{-1} the system is slightly destructured, and the behavior transforms from pseudoplastic to ideally plastic.

Linearization of dependence of apparent viscosities-shear rates gives a value of viscosity at zero shear rate, η_o, of 0.276 Pa.s. This is actually the value of viscosity at the shear rate 1 s^{-1}, low enough for all the fluids behave Newtonian and represents dynamic viscosity of the system.

As a result of destructuring, the rheogram obtained on decreasing of shear rates is placed below that recorded on increasing, forming a hysteresis loop. So the dispersion has a time-dependent rheological behaviour of thixotropic type. When the shear rates decrease the system restores partially its structure. The value of η_o is 0.109 Pa.s, 2.53 times lower than that obtained on increasing rates, so the dispersion remains partially destructured. Thixotropy index, calculated as the ratio of the hysteresis loop area and of the area under the rheogram obtained on increasing shear rates, expressed as a percentage, has the value of 6.4%.

Rheograms obtained for compositions A_1-A_3 on increasing shear rates are shown in Figure 7.19.

The figure shows that for the lowest MMA amount the limiting shear stress preserves their value but the pseudo-plastic behavior is less pronounced, which means that the dispersion is destroyed less under the action of shearing. The rheogram is placeed under that of A0 dispersion at shear rates under 500s^{-1}, when its behavior is pseudo-plastic, and over it its behavior becomes ideally plastic. The MMA amount makes rheograms be under that of dispersion A0; the higher the monomer amount the lower the rheograms are placed. The limiting shear stresses displace towards zero and shearing rates at which the behavior starts to be ideally plastic decrease.

The values of η_o şi η_∞ used in equation (7.7), 1/C and m, and of correlation coefficients, R^2, for A0-A3 dispersions, values resulted from rheorgrams obtained with increasing shear rates are are presented in Table 7.4.

Table 7.4. Values of η_o, η_∞, 1/C, m and R^2 obtained for dispersions A0-A3 with Cross equation

Dispersion	**η_o, Pa.s**	**η_∞, P.as**	**1/C, s^{-1}**	**m**	**R^2**
A0	0.192	0.018	40	0.841	0.99983
A1	0.161	0.023	10	0.565	0.99982
A2	0.125	0.018	17	0.632	0.99975
A3	0.041	0.017	125	1.055	0,99978

It can be seen from the Table that the highest η_0 value was obtained for dispersion with no MMA and the highest η_∞ value for the one containing the lowest quantity. Considering values m, A1 dispersion is the less pseudoplastic, containing minimal amount of MMA quantity, and the most pseudoplastic one that containing the maximal amount. Correlation coefficients are very close to the unit, which means that Cross equation describes very well the behavior of all dispersions. The same thing can be seen in Figure 7.19, red curves representing Cross equation.

Given the very low or even zero limiting shear stress, to obtain the values of flow indices of A2 and A3 dispersions Ostvald-de Waele equation was applied (equation describes the pseudoplastic behavior of fluids without limiting shear stress). [27, 29]

Values obtained for flow indices of A0-A3 dispersions with Ostvald-de Waele equation and of dynamic viscosities, η_0, and R^2 are summarized in Table 7.5.

Table 7.5. Dynamic viscosities, flowing indices and correlation coefficients obtained for samples A0-A3 using Ostvald-de Waele equation

Dispersion	**η_o, Pa.s**	**n**	**R^2**
A0	0,276	0,678	0,99784
A1	0,099	0,840	0,99960
A2	0,090	0,821	0,99937
A3	0,048	0,873	0,99931

The table shows that the η_0 decreases significantly for dispersions containing grafted MMA compared to ungrafted polymer, especially when the monomer was introduced in a larger quantity. Flowing indices vary inverse compared to viscosities, as expected, less viscous dispersions flowing easier. R^2 have very good values, especially for dispersions containing grafted rubber, but all values are a slightly lower than those obtained for Cross equation.

The apparent viscosities, η^*, decrease when shear rates increase, which is characteristic to pseudoplastic systems. Dependence of apparent viscosities on shear rates for dispersions A0-A3 when they are increased are represented in Figure 7.20.

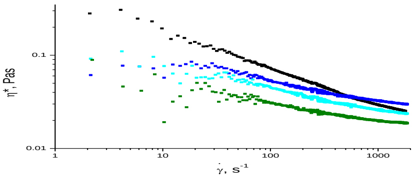


Figure 7.20. Dependence of apparent viscosities on shear rates for dispersions: ▪ – A0, ▪ – A1, ▪ – A2, ▪ – A3

The Figure shows that for dispersion that does not contain MMA the apparent viscosity decreases practically linear with increasing of shear rates, while the decrease is exponential for dispersions containing different amounts of monomer. The viscosity of dispersion A0 drecreases the most in the used shearing speed interval.

The rheograms of dispersions containing MMA obtained when shear rates are increased and decreased superpose, that is these systems do not have time-dependent rheologic behavior.

7.2.1.2. Dynamic rheologic behavior

Rheology describes the behaviour of viscoelastic fuilds by two components: viscosity and elasticity. Viscosity is the resistence of the considered fluid during the flow and elasticity is its property to store the deformation energy in an attempt to recover its original shape.

The viscous and elastic components of a fluid are obtained using rheometers. They record the resistance force generated by the material during its deformation. At low deformation amplitudes the viscoelastic response of material is linear. In such a case dynamic measurements allow determination of storage and loss moduli as function of frequency of the oscillatory motion.

Dependencies of storage moduli on the applied frequencies for dispersions in Table 6.1, subchapter 6.1, are presented in Figure 7.21 and loss moduli in Figure 7.22.

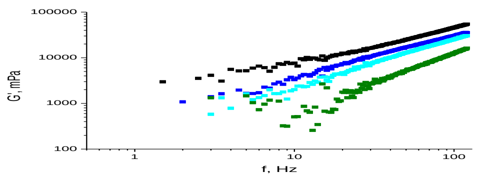


Figure 7.21. Dependencies of G’ on frequency for dispersions: ▪ – A0, ▪ – A1, ▪ – A2, ▪ – A3

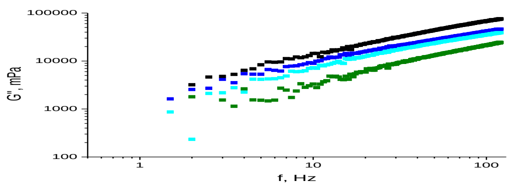


Figure 7.22. Dependencies of G” on frequency for dispersions: ▪ – A0, ▪ – A1, ▪ – A2, ▪ – A3

The two figures show that the values of loss moduli increase almost linearly with frequency for all dispersions, while those of storage ones vary slightly exponentially.

Loss moduli have values only a bit higher than storage ones over the entire frequency range. That is the two components have close values, with a slight predponderace of viscosity.

If the dependence of time of the values of the two moduli at the constant frequency of 10 Hz is considered for the four dispersions, the results given in Figure 7.23 are obtained.

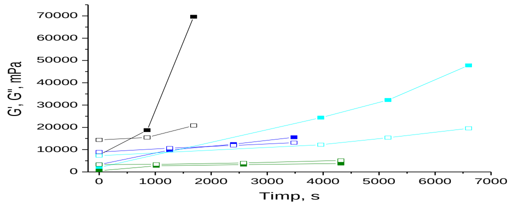


Figure 7.23. Modifications of storage (■) and loss (□) moduli at 10 Hz in time for: ▪ – A0, ▪ – A1, ▪ – A2, ▪ – A3

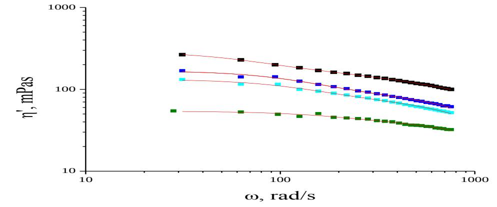


Figure 7.24. Dependencies of dynamic viscosities on frequency for dispersions: ▪ – A0, ▪ – A1, ▪ – A2, ▪ – A3; red curves – fitting with generalized Maxwell model

The Figure shows that initially all dispersions have loss moduli slightly higher than the elasticity ones, that is the viscous behavior is slightly predominant. If the loss modulus increases a bit in with time for dispersion A0, the storage one increases more, almost 2 times in 1000 s and about 7 times in 2000 s, so the dispersion becomes preponderantly elastic under the action of oscillatory motion. On the other hand, for dispersions containing grafted polychloroprene the storage and loss moduli are independent on time of application of oscillatory movement, except for dispersion A2, for which the storage modulus increases approximately 22 times in 6500 s and the loss one almost 2.5 times, which means that the dispersion becomes more and more elastic in time, starting with about 1200 s of application of oscillatory movement (at 6500 s the elasticity modulus becomes 2.4 times higher than the loss one).

Given the linear viscoelastic behaviour of systems within the used frequencz range, the obtained results must be treated with models describing the visoelastic behaviour of bodies. The most general form of a linear model of viscoelasticity is the generalized Maxwell model, known also as Maxwell-Wiechert, [30] consisting of simple Maxwell models joined parallel to consider the spectrum of relaxation times.

The dependence of dynamic viscosities on frequency for dispersions A0-A3 are represented in Figure 7.24. The Figure shows that dynamic viscosities decrease with increasing of applied frequency, systems A0 and A3 having the highest decrease, described accurately by the generalized Maxwell equation.

In table 7.6 the values of dynamic viscosities and relaxation times obtained for the three simple Maxwell models, of viscosities at zero frequency and correlation coefficients obtained using the generalized Maxwell relation consisting of 3 simple models are given.

Table 7.6. Values of dynamic viscosities and relaxation times, viscosities at zero frequency and correlation coefficients for the generalized Maxwell relation consisting of 3 simple models

Dispersion	**η_i, mPas**			**θ_{ri}, ms**			**η'_0, mPas**	**r^2**
	1	2	3	1	2	3		
A0	95	131	60	0.5	14.1	2.2	286	0.99981
A1	80	89	0	0.8	7.7	0	169	0.99213
A2	69	63	0	0.9	7.1	0	132	0.99351
A3	38	16	0	0.7	4.5	0	54	0.97939

The values of correlation coefficients show that the generalized Maxwell equation describes the viscoelastic behavior of dispersions, especially when they do not contain polychloroprene grafted with MMA or the amount of monomer is lower. When the frequency tends toward zero, the dynamic viscosities of the systems become equal to the sum of the viscosities of simple Maxwell models.

When comparing viscosities obtained at a zero frequency to those for zero shearing rate in Table 7.4 resulted from the Cross equation, a pretty good corespondance of values can be noticed.

In conclusion, both the non-grafted polychroloprene rubber and the MMA grafted polymer have a pseudoplastic behavior with a zero limiting shear stress, which becomes less pronounced as the methacrylate amount increases. Viscosities at zero shear rate also drop with increasing of MMA quantity while flow indices increase. Another effects of MMA is the disappearance of the thixotropic behavior obtained for the non-grafted polymer sample, probably because of the stiiffening of the polychloroprene molecules. The pseudoplastic behavior is described very well both by the Cross and Ostwald-de Waele models. Dynamic rheologic measurements show that the two components – elastic and viscous – are very balanced, with just a slight preponderance of the viscous ones. The linear viscoelastic behavior is described very well by the generalized Maxwell model consisting of three simple Maxwell models. Viscosities at zero frequency are in a pretty good accordance with those obtained for zero shear rate resulted from Cross equation.

7.2.2. Rheologic behavior of dispersions obtained from polychloroprene rubber modified on roller

If the polychloroprene rubber is modified with MMA using a roller – B series of samples – the stationary and dynamic rheologic behavior of dispersions is slightly different from those obtained by modifying the latex.

7.2.2.1. Stationary rheologic behavior

Rheograms obtained for the reference sample B0 when shear rates increase and decrease are represented in Figure 7.25.

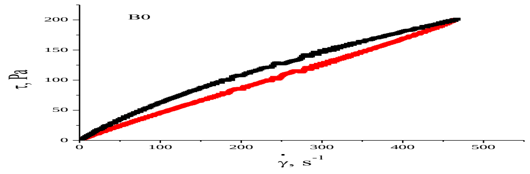
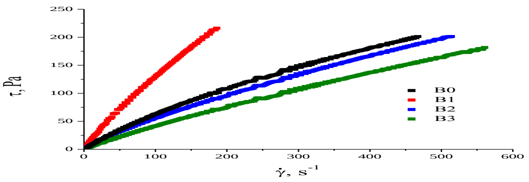
	

Figure 7.25. Rheograms of the B0 dispersion when shear rates: ■ – increase; 🟥 – decrease	Figure 7.26. Rheograms obtained for dispersions B0-B3 when shear rates increase

When shear rates increase, the dispersion has a pseudoplastic behavior and no limiting shear stress. The system B0 behave pseudoplastic over the entire shear rates range.

When shear rates decrease, the rheogram does not superpose with that obtained during their increase, indicating a thixotropic behavior, with a complete restoration of the structure at a zero shear rate. The hysteresis loop is larger than the one for dispersion A0, which proves that the thixotropy is also more pronounced. The same thing is shown by viscosity at zero shear rate obtained by linearising the apparent viscosity-shear rate data recorded when shear rates decrease, which is almost 3.7 times smaller than that obtained from data resulted when they increase (0.526 Pa.s, compared to 1.922 Pa.s).

The dispersions B1-B3, obtained from polychloroprene rubber grafted with increasing amounts of MMA, do not present a time-dependent rheologic behavior (thixotropy) anymore, but the rheograms obtained when shear rates increase and decrease superpose practically.

The superposed rheorgrams represented in Figure 7.26 show that their position is the same as those of dispersions belonging to series A.

In figure 7.27, in which dependencies of apparent viscosities on shear rates for the four dispersions are represented, it can be seen that the curve for dispersion B1 is indeed placed well above the one for dispersion B0 over the entire shear rate interval.

Given the absence of limiting shear stress, the rheological parameters for dispersions B0-B3 were calculated using the Ostwald-de Waele equation. The results are presented in table 7.7.

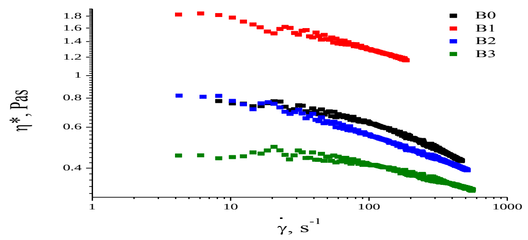


Figure 7.27. Dependencies of apparent viscosities on shear rates for indicated samples

Table 7.7. Dynamic viscosities, flow indices and correlation coefficients of samples B0-B3 obtained using Ostwald-de Waele equation

Dispersion	**η_o, Pa.s**	**n**	**R^2**
B0	1.922	0.759	0.99884
B1	2.657	0.842	0.99921
B2	1.471	0.789	0.99978
B3	0.820	0.853	0.99962

The Table shows that the higest dynamic viscosity is presented by sample B1, followed by B0, B2 and B3. Therefore, the viscosity decreases when the amount of MMA decreases. The flow indices do not follow strictly the variations of the viscosities: the increase order should be B3 > B2 > B0 > B1, while the one obtained using Ostwald-de Waele equation is B3 > B1 > B2 > B0, although it is very well followed by the rheograms of all dispersions, as the values of correlation coefficients show.

The Cross model is followed even better than the Ostwald-de Waele one, as the values of correlation coefficients in Table 7.8 show.

When considering 1/C values, the narrowest ideal plastic behavior range is presented by dispersion B2 (shear rates only between 0 and 24 s^{-1}) and the widest by sample B3 (0-395 s^{-1}).

Table 7.8. η_0, η_∞, 1/C, m and R^2 values obtained using Cross equation for dispersions B0-B3

Dispersion	**η_0, Pas**	**η_∞, Pas**	**1/C, s^{-1}**	**m**	**R^2**
B0	0.833	0.103	352	0.73	0.99969
B1	2.137	0.208	182	0.44	0.99975
B2	1.421	0.000	24	0.31	0.99984
B3	0.556	0.128	394	0.50	0,99970

Values obtained for parameter m show the weakest pseudoplastic behavior for dispersion B2 and the most pronounced for B0.

The fact that all m values are smaller than for A series proves that dispersions thus obtained have a less pronounced pseudoplastic behavior than those belonging to series A.

7.2.2.2. Dynamic rheologic behavior

Dependencies of storage moduli and loss moduli on applied frequencies are represented in Figure 7.28 and 7.29 respectively dispersions B0-B3.

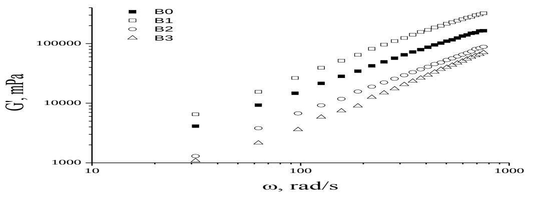


Figure 7.28. Dependence of storage moduli on frequency for indicated systems

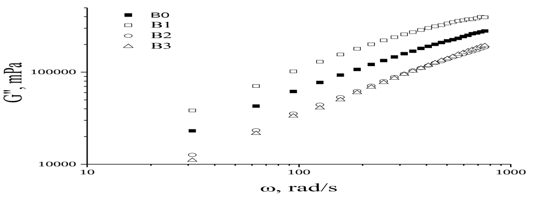


Figure 7.29. Dependence of the loss moduli on frequency for the mentioned dispersions

The figures show that the moduli increase with frequency. Dispersion B1 have the smallest values for both moduli, followed by B0, while B2 and B3 have close values. All samples are predominantly viscous.

The dependence of viscosities on frequency, Figure 7.30, shows that viscosities decrease when frequency increases, more for viscous dispersions and less for the fluid ones.

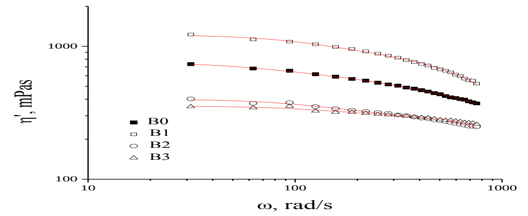


Figure 7.30. Dependencies of dynamic viscosities on frequency for indicated dispersions; red loops – fitting with generalized Maxwell model consisting of 3 simple Maxwell models

Red curves in the Figure are the results obtained for fitting with the generalized Maxwell model consisting of 3 simple Maxwell models.

The values of dynamic viscosities and relaxation times obtained for the three simple Maxwell models, of viscosities at zero frequency and of R^2 obtained using the generalized Maxwell equation consisting of 3 simple models are presented in table 7.9.

Table 7.9. Fiting parameters obtained for the generalized Maxwell equation

Sample	**η_i, mPa.s**			**θ_{ri}, ms**			**η'_0, mPa..s**	**R^2**
	1	**2**	**3**	**1**	**2**	**3**		
B0	200	395	160	2,9	0,6	12,6	755	0,99932
B1	378	843	0	7,1	1,1	0	1221	0,99765
B2	102	299	0	7,1	0,7	0	401	0,99330
B3	62	294	0	6,3	0,5	0	356	0,98323

The viscoelastic behavior of dispersions is also accurately described by this equation, as can be seen from the values of correlation coefficients in Table 7.9.

Viscosities at zero frequency also correlate for these dispersions with those at zero shear rate resulted from the Cross equation (Table 7.8).

The modifications of the two moduli's values in time are represented in figure 7.31.

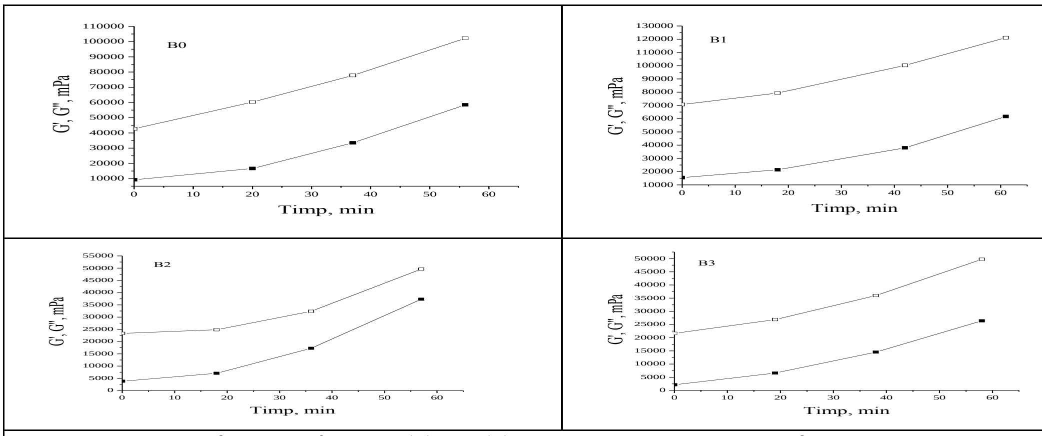


Figure 7.31. Modifications of storage (■) and (□) loss moduli at 10 Hz in time for the indicated samples

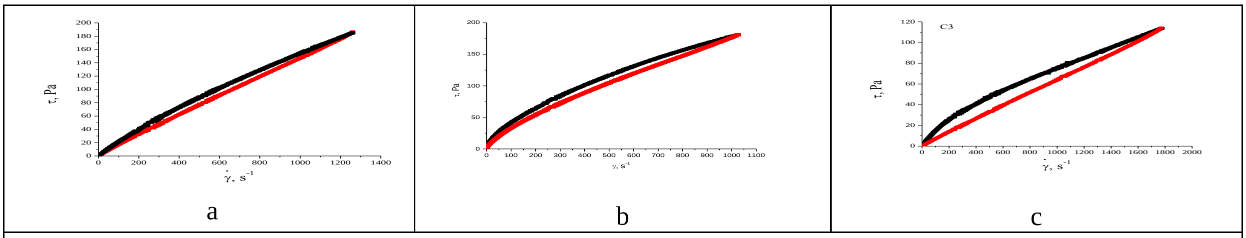
The figures show that loss moduli are higer than the elasticity ones for all dispersions, which proves that the samples are predominantly viscous and their ratios maintain practically constant in 60 min, the time of application of oscillatory movement. The B2 dispersion is an exception, the elasticity modulus increasing in time. The G"/G' ratio thus decreases from approximately 4.0 to almost 1.3 in 1 hour, which means that time increases the elasticity.

7.2.3. Rheologic behavior of dispersions obtained from polychloroprene rubber containing montmorillonite modified on roller

The series samples of C consists of three samples containing increasing amounts of montmorillonite (C1-C3) and three with the same quantity as C2 and increasing MMA amounts (C4-C6). The montmorillonite was introduced to modify rheologic properties, namely to enhance the pseudo-plastic behavior and thixotropy.

7.2.3.1. Stationary rheologic behavior

The rheograms of samples C1-C3 are presented in Figure 7.32.



a b c

Figure 7.32. Rheograms of dispersions: a – C1; b – C2; c – C3

The Figures show that all the samples have pseudoplastic behavior with no limiting shear stress and become more thixotropic with increasing of montmorillonite amount (the surfaces of hysteresis loop increase).

By applying the Qstwald-de Waele equation the results in Table 7.10 were obtained.

Table 7.10. Rheologic parameters obtained for dispersions C1-C3 with Qstwald-de Waele equation using rheograms resulted when shear rates increase

Dispersion	**η_0, Pa.s**	**n**	**R^2**
C1	0.527	0.822	0.99960
C2	1.084	0.858	0.99961
C3	0.648	0.689	0.99936

The rheograms follow pretty well the Qstwald-de Waele equation, as correlation coefficients show, but the values of viscosities at zero shear rate and flow indices do not show a clear tendency when the montorillonite quantity increases.

By using the Cross equation, the values in Table 7.11 were obtained.

Table 7.11. Rheologic parameters of Cross equation for dispersions C1-C3 resulted from rheograms obtained when shear rates increase

Sample	**η_0, Pa.s**	**η_∞, Pas**	**1/C, s^{-1}**	**m**	**r^2**
C1	0.240	0.079	847	0.78	0.99987
C2	0.718	0.342	156	0.81	0.99965
C3	0.175	0.049	309	1.13	0.99980

If η_0, η_∞ and 1/C do not present a regular variations when the amount of montmorillonite increases, m values increase, showing that the dispersions become more and more pseudoplastic.

The samples C4-C6, containing the same montmorillonite quantity and increasing MMA amounts, present the rheograms in Figure 7.33.

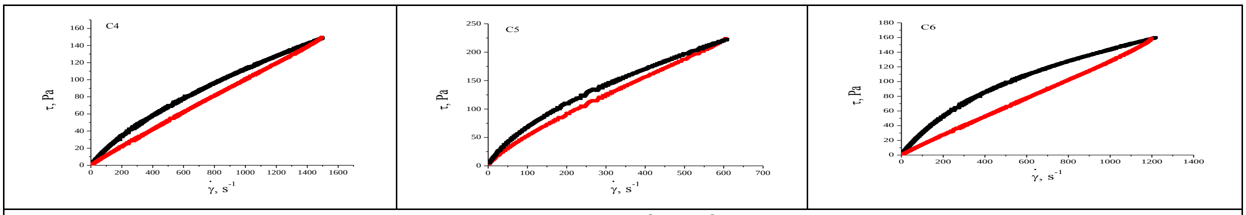


Figure 7.33. Rheograms of specified dispersions

The rheograms are characteristic to pseudoplastic bodies with a zero limiting shear stress and thixotropic time-dependent behavior, more pronounced for the maximum amount of MMA, contrary to expectations, the poly(methyl methacrylate) chains being rigid.

The rheologic parameters in Table 7.12, obtained applying Ostwald-de Waele equation to data of rheorgrams obtained with increasing shear rates, do not show a regular variation of viscosity with MMA amount, but n values decrease, showing a more difficult flowing.

The rheologic parameters obtained using Cross equation are presented in table 7.13.

If the first three parameters do not indicate regularity, the fourth – m value – proves that C4 and C5 dispersions have a similar pseudoplastic behavior (m values are very close), while the C6 dispersion is more pseudoplastic (the m value is practically equal to the unit).

Table 7.12. Values of flowing parameters obtained with Ostwald-de Waele equation

Dispersion	**η_0, Pa.s**	**n**	**r^2**
C4	0.762	0.722	0.99937
C5	3.432	0.652	0.99926
C6	2.187	0.607	0.99554

Table 7.13. Values of flowing parameters resulted by applying the Cross equation

Dispersion	η_0, Pa.s	η_∞, Pa.s	1/C, s^{-1}	m	r^2
C4	0,256	0,032	413	0,65	0,99984
C5	1,520	0,078	58	0,59	0,99972
C6	0,356	0,046	465	1,02	0,99986

7.2.3.2. Dynamic rheologic behavior

The variations of storage moduli with applied frequency are represented in Figure 7.34, which shows that they increase practically linearly with frequency, C6 dispersion (containing montmorillonite and the maximum amount of grafted MMA) having the higest values, and the C1 (containing the lowest amount of montmorillonite) the smallest ones. C2-C5 dispersions present pretty close intermediate values, those of C3 and C5 practically superposing, which shows that effect of montmorillonite is similar to that of MMA, being able to compensate for each other.

Figure 7.35 shows the dependence of loss moduli on frequency.

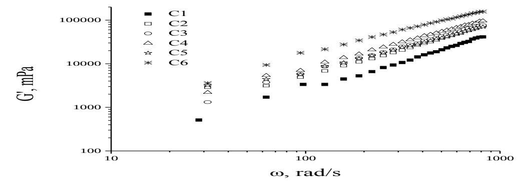


Figure 7.34. Dependence of storage moduli on frequency for dispersions C1-C6

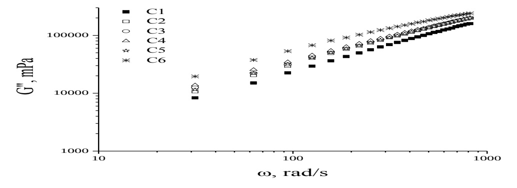


Figure 7.35. Dependence of loss moduli on frequency for dispersions C1-C6

Loss moduli increase exponentially with frequency. As regards this modulus, the biggest values were obtained for the C6 sample as well and the smallest ones for C1. For the other samples, values overlap within the limit of experimental errors.

For all samples, loss moduli are bigger than elasticity ones in the entire frequency field used, which shows that the dispersions are predominantly viscous.

The variation of dynamic viscosities on applied frequency is presented in Figure 7.36.

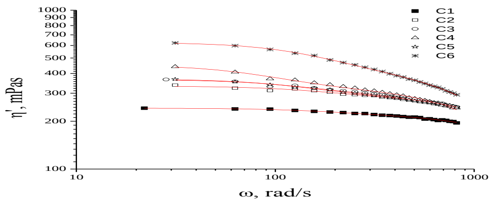


Figure 7.36. Dependence of dynamic viscosity on frequency for the mentioned dispersions

The Figure shows that viscosities of dispersions C3 and C5 are the same over the entire frequency range, showing the same compensation of properties as in the case of storage moduli.

The viscoelastic behavior of samples C1-C6 is well described by the generalized Maxwell model consisting of two simple Maxwell models connected in parallel, as shown by the red lines in Figure 7.36, which represent the respective equations.

The fitting parameters of the generalized Maxwell equation are given in Table 7.14.

The values of correlation coefficients are very good, ranging between 0.9945 and 0.9994.

For the samples C1-C3 viscosities at zero frequency increase with the montmorillonite quantity, while no regularity is found for the others.

The variation of values of the two moduli at 10 Hz in time is presented in Figure 7.37.

Table 7.14. Fiting parameters for generalized Maxwell equation consisting of two simple models

Dispersion	**η_i, mPas**		**θ_{ri}, ms**		**η'_0, mPa.s**	**R^2**
	1	**2**	**1,0**	**2**		
C1	26	215	4,5	0,4	241	0,99523
C2	53	280	5,5	0,5	333	0,98797
C3	75	290	7,1	0,6	365	0,99144
C4	141	311	10,5	0,7	452	0,99453
C5	88	281	7,1	0,5	369	0,99678
C6	245	381	5,5	0,7	626	0,99941

The figure shows that the variation is different from sample to sample:

for C1 sample the storage modulus increases faster the loss one starting with about 28 min and the values become close at 45 min;

- the ratio G”/G’ values increases in time till 35 min for C2, then remains practically the same, without getting close;
- for C3 the values also increase in time (a little more the value of G’ above 37 min);
- increasing of G’ for C4 is higher starting with about 24 min, the values become the same at ca 52 min and then G’ becomes higer; the crossover point indicates a sol-gel transition;
- the same phenomenon occurs for dispersion C5, but values become equal after 55 min;

elasticity modulus increases also more for the last sample, the values become close but not equal, so a crossover point is not obtained.

Concluding, dispersions belonging to A series are more fluid than those obtained by dispersing polychloroprene solutions in aqueous mediun (series B, and C4-C6 dispersions). [31]

In the case of series A dynamic viscosity decreases whith increasing amount of grafted MMA and the flowing index increases. Unlike the reference, grafted copolymer dispersions are not thixotropic. G’ and G" have close values, with the first a little higer over the entire frequency range. G’ values measured at 10 Hz increase significantly in time for A0 and A2 samples.

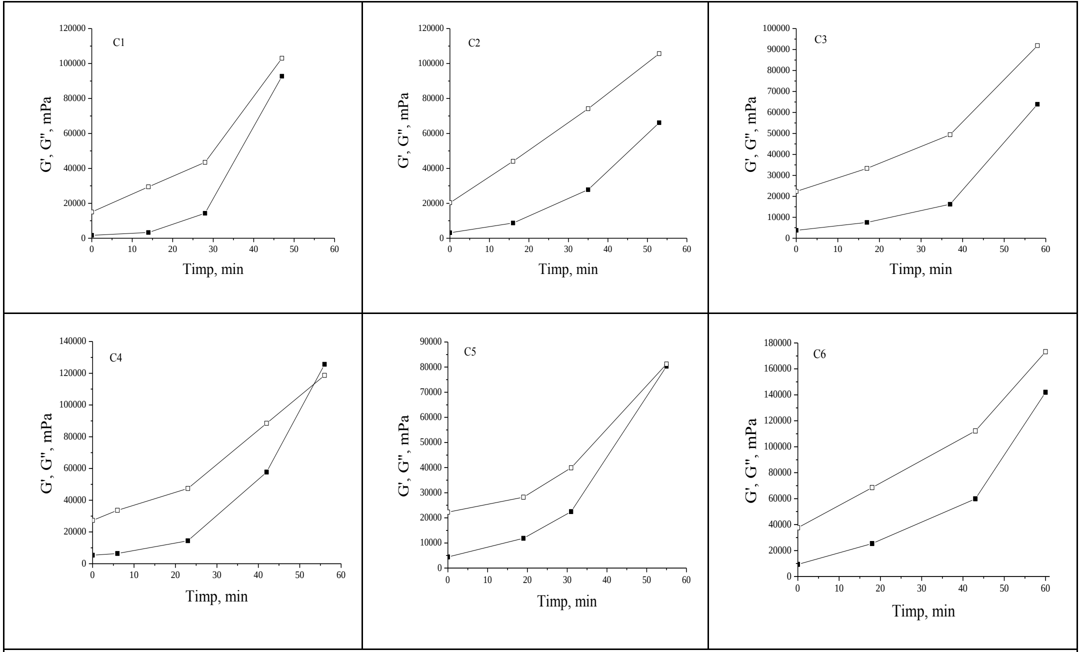


Figure 7.37. The modifications of storage (■) and loss (□) moduli at 10 Hz

The samples in B series have higer dynamic viscosities than A series and grafting with MMA has the same effect, except for the sample with the lower amount of methacrylate, for which the higest viscosity is obtained. The flow indices do not follow strictly the variation of viscosities. G’ values are a little lower than G” over the entire frequency range. Both increase in time approximately in the same measure.

Dispersions C1-C3, which contain increasing montmorillonite quantities, are thixotropic and less viscous than those in B series. G’ increases linearly with frequency and G” slightly exponential, the former remaining a little lower that the latter. Both moduli increase in time, G' more than G", but after 55 min the values become close.

Dispersions C4-C6, with constant montmorillonite amount and increased of grafted methacrylate, are more viscous than the previous ones. G' and G" vary in the same waz as for C1-C3 dispersions, the latter's value being higer. The two moduli become equal for C4 and C5 samples, after about 24 min in the first case and 55 min in the second one, which could indicate a sol-gel transition in these dispersions

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8. CHARACTERISATION OF FILMS OBTAINED FROM ADHESIVE DISPERSIONS

Films obtained from adhesive dispersions were characterized bz optical and electronic scanning microscopy, x-ray diffraction, photo-electronic x-ray spectroscopy and FT-IR.

8.1. Analysis of films by optical microscopy

Optical miscroscopy, a non-destructive analysis method, is often used as a first technique to examine films before performing more sophisticated analyses. [1]

8.1.1. Analysis of particles in films obtained from dispersions obtained by chemical grafting of rubber from latex

In Figure 8.1 the 50X images of films obtained for A0-A3 dispersions are presented.

Images emphasize rough and porous surfaces, which produce the increase of adherence on other surfaces. The pleated aspect increases when the amount of grafted monomer is higher.

All the analysed films present a tendency of phase separation, with formation of incipient cluster in the spinodal structure of biphasic mixtures resulted from separation in the temperature and composition conditions the samples were obtained. The spinodal structure has a granular aspect, with cracks in some areas, the fragments re-locating to form areas relatively ordered as size and in space. The films form composite structures with introduced auxiliaries (ZnO, SiO_2).

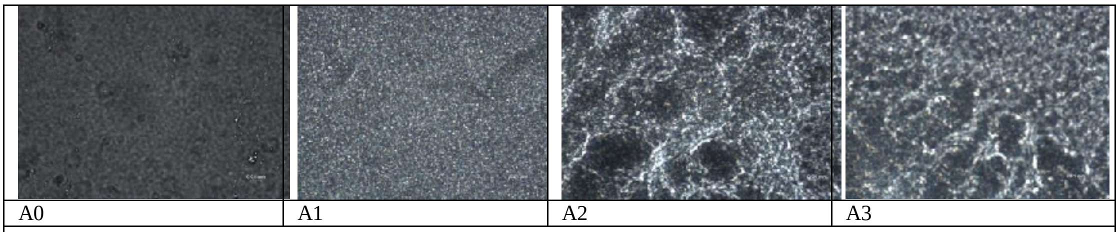

A0 A1 A2 A3

Figure 8.1. Images of films obtained for A0-A3 dispersions, 50X

8.1.2. Analysis of particles in films obtained from dispersions obtained from rubber modified by grafting on roller

The 50X microscopic images for the surfaces of films obtained from polychloroprene rubber modified by grafting on roller (samples B in Table 6.3) are shown in Figure 8.2.

The images show a rougher structure of surfaces for films obtained from B type dispersions than for A type. The granular aspect shows a tendency of phase separation and incipient cluster formation. B2 sample has the most nonhomogenous aspect, particles of different dimensions and consistencies being observed.

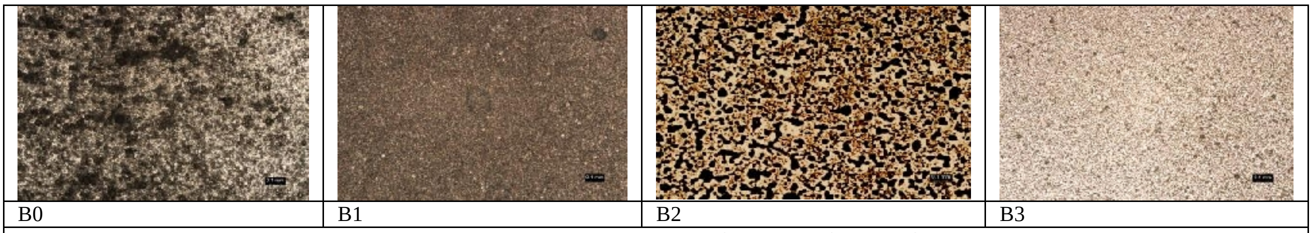
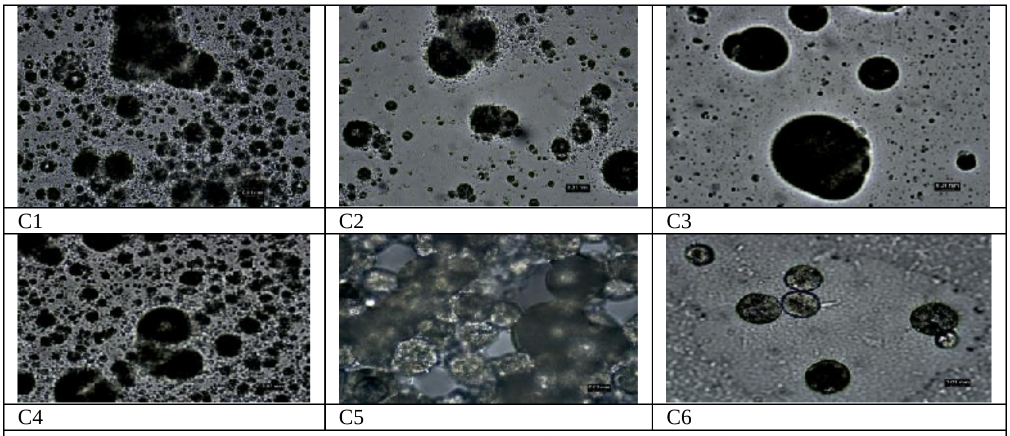

B0 B1 B2 B3

Figure 8.2. Optical images, 50X, of B series film surfaces

8.1.3. Analysis of particles in films obtained from dispersions obtained from rubber modified by grafting on roller in presence of montmorillonite

Images of film surfaces obtained from series C of dispersions are presented in Figure 8.3.


C1 C2 C3

C4 C5 C6

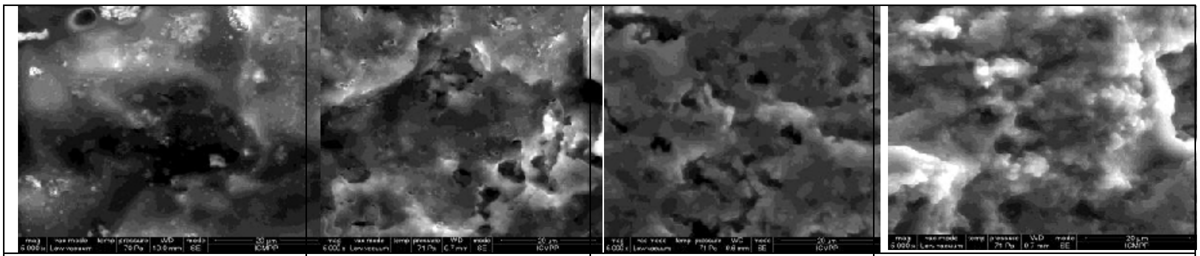
Figura 8.3. Optical images of C1-C6 film surfaces

The morphologies of surfaces of these films show randomly distributed microparticles, together with dispersed auxiliaries. All the films show a phase separation tendency, with formation of incipient cluster. The spinodal structure has a granular aspect, with cracks in some areas. The microparticles have a superficial, thin and rigid layer, namely a “shell” that includes polymer or even more microparticles. These collapsed probably and sticked together. The high rigidity of the “shell” is due to the extensive crosslinking of polymer chains from surfaces. This layer is the result of competition between the effects of deformation of “shell” and compression of the interior mass during the evaporation of water and particles’ pleating.

8.2. Analysis of films by electron microscopy

Scanning electron microscopy is the imagistic and analyis technique based on detection of electrons and x-rays emitted by materials when irradiated by scanning using an electron beam. [2]

The study of morphologic aspects was made by direct observation of topography of cross sections of films' fractures obtained from adhesive dispersion. The fracturing was made after cooling in liquid nitrogen. The obtained cross sections were fixed in aluminium supports and the samples examined using the low vacuum ESEM QUANTA 200 instrument, equiped with an LFD detector. The work voltage was 20 KV. The obtained results are presented in figures 8.4-8.6.



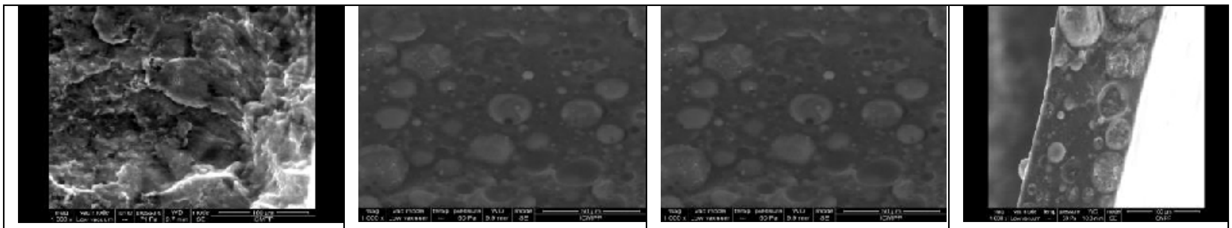
A0, 5000X A1, 5000X A2, 50000X A3, 5000X

Figura 8.4. SEM Images of film sections obtained from A series of dispersion

The images, 1000 X, of A0 sample show a lamellar structure for. When magnification is 5000X, it can be seen that the auxiliary filling elements are finely dispersed inside the film.

A1-A3 samples, made from polychloroprene grafted with various MMA quantities, have aspects different from A0 sample: the morphology is biphasic, with spheroidal particles distributed in a lamellar matrix, their number increasing with the grafting degree.

In figure 8.5 the images for cryogenically fractured surfaces of films obtained from non-modified Denka AD 20 polychloroprene and modified with MMA by grafting on roller.



B0, 1000X B1, 1000X B2, 1000X B3, 1000X

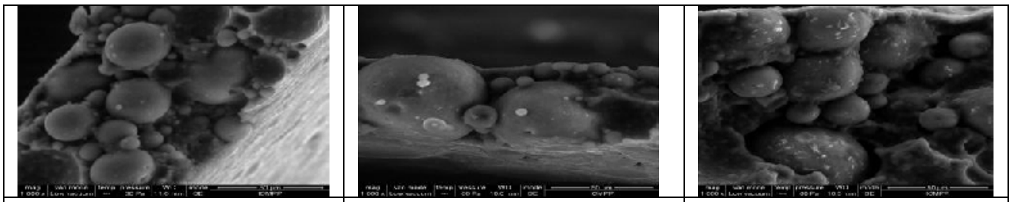
Figura 8.5. SEM images of films sections obtained from B series of dispersions

The surface of film fracture obtained from B0 sample has a heterogeneous aspect, with areas that present different roughness. Strongly segregated particles can be seen in different sections, in which the surface is rougher, the section appearing very rippled, or with less segregated and more evenly distributed particles, for which the image of the section is smoother.

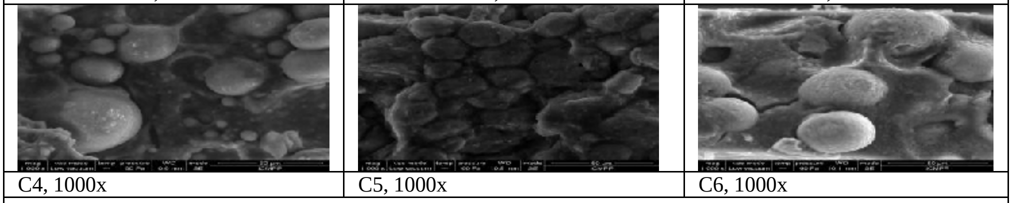
The sections of films obtained from samples modified grafting on roller, with images presented in the same figure, present biphasic morphology, particles having micronic dimensions, so the dispersion is relatively coarse. The auxiliaries resulted in composite structures, with granular aspect, but with no well defined biphasic character. The increase of degree of grafting gives more finely structured spherical areas. The coalescence tendency can also be seen, which can be explained by the inclusion of auxiliaries between the individual particles, which determines their inter-connection as clusters.

In Figure 8.6 the images of fractures of films obtained from dispersions C1-C6 are presented.

The samples C1-C3, which contain non-grafted polychloroprene, but that have 2, 4, and 7% montmorillonite, respectively, present a globular morphology, consisting of large spherical particles (tens of microns). However, an non-structured material can be also observed. Montmorillonite dispersed aggregates are present both in spherical particles and in the unstructured material.



C1, 1000x C2, 1000x C3, 1000x



C4, 1000x C5, 1000x C6, 1000x

Figura 8.6. SEM images of sections and surfaces of films obtained from dispersions C1-C6, certaining montmorillonite

SEM images for the sections of films obtained from C4-C6 dispersions are also presented in Figure 8.6. Their morphology is also globular but the spherical particles are more finely dispersed. The particles present an obvious coalescence, resulting in globules of hundreds of microns distributed in a matrix of non-structured material. The spherical particles and the non-structured material contain dispersed aggregates consisting of montmorillonite.

The presence of montmorillonite is also proved by EDX spectra, which present an absorption specific to elements from which the clay is made: Na, Si, Al.

Energy dispersive X-ray spectra allow, based on characteristic emission energies, the identification of elements present into the micro-area examined with secondary electrons. The total number of captured impulses characteristic to an element is proportional to its amount in the area. In this waz the existing elements and their concentration are identified. [7, 8] Figure 8.12 shows the presence of montmorillonite for the C6 sample.

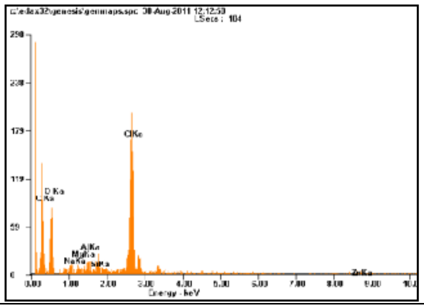


Figure 8.12. EDX spectrum for C6 sample

8.3. Film analysis by FT-IR spectrometry

Determinations were made using a double-beam IR molecular absorption spectrometer, in the range 4000-400 cm^{-1}, using the FT-IR 4200 device equiped with a diamond crystal and sapphire head ATR. Adhesive dispersions were dried on glass blades. Films were cutted and analyzed.

The FT-IR spectrum of A0 sample is presented in Figure 8.14.

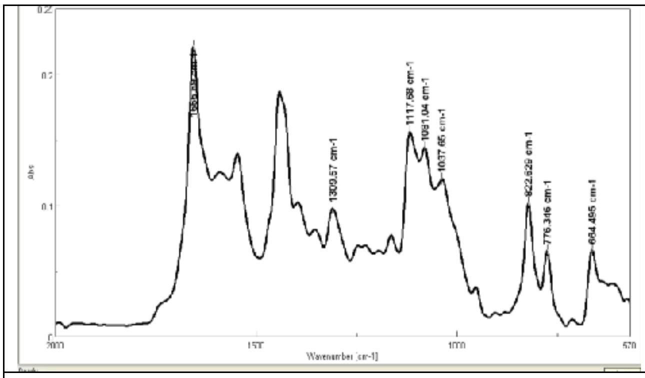


Figure 8.14. FT-IR spectum of A0 sample

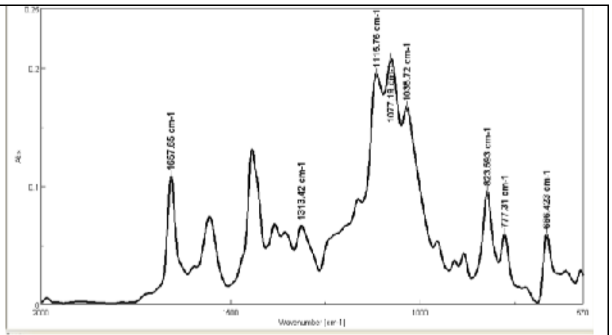


Figure 8.17. FT-IR spectum of A3 sample

Comparing the spectra of reference polychloroprene mixtures A0, B0 and C1-C3 to that of the raw chloroprene it can be seen that weak bands are present in mixtures at about 1150 cm^{-1}, which correspond to some vibrations of C-C1 bond. The small shifts can be assigned to the rubber's plastificization due to processing on roller.

The FT-IR spectra of the grafted samples within the spectral range 2500-570 cm^{-1} are presented in the work in Figures 8.15-8.27 but here only the spectrum of sample A3 is presented.

The intensity of som bands modifies compared to those of the reference: the intensity of the the band from 1150 cm^{-1} creases, proportional to the amount of methacrylate introduced, more intense being those of samples B1-B3 and C4-C6. The band at 1730 cm^{-1} from MMA spectrum can be assigned to its bonding on polychloroprene chain. A weak band at 1200 cm^{-1} also appears, assigned to $\nu C{=}O$ vibration from $-COOCH_3$ group. The decrease of intensity of band from 1150 cm^{-1} can be a result of grafting of MMA on polychroloprene chain. [17, 18]

The above-mentioned assignements are also supported by the absence of methacrylate and poly(methyl methacrylate) from all the dispersions in which the monomer was introduced.

The maximum monomer and polymer amounts were found experimentally for sample C6, but they are very low: 0.22% methacrylate and 1% poly(methyl methacrylate).

8.4. Characterization of adhesive dispersions by x-ray diffraction

X ray diffraction is a versatile, non-destructive technique that provides information on crystalline structure, [19-21] offering complete solutions for the characterization of materials.

Diffractograms of polymer films obtained from series A and B of dispersions were recorded using the Bruker D8 Advance diffractometer, in the Bragg-Brentano configuration, using the CuKθ (θ = 1.5406 Å) radiation. [26, 27]

The superposed diffractograms for samples in A series are presented in Figure 8.29.

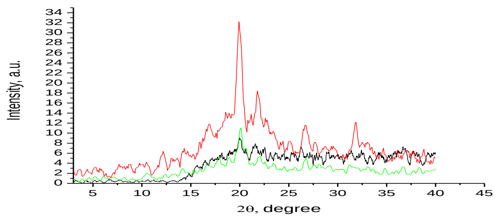


Figure 8.29. Superposed diffractograms for A series of samples: **(–)** A1; (–) A2; (–) A3

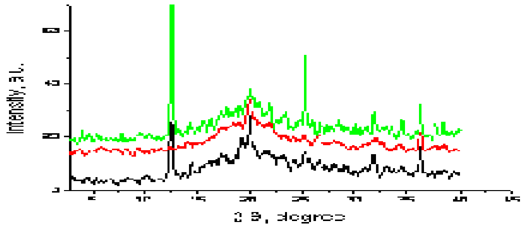


Figure 8.33. Superposed diffractograms for B series of samples: **(–)** B0; (–) B1; (–) B3

The figures show that grafting modifa the aspect of diffractograms: the wide diffraction characteristic to poly(methyl methacrylate) appears and increases in amplitude, simultanious with decreasing of amplitude of maximum characteristic for polychloroprene from 2θ about $19^{o}30'$.

Diffractograms of samples from B series, presented in figure 8.33, lool similar with those of A series, with haloes for the amorphous phase increasing in amplitudes with MMA amount.

In conclusion, the X ray diffraction spectra show the increase of amount of poly(methyl methacrylate) with increase of amount of monomer introduced, aassigned to monomer grafting.

8.5. Determination of glass transition temperatures of grafted rubbers by differential scanning calorimetry

Differential scanning calorimetry is the most used method to determine thermal transitions and physico-chemical processes occuring in polymers and polymer composites.

DSC analyses were made using the Diamond DSC – Perkin Ekmer equipment calibrated with indium (99% purity) both for temperature and energy, in the range (-60)÷140°C, using a heating rate of 5°C/min. The 5-7 mg samples were placed in non-hermetic aluminium crucibles. To ensure a thermal homogeneity, nitrogen was intoduces into the cell. DSC curves for A0, A3, B0, B2, C2 and C6 samples are presented in Figure 8.34. Glass transition temperatures, T_g, are indicated on each thermogram.

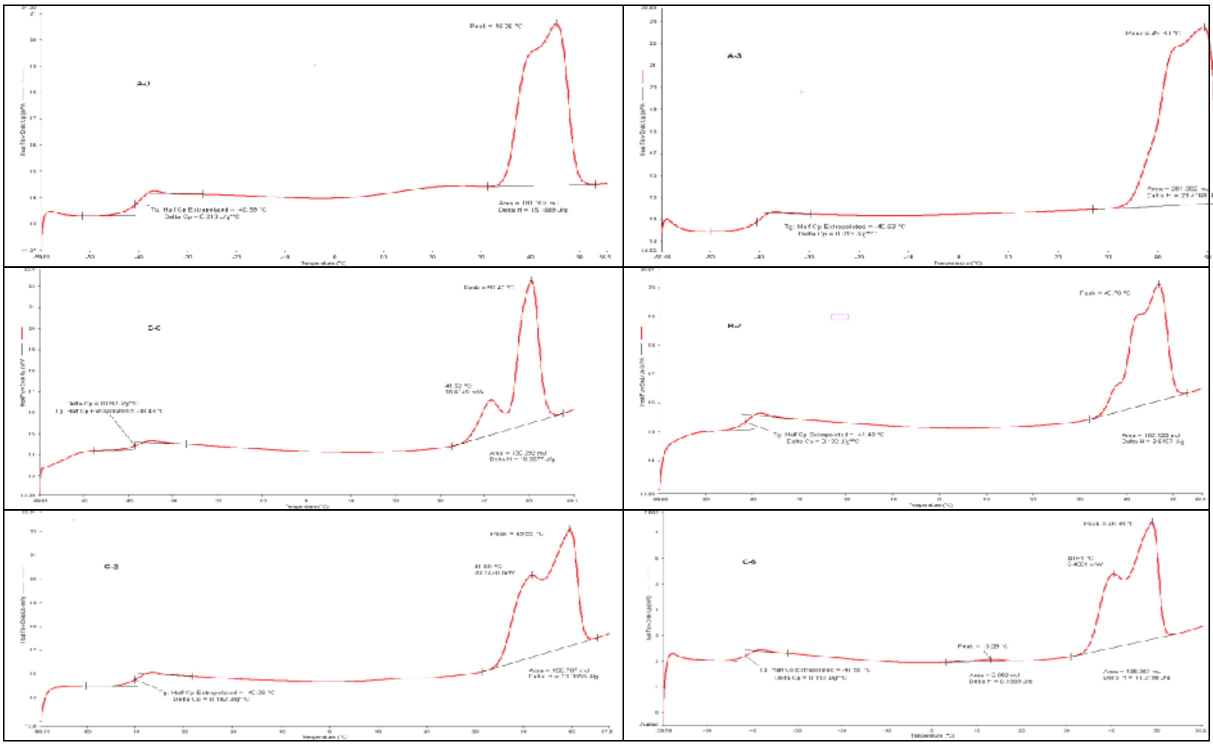


Figure 8.34. DSC thermograms for the indicated samples

T_g values generally reflect minor sample modifications. For A0 and A3 samples (Dispercoll 84), grafting does not bring significant differences in glass transition temperatures.

In the case of B0 and B2 samples (polychloroprene Denka AD 20), grafting decreases T_g by almost 3°C due to the increase in the free volume produced by grafts.

The introduction of 4% montmorillonite reduces T_g of the non-grafted polychloroprene by almost 1.5 °C (B0 and C2 samples), montmorillonite being an agent for modification of viscosity.

In the presence of montmorillonite grafting reduces less T_g of polychloroprene, only with 1,5°C (C2 and C6 samples).

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9. DETERMINATION OF BONDING CAPACITY

The bonding capacity was determined according to SR EN 1392:2006 standard, test known as "(23 ± 2)°C detachment trial".

To ensure a comparison between adhesive and cohesive properties of studied dispersions with reference samples, as well as each other, the used methodology was the following:

1. Adherence tests were made on the following types of supports: standard rubber mixture with a hardness of 85ºShA; rubber mixture for fitting of the lower part of the footwear BTA_5; cotton fabric; linen; leather; split; synthetic leather.
2. Carrying out of experiments in the same technological conditions; in the absence of a conditioning room, the measurements were made during the same day or the same period of different days.

Determination of adherence included the following stages: preparing the support; applying the adhesive on the surfaces; putting the samples together; detachment.

Agents for increasing bonding capacity have been added in composition of adhesive dispersions prepared: colophony resin and crosslinking agent **Desmodur RE** – solution 27% of triphenylmethane triisocyanate in ethyl acetate, separately or combined. The resin solution was prepared separately and dosed directly in adhesive dispersions, in the following proportions resin/adhesive dispersion: 5/100, 10/100 and 15/100. Before using, the resin was pre-reacted with magnesium oxyde, to form chelates which increase cohesion of adhesive films at high temperatures. Preliminary tests have shown that when adding resin and/or crosslinker, the last two ratios do not improve visibly the peel resistance, so they were not used.

The values of peelling resistance are given for adhesive dispersions A0-A3 in the absence and presence of the two agents for increasing bonding capacity, introduced separately or as a mixture in equal amounts, are presented in the paper in Tables 9.1-9.4.

Results show that, after conditioning for 24 hour at room temperature, rubber latex gives very low peelling resistances, of maximum 0.2 N/mm in the case of Cs/Cs substrates. Increasing of conditioning time results into increasing of value. Conditioning for 3 h at 50^{o}C followed by mantaining for 72 h at room temperature does not change the value, whle heating for 168 h at 70^{o}C followed by conditioning the same time at room temperature increases peelling resistance 34 times, reaching the value of 6.8 N/mm, much higher than that imposed for solvent-based adhesives according to SREN 15307/2007: 3 N/mm for binding uppers together and 4 N/mm for binding uppers to soles. The most effective water-based polychloroprene adhesives, produced by Bayer, Germany, have a peelling resistance of maximum 2 N/mm, according to their prospectus.

Adding 5% isocyanate increases peelling resistance 18 times for the Cs/split joint, 10 times for Cs/flax, 8 times for Cs/cotton, 5 times for Cs/Cs and Cs/synthetic leather and only 2 times for C/leather, but values remain inferior to those required for solvent-based adhesives. On the other hand, heating for 168 h at 70^{o}C followed by mantaining for 72 h at room temperature brings peelling resistance value to 8.7 N/mm, 2.9 and respectively 2.2 times higher than the values provided in the standard for solvent-based adhesives.

Adding 5% colophony resn increases adherence 20 times for Cs/cotton, 19 times for Cs/flax, 18 times for Cs/split, 8 times for Cs/Cs, 7 times for Cs/synthetic leather and 4 times for Cs/leather, but all values are below 2 N/mm, except the last value, of 3.1 N/mm. The mixture of the two agents determines a low increases in peelling resistance compared to their individual use.

If chloroprene is grafted with the minimum amount of MMA, peel resistances increase, especially for Cs/split, Cs/cotton, Cs/flax, Cs/synthetic leather, but values remain below 3 N/mm, except when heated at 70^{o}C, when values reach 3.8 N/mm.

Isocyanate determines tensile strength values to become closer to those required for solvent-based adhesives for Cs/split and Cs/flax, but remain below 3 N/mm.

Resin also increases peelling resistance, values above 3 N/mm being obtained for Cs/flax – 3.5 N/mm and Cs/Cs conditioned at 70^{o}C. Again, introducing the blend of the two agents is only justified for conditioning at 70^{o}C (Table 9.2).

For the maximum amount of grafted methacrylate, peelling resistance has a high value, close to that of solvent-based adhesives: 3.8 N/mm for Cs/cotton, followed by Cs/Cs – 3.1 N/mm, but remains low for C/leather and is zero for C/synthetic leather. The highest value – 5.6 N/mm – is obtained by heating for 168 h at 70^{o}C. Isocyanate increases considerably the value for Cs/flax (5.2 N/mm), but remains zero for Cs/synthetic leather. Resin leads to lower values, increasing them only for Cs/leather, Cs/synthetic leather and Cs/Cs heated at 70^{o}C. The mixture gives very high values for Cs/flax – 8.3 N/mm, followed by Cs/Cs conditioned at 70°C – 8.0 N/MM, Cs/Cs conditioned at room temperature – 5.9 N/mm and by Cs/cotton – 5.3 N/mm.

Figures 9.4-9.15 show the peel resistances for samples A0-A3.

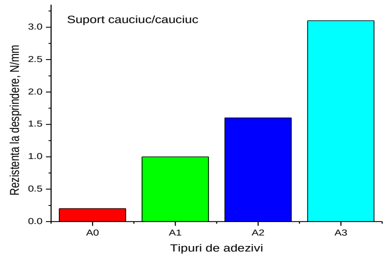

Figure 9.4. Peelling resistance for adhesives A0-A3 on rubber/rubber substrate

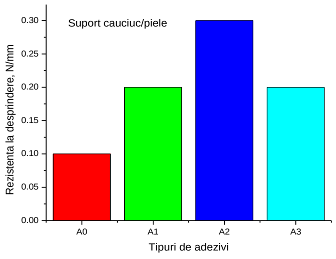

Figure 9.5. Peelling resistance for adhesives A0-A3 on rubber/leather

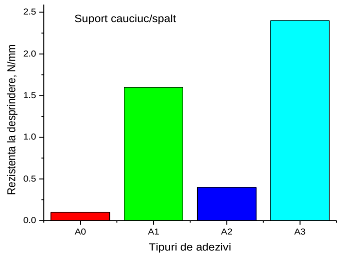

Figure 9.6. Peelling resistance for adhesives A0-A3 on rubber/split substrate

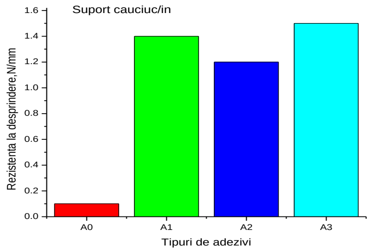

Figure 9.7. Peelling resistance for adhesives A0-A3 on rubber/flax substrate

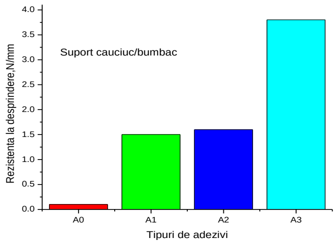

Figure 9.7. Peelling resistance for adhesives A0-A3 on rubber/cotton

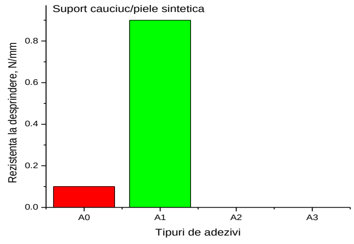

Figure 9.7. Peelling resistance for adhesives A0-A3 on rubber/synthetic leather substrate

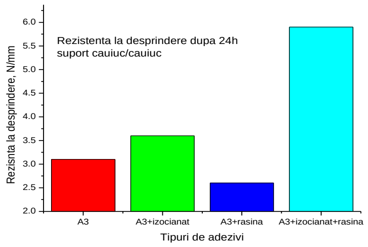

Figure 9.12. Peelling resistance for adhesive A3 under specified conditions

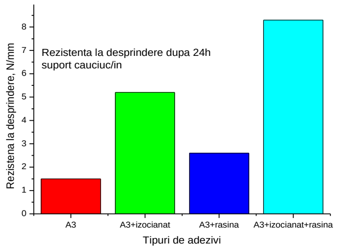

Figure 9.12. Peelling resistance for adhesive A3 under specified conditions

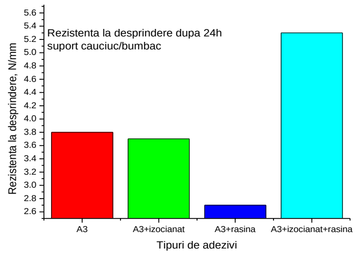

Figure 9.12. Peelling resistance for adhesive A3 under specified conditions

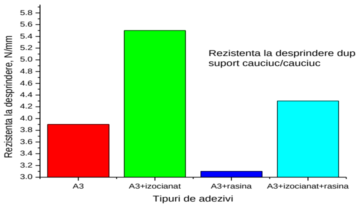

Figure 9.12. Peelling resistance for adhesive A3 under specified conditions

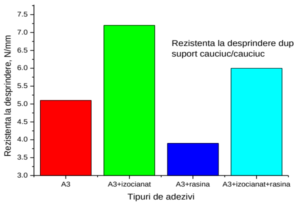

Figure 9.12. Peelling resistance for adhesive A3 under specified conditions

Tables 9.5.-9.8 give the peelling resistance values for adhesive dispersions obtained from rubber grafted on roll from series.

In the absence of adherence improving agents – dispersion B0 – values are higher than those obtained for latex, and the two agents and their mixture do not bring improvements. Grafting also does not contribute too much to increasing of peelling resistance. The highest value – 1.9 N/mm – was obtained for Cs/leather when using dispersion B3 in the presence of the mixture of the two additives.

Tables 9.8.-9.14 present peel resistance values for ungrafted rubber dispersions containing montmorillonite – C1-C3 – and for those grafted on roll, C3-C6.

Dispersions C1-C3 give low peelling resistance values. They are slightly increased by the adherence improving agents, by increasing conditioning time at room temperature, by conditioning at 50°C, but get even higher when conditioning is done at 70°C. The highest values were obtained for sample containing 4 g montmorillonite/100 g rubber in the presence of the mixture of agents when conditioning is done for 168h at room temperature (1.8 N/mm), or in the absence of additives (1.7 N/mm). The lowest values were obtained for all pairs of substrates when the sample contained 8 g montmorillonite/100 g rubber.

Dispersions C4-C6, containing 4 g montmorillonite/100 g and grafted rubber have higher bonding capacities than those obtained from C2, in which rubber is not grafted, for all types of substrate pairs and for situations where conditioning was done. Thus, for samples grafted using the minimum amount of monomer, none of the resistance values is under 1 N/mm and the maximum value is 2.3 N/mm for the sample containing the mixture of adherence improving agent and for Cs/Cs pair conditioned for 168 h at room temperatre; for samples grafted with a higher amount, values do not decrease under 1.3 N/mm and the maximum value is 2.5 N/mm, while for the maximum amount of monomer values are not lower than 1.5 N/mm and the maximum value is 3.5 N/mm for C/split pair conditioned for 24 h at room temperature.

Grafting with methyl methacrylate of the samples having this composition has as result an increase in peelling resistance, which increases with the amount of monomer used, but values remain inferior compared to those btained with dispersions in series A.

10. CONCLUSIONS

TECHNOLOGIES FOR OBTAINING ADHESIVE DISPERSIONS

- ➢ The basic material is polychloroprene, due to its property of crystallizing, which gives remarkable mechanical resistance to adhesives.
- ➢ Modification of polychloroprene by grafting with MMA was done by two different technologies: latex grafting and mass grafting of polymer by processing on roll.
- ➢ The first method gives directly dispersions of grafted polychloroprene –series A0-A3 of samples, while using the second one grafted rubber must be obtained, then dissolved in a convenient solvent or solvent mixture and dispersed under mechanical stirring in water containing agents for stabilization of dispersion and pH adjustment.

CHARACTERIZATION OF ADHESIVE DISPERSIONS

Particle size and size distribution have the following aspects:

- Grafting of latex particles preserves:
  - ➢ unimodal distribution of the initial rubber latex;
  - ➢ particles slightly increase their average sizes;
  - ➢ the maximum limit of particle size shifts towards higher values;
  - ➢ distribution range increasing, the weight of preponderant fraction in dispersions decreases.
- Dispersions obtained by mechanical dispersion of solutions of rubber grafted on roll:
  - ➢ much wider particle sizes and particularly particle size distributions,
  - ➢ bimodal or even polymodal distribution.

CHARACTERIZATION OF FILMS OBTAINED FROM ADHESIVE DISPERSIONS

- Optical microscopy shows that:
  - ➢ films obtained from series A of dispersions have a coarse, porous structure of surfaces;
  - ➢ surfaces of films obtained from series B are coarser than those obtained from the A series;
  - ➢ films obtained from dispersions C1-C3 contain randomly distributed microparticles, together with those formed by dispersed auxiliaries. All have the tendency of phase separation, with formation of clusters in incipient state;
  - ➢ microparticles have a thin and rigid superficial layer, a “shell”, which incorporates the polymer mass or even several microparticles in films obtained from dispersions C4-C6.
- SEM images:
  - ➢ Aspects of samples A1-A3 are different from that of sample A0: morphology is of biphasic type and consists of spherical particles distributed in a matrix with lamellar morphology, whose number increases as the grafting degree increases.

- Samples modified by roll grafting have biphasic morphology, with particles of micronic size. Auxiliary compounds result in composite structures with grainy aspect, without a well-defined biphasic character. Increasing the degree of grafting domains with more finely spherical structures can be seen. The coalescence tendency also appears, explained by the inclusion of auxiliary materials between individual particles, determining their interconnection in clusters.
- Surfaces of films obtaied from dispersions C1-C3 have globular morphology, large spherical particles, of tens of microns, coexisting with unstructured material. Aggregates of montmorillonite are dispersed both within particles and non-structured material.
- Films obtained from dispersions C4-C6, containing 4% montmorillonite and rubber grafted with 10, 15 and 20% MMA, also have a globular morphology, but the spherical particles are smaller. Coalescence gives rise to globules with sizes of hundreds of microns distributed within the matrix of non-structured material. Dispersed montmorillonite aggregates both within particles and non-structured material can be seen as in the case of samples B.
- ***X-ray photoelectron spectroscopy***, performed for samples C1-C6, emphasizes the presence of montmorillonite, showing the peaks specific to elements from which clay is made.

FT-IR spectrometry, combined with the absence of MMA and poly(methyl methacrylate) even in the sample with maximum amount of methacrylate – C6 (20%) – allow the conclusion that the band at 1730 cm^{-1} can be assigned to grafting of MMA on polychloroprene chains.

X-ray diffraction, done for films obtained from dispersions from series A and B, shows a decrease in intensity for peak at $19^{o}30'$ characteristic to polychloroprene as the amount of MMA increases, and an increase of diffuse diffraction characteristic to poly(methyl methacrylate).

DETERMINING BONDING CAPACITY

- Grafting of MMA on polychloroprene chains results in increasing of adherence by 15-40% for all the used substrates, depending on the amount introduced.
- Introducing 4 % montmorillonite determines increases of adherence.
- Higher percentages of montmorillonite produce crosslinking of elastomer, which result in agglomeration of particles in dispersions.
- Stability of dispersions ranges between 30 and 40 days from preparation.
- Dispersions obtained by chemical grafting in the presence of 4 % montmorillonite present peelling resistance values close to or even higher than those imposed to classic adhesives (3 N/mm) on leather, split, flax and cotton substrates.
- Colophony increases significantly the peelling resistance for all types of dispersions.
- Increased peelling resistances were also obtained when joinings were done at high temperature ($100^{o}C$), which allows the conclusion that the prepared adhesive dispersions can also be used for bondings resistant to high temperatures.