Studies Regarding the Performance of Pressure Sensitive Adhesives Based on Carbocatenary Elastomers

I. Peel strength

IOANA DUSESCU[1], PAUL OCTAVIAN STANESCU[2], CATALIN ZAHARIA[2], GHEORGHE HUBCA[2]*
[1] S.C. Haas–C-Impex S.R.L., Ploieşti, 1 Lăpuşna Str., 100002, Prahova, Romania
[2] Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Science and Engineering of Polymers, 1-3 Polizu Str., 010072, Bucharest, Romania

This work presents the main mechanical properties of the pressure sensitive adhesives solutions based on carbocatenary elastomers: peel, shear and tensile strength. Polychloroprene rubber was chosen as the main component of the adhesive system and its adhesive performances were evaluated. The mechanisms of fracture of the adhesive bond and breaking at the tensile test were also discussed.

Keywords: pressure sensitive, adhesives, elastomers, polychloroprene rubber

Polymers are frequently used for adhesives fabrication. Nowadays, adhesives are indispensable products for most of the technical applications. The mechanical properties and easy processing make the polymers ideal candidates for adhesives obtaining. The adhesives are mainly subdivided in two major classes: structural and pressure sensitive adhesives.

The structural adhesives have permanent character and impart high strengths for the adhesive assemblies (sometimes their strength is higher than the strength of the substrate). During the assembly process the adhesive changes from fluid to solid state as a result of polymerization, polycondensation, cross-linking processes etc.

Pressure sensitive adhesives impart moderate strengths for the adhesive assemblies. Their main peculiarity relies on the special viscoelastic behaviour, expressed by a cold permanent flow. Therefore, during the assembly process these systems maintain their fluid state [1-15].

According to literature definition [16] the pressure sensitive adhesives, known as "Haftkleber" in Germany, "Autocollants" in France and "Pressure-sensitive adhesives" in Great Britain can be classified in three main classes: adhesives based on carbocatenary elastomers, adhesives based on acrylic polymers and adhesives based on silicon elastomers [17].

The main goal of this paper consisted in the evaluation of the main characteristics of the adhesive assemblies with pressure sensitive adhesives based on carbocatenary elastomers.

Pressure sensitive adhesives based on carbocatenary elastomers can be applied as solutions in organic solvents, aqueous dispersions or hot-melts. The elastomer solutions in organic solvents were chosen according to the technical and economical performances of the pressure sensitive adhesives and their physical state (table 1).

PROPERTY		Physical state of the adhesive		
		Solution	Emulsion	Hot-melt
Adhesive properties	Bonding	Excellent	Excellent	Excellent
	Peeling	Excellent	Excellent	Good
	Shearing	Excellent	Good	Poor
End use properties	Ageing resistance	Excellent	Good-acceptable	Poor
	Adaptability	Excellent	Good	Poor
Exuding		Good	Acceptable	Satisfactory-poor
Conversion properties	Cutting though punching	Good	Acceptable	Poor
	Printing	Excellent	Acceptable	Good
Cost		Very high	Moderate	Low

Table 1
TECHNICAL AND ECONOMICAL PERFORMANCES OF THE PRESSURE SENSITIVE ADHESIVES VERSUS THEIR PHYSICAL STATE [5, 10]

* *e-mail: gheorghe_hubca@yahoo.com; Tel. 0214022703*

Table 2
COMPOSITIONS OF THE ELASTOMER-BASED ADHESIVE SOLUTIONS

No.	Material	Elastomer				Role in the recipe
		Polychloroprene	Natural	NBR	SBR	
1	Colophonium	10	10	10	10	Tack agent
2	BHT	2	2	2	2	Antioxidant
3	MgO	8	8	8	8	Filler*
4	ZnO	5	5	5	5	Filler*
5	Mineral oil	-	5	-	5	Plasticizer
6	Solvent**	375	370	375	370	

* active filler for polychloroprene rubber

** toluene for polychloroprene rubber and styrene-butadiene rubber, methyl-ethyl-ketone/toluene, 80/20 for nitrile butadiene rubber and cyclohexane for natural rubber

The solids concentration in the final adhesives solutions was 25%, and the concentration with respect to elastomer was 20%.

Table 3
MAIN CHARACTERISTICS OF THE ELASTOMER-BASED ADHESIVES

Rubber-based mixture	Cohesive resistance, MPa	Relative sticking*	Elongation resistance at 100 °C, MPa
Natural	1.37	100	20
Polychloroprene	0.17	90	8.28
Nitrile butadiene	0.26	89	9.16
Styrene butadiene	0.34	85	10.35

*against the natural rubber

Some other advantages could be mentioned:

-the solids content and viscosity, which are among the most important parameters of these adhesives could be easily and precisely adjusted as the mechanical stability of the system does not depend on these parameters;

-these adhesives could be easily applied with various coating devices and high rates due to the high drying rate.

Experimental part

Materials and methods

The following types of elastomers were used as main components of the adhesive solutions: blended SMR natural rubber (Wagn Rubber Technology) characterized by Mooney viscosity of 48; polychloroprene rubber (Denka chloroprene, Japan); nitrile butadiene rubber (Europrene, Italy), NBI sort with 26% acrylonitrile and Mooney viscosity of 45; styrene-butadiene rubber (Europrene sort, Stöff Rudolf Gmbh, Austria) characterized by Mooney viscosity of 35.

Toluene, methyl-ethyl-ketone and cyclohexane were provided by Merck and used without any further purification. The following ancillary materials were employed: hydrogenated colophonium, zinc oxide, magnesium oxide, 2,6-di-t-butyl phenol (BHT) and mineral oil.

All adhesive solutions except natural rubber and styrene-butadiene rubber had the same composition to better compare the results (table 2). The natural rubber and styrene-butadiene rubber contain also mineral oil as plasticizer.

Mechanical tests were performed on a Universal Testing Machine (INSTRON 3382, US) at 20°C and 50-55 % relative humidity. T-peel test was employed for flexible substrates and 180 ° peel test for hybrid rigid/flexible substrates. Shear and tensile tests were also performed.

The fracture of the adhesive assembly was monitored by optical means. The optical images were achieved with an Olympus BX41 Microscope equipped with Live view digital SLR camera E-330 (7.5 Mpxl) and special software Quick Photo Micro 2.3.

Results and discussions

Four types of elastomers were chosen: polychloroprene rubber, nitrile butadiene rubber, natural rubber and styrene-butadiene rubber. The main characteristics of the adhesive solutions are shown in table 3.

The adhesives were applied onto flexible bands made out of plasticized PVC deposited in one layer on textile substrate with a 25.4x10 mm^2 surface. The bands were washed with isopropyl alcohol and then dried. After applying the adhesive and solvent evaporation (30 min), the two substrates were assembled by mechanical means (force of 5 kgf, 50N) and maintained for a period of time under pressure. Then, the assembly was subject to peel test. As we may notice from figure 1, polychloroprene rubber is the best elastomer for pressure sensitive adhesives. There are also other advantages and reasons for using polychloroprene rubber for this type of adhesives:

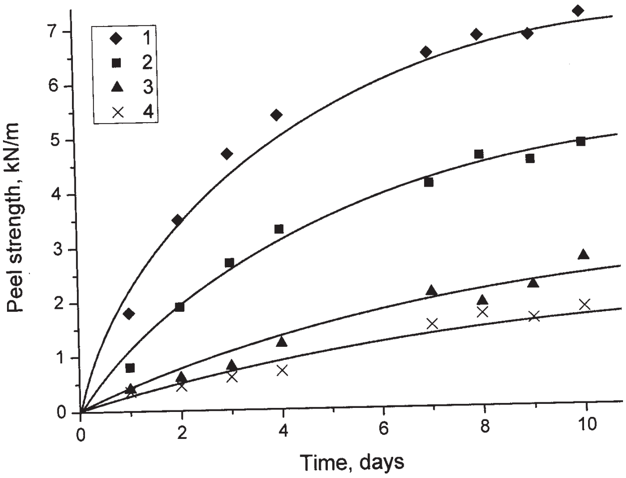

Fig.1.Peel strength versus time for adhesive assemblies with different elastomers 1. polychloroprene rubber; 2. nitrile rubber; 3. natural rubber; 4. styrene-butadiene rubber temperature 25 °C, relative humidity 50 %, flexible PVC, bond surface 25.4x100 mm^2, pressure 2N/cm^2, peel rate 50 mm/min

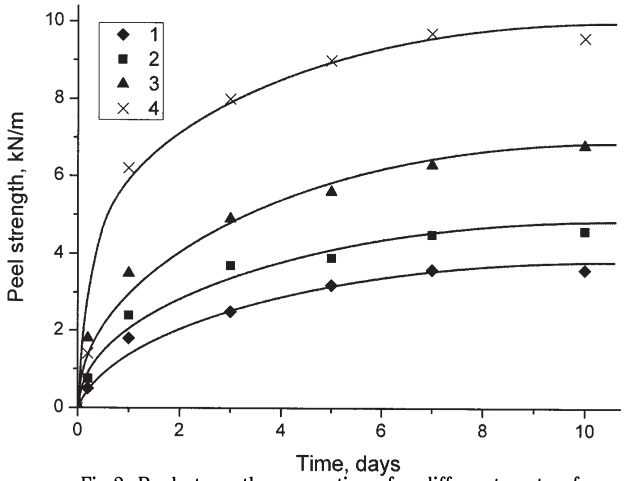

Fig.2. Peel strength versus time for different sorts of polychloroprene rubber 1. S-40; 2. M-40; 3. M-130H; 4. A-90 temperature 25 °C, relative humidity 50 %, flexible PVC, bond surface 25.4x100 mm^2, pressure 4 N/cm^2, peel rate 50 mm/min

-adhesives based on polychloroprene rubber present 80 % of the total number of elastomer-based adhesives (structural and pressure-sensitive adhesives);

-polychloroprene rubber is highly polar, thus enhancing the adhesive ability for different substrates;

-polychloroprene rubber easily crystallizes so that the adhesive assembly has high resistance;

-easy processing and application;

-excellent flexibility and high resistance at ageing and chemical agents.

The industry offers a diversity of sorts of polychloroprene rubber with different molecular weights, crystallization rates and Mooney viscosities. Four sorts of polychloroprene rubbers were chosen in this study and their main characteristics are shown in table 4.

Adhesive solutions in toluene (20 % concentration of elastomer) were obtained according to the composition from table 2. Results of the peel test are shown in figure 2. In this way the pressure sensitive adhesive based on polychloroprene rubber (A-90) was selected for future tests.

The following studies allowed the determination of some parameters correlated with the peel resistance: contact time, peel rate, contact pressure and nature of the substrate.

The influence of the type of substrate on peel strength was evaluated both for flexible substrates (PVC/PVC) and hybrid substrates (flexible PVC/Al alloy 2024T3). Results are shown in figure 3. As one may notice from figure 3, the final strengths of the adhesive assemblies could be reached after 10 days contact time. The results are in good agreement with literature data for other pressure sensitive adhesives.

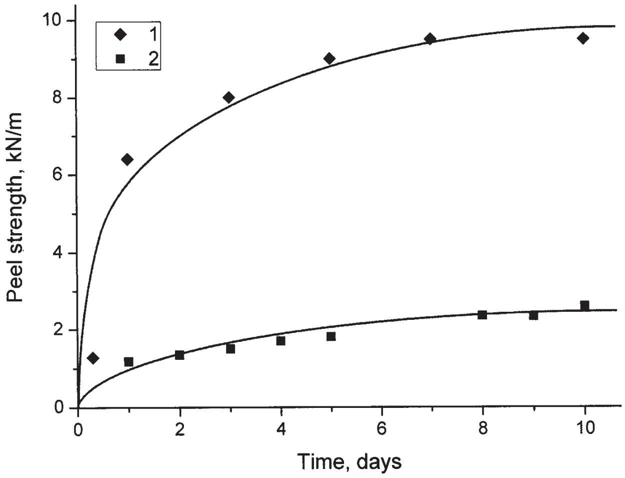

Fig.3. Influence of the substrate on the peel strength temperature 25 °C, relative humidity 50 %, flexible PVC, peel rate 50 mm/min (curve 1) and 300 mm/min (curve 2) , pressure 4 N/cm^2 (curve 1) and 2 N/cm^2 (curve 2), bond surface 25.4x100 mm^2 (curve 1) and 25.4x50 mm^2 (curve 2)

The application rate of force release plays a major role in the determination of peel resistance for adhesive assemblies based on pressure sensitive adhesives. Table 5 presents the influence of peel rate on the resistance of adhesive assembly. We may notice the most notable differences at low peel rates, no matter the nature of the substrate on which the pressure sensitive adhesive is applied.

The normally applied force onto the substrates influences the strength of the bonds. Figure 4 shows the

Table 4

SORTS OF POLYCHLOROPRENE RUBBER FOR PRESSURE SENSITIVE ADHESIVE SOLUTIONS

No.	Sort of polychloroprene rubber	Crystallization rate	Mooney viscosity (ML1+4)
1	S-40	Slow	48±5
2	M-40	Average	48±5
3	M-130H	Average	1510-2600*
4	A-90	Fast	48±5

- Viscosity of 10% solution in toluene (cP)

Table 5
INFLUENCE OF PEEL STRENGTH ON THE RESISTANCE OF ADHESIVE ASSEMBLY BASED ON POLYCHLOROPRENE RUBBER. TEMPERATURE 25 °C, 10 DAYS CONTACT TIME, BOND SURFACE 25.4X100 mm^2, CONTACT PRESSURE 4 N/cm^2

No.	Peel rate, mm/min	Assembly strength, kN/m	
		PVC/PVC	PVC/Al alloy 2024T3
1	5	0.79	0.4
2	25	1.02	0.64
3	50	1.84	0.92
4	150	2.76	1.3
5	300	3.43	2.6

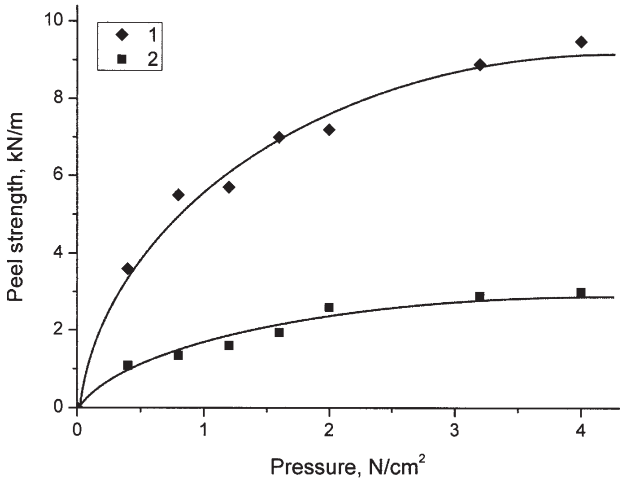

Fig.4. Influence of pressure on peel strength
1. flexible PVC/flexible PVC; 2. flexible PVC/Al alloy temperature 25 °C, 10 days contact time, bond surface 25.4x100 mm^2, peel rate 50 mm/min (curve 1) and 300 mm/min (curve 2)

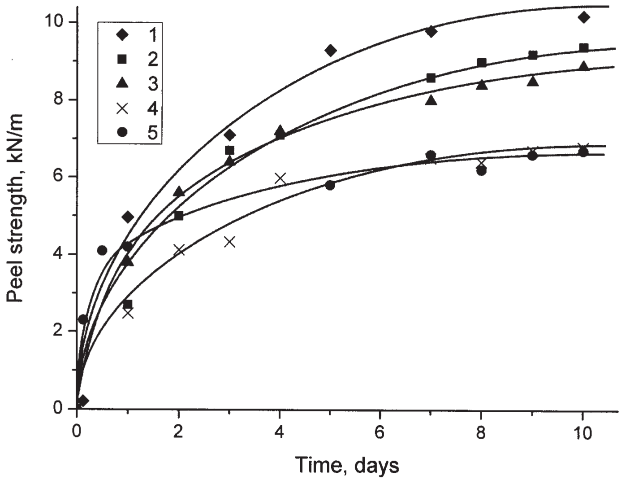

Fig.5. Influence of nature of the flexible substrate on peel strength 1.fabric/fabric; 2. fabric/PVC; 3. fabric/leather; 4. PVC/PVC; 5. leather/leather temperature 25 °C, relative humidity 50%, applied pressure 2 N/cm^2, bond surface 25.4x100 mm^2, peel rate 50 mm/min

influence of pressure on peel strength of the assemblies with adhesive based on polychloroprene rubber on flexible (PVC/PVC) and hybrid supports (flexible PVC/Al alloy 2024T3). Data from figure 4 show that the influence of pressure on peel strength is more important at lower values and it finally enters a plateau (in time).

In order to better identify and expand the applications of pressure sensitive adhesives, adhesive systems based on polychloroprene rubber were tested onto flexible substrates, flexible/rigid substrates and rigid substrates.

The influence of the flexible substrate upon the peel strength is presented in figure 5. Peel strengths of the assemblies based on cotton fabric/cotton fabric have the highest values. Similar results were obtained for assemblies based on fabric/PVC and fabric/leather. This could be explained by the printing of the adhesive within the cotton fabric.

Optical analysis of the substrates after the peel tests showed that the fracture of the adhesive assembly took place in the adhesive layer (cohesive fracture, fig. 6).

The peel strengths of the hybrid assemblies based on flexible PVC/rigid substrates are shown in table 6 (after 5 and 10 days). The highest values of the peel strength could be noticed for hybrid substrates like PVC/textolite and PVC/PMMA.

The peel strength for the assembly with rigid substrates was performed on aluminium and steel samples (25.4x100 mm), which were conditioned by polishing and degreasing with methyl-ethyl-ketone.

In all the cases, the fracture of adhesive assembly took place at the interface adhesive-substrate (fig.7).

The peel strength for the assembly with rigid substrates was performed on aluminium and steel samples (25.4x100 mm), which were conditioned by polishing and degreasing with methyl-ethyl-ketone.

The peel strength was determined after 5 and 10 days and the results are presented in table 7.

The following conclusions could be drawn from this last test:

-the strength of hybrid assembly Al/steel is higher than the peel strength of the assemblies with similar substrates

-the fracture of the adhesive assembly took place completely different. The fracture for the Al/Al adhesive assembly takes place within the adhesive layer (fig. 7A), while the fracture of the hybrid assemblies Al/steel at the adhesive/steel interface (fig. 7B).

Conclusions

The research study conducted on pressure sensitive adhesives based on polychoroprene rubber led on the following conclusions:

-the maximum peel strength is reached after minimum 10 days contact time both for flexible substrates and for hybrid substrates: flexible/rigid or rigid/rigid;

-the peel rate influences the resistance of adhesive assemblies (it could increase within certain limits); the major differences are recorded at low peel rates;

-the contact pressure plays a major role in the adhesion process. Good strengths are obtained for 2-4 N/cm^2;

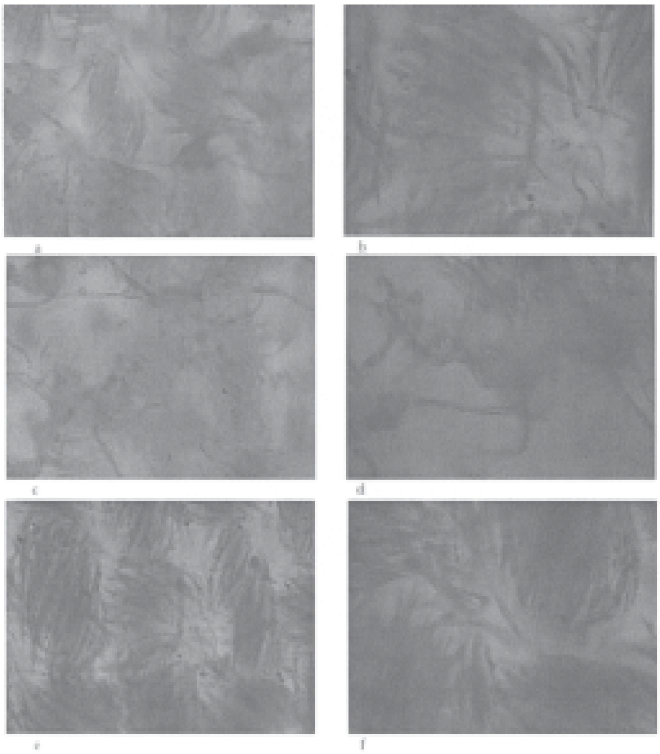

Fig.6. Optical microphotographs of the surfaces after peel test for flexible/flexible substrates a.fabric/fabric; b. fabric/PVCA; c,d. PVC/PVC; e. fabric/leather; f. leather/leather

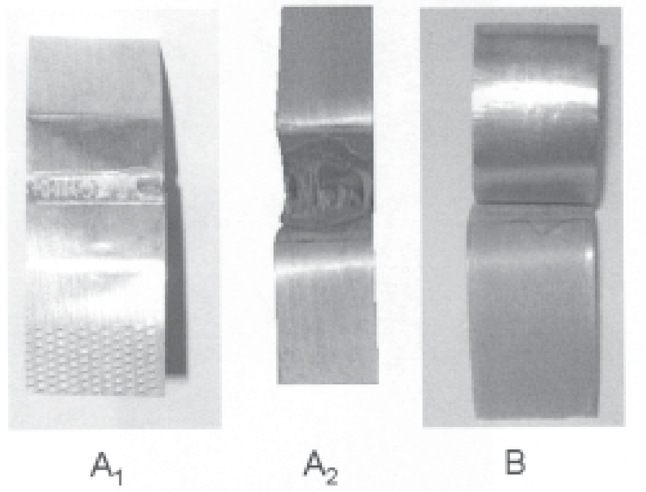

Fig.7. Fracture of adhesive assemblies between rigid substrates A. Al substrates; B. Al/steel A_1 – initiation of the fracture process; A_2 – fracture of the adhesive assembly

Table 6
PEEL STRENGTH VERSUS NATURE OF THE RIGID SUBSTRATE. FLEXIBLE SUBSTRATE: PVC ON TEXTILE SUPPORT, TEMPERATURE 25 °C, CONTACT PRESSURE 2 N/cm^2, PEEL RATE 300 mm/min, RELATIVE HUMIDITY 50 %, BOND SURFACE 25.4X50 mm^2

No.	Rigid substrate	Peel strength, kN/m	
		5 days	10 days
1	Al alloy 2024T3	1.84	2.60
2	Royalite (rigid PVC)	2.12	2.85
3	PMMA	2.24	3.12
4	Steel	1.92	2.74
5	Textolite	3.12	4.72

Table 7
PEEL STRENGTH VERSUS SUBSTRATE NATURE. TEMPERATURE 25 °C, CONTACT PRESSURE 4 N/CM^2, PEEL RATE 50 mm/min, RELATIVE HUMIDITY 50 %, BOND SURFACe 25.4x50 mm^2

No.	Rigid substrate	Peel strength, kN/cm^2	
		5 days	10 days
1	Al/Al	2.05	2.76
2	Steel/Steel	2.76	3.12
3	Al/Steel	3.26	3.86

-substrate nature has also a major impact upon the peel strength. There is a clear difference between adhesive assemblies based on flexible substrates (fabric/fabric, PVC/PVC, leather/leather), hybrid substrates (flexible PVC and rigid substrates) or rigid substrates. The polarity and porosity of the substrate is also important although the literature does not mention a significant influence of the substrate nature upon the pressure sensitive adhesives;

-the fracture of adhesive assemblies based on flexible substrates takes place within the adhesive layer (cohesive fracture). In the case of adhesive assemblies based on flexible PVC/rigid substrates, the fracture takes place at the interface rigid substrate/adhesive (adhesive fracture). For the rigid substrates, the fracture appears in the adhesive layer (for similar substrates) or at the interface steel/adhesive for Al/steel hybrid assemblies.

References

1. PETRIE, E.M., Handbook of adhesives and sealants, Mc Graw-Hill, New York, 2000
2. PIZZI, A., MITTAL, K.L., Handbook of adhesive technology, 2nd Ed., Marcel Dekker, 2003
3. BENNETT, G., KLINGEN, J., GEISS, P.L., NEEB, T., Adhesives Age, 39, no. 10, 1996, p. 19
4. PLANT, R.H., The Journal of Adhesion, 86, 2010, p. 675
5. JOSSE, G., SERGOT, P., DORGET, M., and CRETON, C., The Journal of Adhesion, 80, no. 1-2, 2004, p. 87

6. CROSBY, A., SCHULL, K.R., LAKVOUT, H., and CRETON, C., J. Appl. Phys., 88, 2000, p. 2956
7. AZARI, S., PAPINI, M., SPELT, J.K, The Journal of Adhesion, 86, no. 7, 2010, p. 742
8. BENEDEK, I., Pressure sensitive adhesives and applications, 2nd Ed., CRC Press, 2004
9. BENEDEK, I., FELDSTEIN, M.M., Technology of Pressure Sensitive Adhesives and Products, CRC Press, 2008
10.*** Pressure sensitive adhesive – Wikipedia, the free encyclopedia,http://em.wikipedia.org/wiki/Pressure-sensitive_adhesive
11. *** Pressure sensitive adhesive information//Chemsultants International, http://www.chemsultants.com/technical-resources/pressure-sensitive-adheisve-info.aspx
12. *** Pressure sensitive adhesives (PSA), http://www.globalspec.com/learn more/materials_chemicals/adhesives/pressure_sensitive
13.*** Pressure sensitive adhesives, http://www.thomasnet.com/articles/adhesives-sealant/pressure-sensitive-adhesives
14. HARRINGTON, W.F., Elastomeric Adhesives, in Adhesives and Sealants, vol.3. Engineered Materials Handbook, ASM International, 1990
15.*** Pressure sensitive adhesives, http://www.stockwell.com/pages/materials_adhesives.php
16. MĂRCULESCU, B., RUSEN, E., BUTAC, L.M., Adezivi, lacuri şi vopsele, Ars Docendi, Universitatea din Bucuresti, 2009
17. BENEDEK, I., Developments in pressure sensitive products, 2nd Ed., CRC Press Taylor and Francis Group, 2005

Manuscript received:24.11.2010