

# Studies regarding the Adhesive Performances of Hybrid Acrylic Polymer Solutions - New Generation of Pressure Sensitive Adhesives

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*Acrylic adhesives show high stability towards atmospheric agents and degradation resistance. On the other hand they have low adhesion for low energy surfaces (non-polar thermoplastics: polyethylene, polypropylene etc.). Pressure sensitive adhesives based on hybrid acrylic polymers could eliminate these drawbacks by combining the performances of classical acrylic adhesive with those of elastomeric adhesives. This work is focused on the study regarding the performances of pressure sensitive adhesives based on hybrid acrylic polymers. Peel strength, shear strength and tensile strength are also determined.*

**Keywords:** acrylic adhesives, pressure sensitive adhesives, acrylic saturated rubber, hybrid pressure sensitive adhesives

Acrylic adhesives have been discovered quite recently. The first patents have been published in 1995-1997 [1-2], and the first scientific communications in 2001 [3]. More information on these types of pressure sensitive adhesives has been published in the last years [4-8].

The idea of obtaining hybrid acrylic adhesives started from the necessity of combining the excellent performances of acrylic adhesives with those based on elastomers.

Therefore, acrylic adhesives have high stability towards atmospheric agents and degradation, but they have low adhesion for low energy surfaces (polyethylene, polypropylene).

On the other hand, the elastomeric adhesives show high adhesive character towards low surface energies, but their stability in time is low and the cohesive resistance is limited. The combination of these two types of adhesives leads to products that adhere to a high number of surfaces with different energies.

Combination of these two types of adhesives was achieved through the obtaining of grafted copolymers having polyacrylic main chain and saturated hydrocarbon chain as grafts (fig 1).

The polyacrylic chain contains specific elements for acrylic pressure sensitive adhesives.

-Low  $T_g$  monomers: 2-ethyl-hexil acrylate, butyl acrylate or iso-octylacrylate, which offer tacking properties.

-High  $T_g$  monomers: methyl methacrylate or methyl acrylate, which offer cohesive resistance.

-Functional monomers: acrylic acid or  $\beta$ -hydroxyethyl acrylate, which offer specific adhesion and cross-linking.

Hydrocarbon grafts are composed of low molecular weight copolymers (2000-30000 g/mole): ethylene-butylene, ethylene-propylene or their mixture, with acrylate or methacrylate end groups and  $T_g$  between (-20) – (-50 °C), obtained by hydrogenation of 1,4 and 1,2 polybutadiene or 1,4-cis-polyisoprene with hydroxyl end groups.

The acrylic polymer is not compatible with the hydrocarbon graft that leads to the following structure of the hybrid acrylic polymer.

Due to this structure the hybrid acrylic polymer shows two distinct  $T_g$  temperatures by DMA analysis, the lowest one being characteristic to the elastomeric phase [4].

Due to the incompatibility between the two components, colophonium esters or phenol-terpene resins are used as tacking agents for the acrylic phase. C5 resins are usually used as tacking agents for the elastomeric hydrocarbon phase.

The presence of hydrocarbon tacking agents does not alter the temperature of glassy state of the acrylic phase (the tacking agent is incompatible with this phase and does not react). It increases the  $T_g$  of the elastomeric phase.

This paper reports on the evaluation of the mechanical properties of this new class of pressure sensitive adhesives such as peel strength, shear strength and tensile strength.

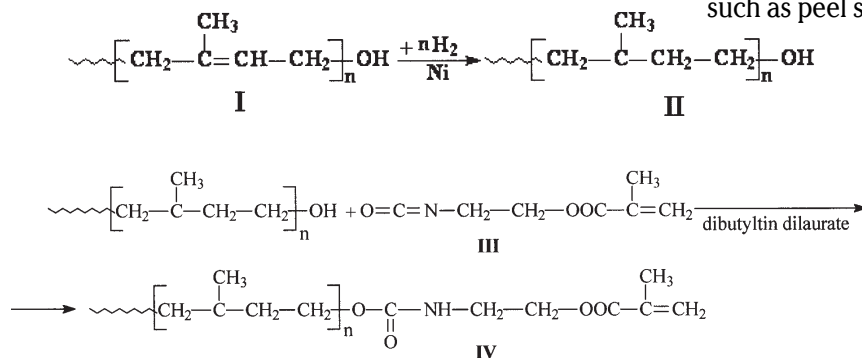


Fig. 1. Chemical reactions for the synthesis of macromer with methacrylic end groups (scheme I): I - polyisoprene with hydroxyl end groups; II - ethene-propene random copolymer; III -  $\beta$ -isocyanate-ethyl-methacrylate; IV - macromonomer with methacrylic end groups

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**Experimental part**

The hybrid acrylic adhesive was provided by National Starch & Chemical Company, Adhesive Division, USA (DURO-TAK® AH 100, no.80-131A).

Ethene-propene copolymer with methacrylic end groups was provided by KRATON™ Polymers, USA (KRAFTON

LIQUID® Polymers, L 1253). IR spectrum of this polymer obtained through the reaction sequences presented in scheme I (fig. 3) is shown in figure 4.

This macromer was copolymerized with 2-ethyl-hexyl acrylate and acrylic acid in hexane/ethyl acetate resulting in a solution of grafted copolymer.

IR spectrum of the hybrid adhesive is presented in figure 5. The spectrum shows the characteristic bands for esteric, methyl and methylene groups from the hydrocarbon graft. Peaks assignment is in good agreement with those obtained by SFG-IR (Sun frequency generation) from literature data [9-10].

Due the incompatibility of the two phases (acrylic copolymer and hydrocarbon copolymer) solvent mixtures were used for the obtaining of adhesive solution: ethyl acetate (1-30 %); n-hexane (10-30 %); naphtha solvent (aliphatic) (10-30 %); toluene (1-5 %) and mixture of hexane isomers (1-5 %).

Mechanical tests for the adhesive assemblies were performed on a Universal Tensile Machine INSTRON 3382. 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.

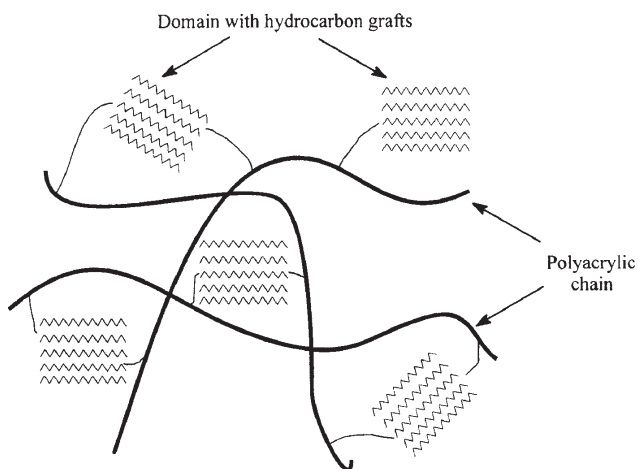


Fig. 2. Schematic representation of hybrid acrylic polymer

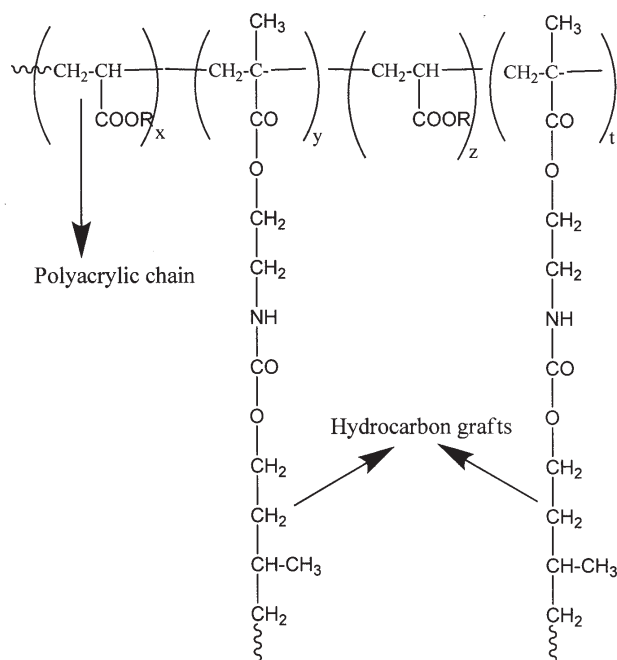


Fig. 3. Structure of hybrid acrylic polymer

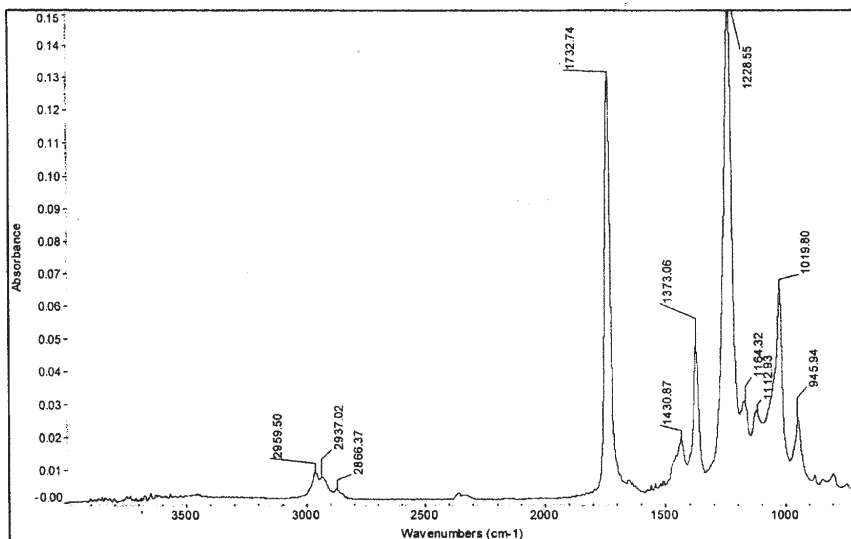


Fig. 4. IR spectrum of ethene-propene copolymer with methacrylic end groups

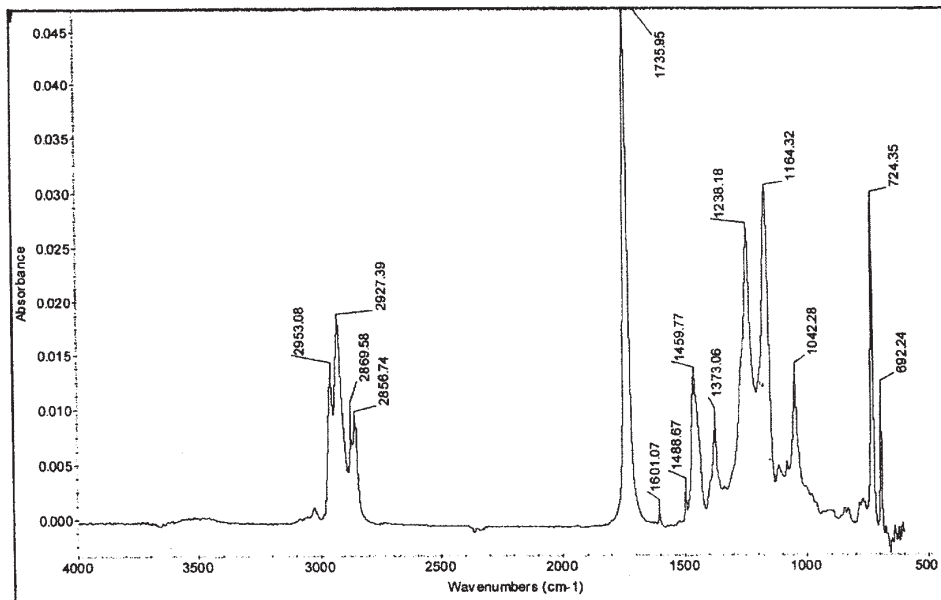


Fig. 5. IR spectrum of hybrid acrylic adhesive

### Results and discussions

The following parameters were determined to establish the influence of the hybrid acrylic adhesive on the performance of the adhesive assemblies: influence of the contact time, influence of the peel rate, influence of the contact pressure and nature of the substrate.

The influence of the contact time upon the peel strength of the adhesive assemblies was performed on two

substrates: flexible PVC/alloy Al2024 T<sub>3</sub> and steel/steel. The results are presented in figure 6.

As shown in figure 6, the peel strength increases with the contact time. Higher strengths are obtained for steel/steel assemblies.

Mixed substrates Al/steel were used to study the influence of the peel rate upon the strength of the adhesive assemblies based on hybrid acrylic adhesive. The obtained results are shown in table 1.

These data show the dependence of the peel strength on the peel rate for the Al/steel assemblies. The peel strength increases with the increase of fracture rate of the assembly.

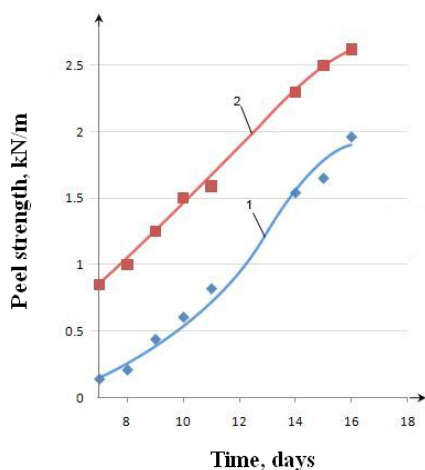


Fig. 6. Influence of the contact time upon peel strength  
Temperature: 25 °C ; R.U. 50% ; contact pressure: 2 N/cm<sup>2</sup>; peel rate: 300 mm/min; surface covered with adhesive: 25.4x50 mm.  
1-flexible PVC /alloy Al 2024T<sub>3</sub>; 2-steel/steel

Table 1

INFLUENCE OF PEEL RATE UPON STRENGTH OF AL/STEEL ASSEMBLIES; TEMPERATURE: 25 °C; R.U. 50%; CONTACT PRESSURE 2 N/cm<sup>2</sup>, SURFACE COVERED WITH ADHESIVE 25.4X50 mm, CONTACT TIME 10 DAYS

No.	Peel rate, mm/min	Strength, kN/m
1	5	0.42
2	50	0.54
3	300	0.65
4	500	0.82

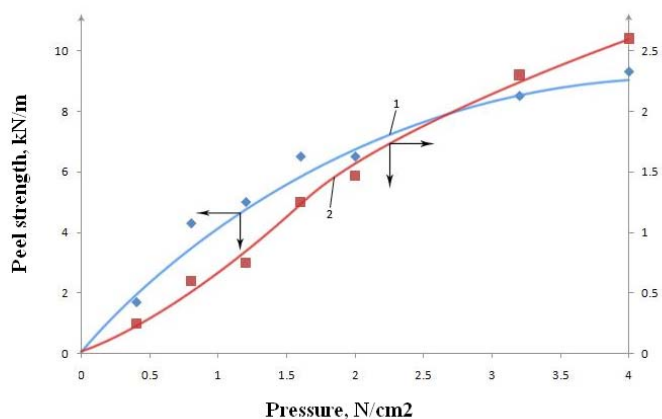


Fig. 7. Influence of pressure upon the peel strength of hybrid acrylic adhesive assembly  
t=25 °C; R.U. 50%; contact time 10 days, surface covered with adhesive 25.4x100 mm, peel rate 50 mm/min (curve 1) and 300 mm/min (curve 2) 1-flexible PVC /flexible PVC; 2-alloy Al 2024T<sub>3</sub>/flexible PVC

**Table 2**

INFLUENCE OF SUBSTRATE NATURE UPON PEEL STRENGTH;  
 TEMPERATURE: 25 °C; R.U. 50%; PEEL RATE 300 MM/MIN; SURFACE  
 COVERED WITH ADHESIVE 25.4X50 MM; CONTACT TIME 10 DAYS,  
 CONTACT PRESSURE 2 N/cm<sup>2</sup>

No.	Substrate	Peel strength, kN/m
1	Flexible PVC /rigid PVC	2.16
No.	Substrate	Peel strength, kN/m
2	Flexible PVC/textolite	3.68
3	Flexible PVC/ PMMA	2.45
4	Flexible PVC /Al 2024 T <sub>3</sub>	1.46
5	Flexible PVC /steel	1.74
6	Al/Al	0.54
7	steel/steel	0.606
8	Al/steel	0.65

The influence of pressure upon the peel strength of adhesive assemblies based on flexible substrates (plasticized PVC on textile support) and mixed substrates (alloy Al 2024 T<sub>3</sub>/flexible PVC) is presented in figure 7.

The contact pressure is kept constant during set up of the substrates assembly. This factor has a major role on the peel strength. The significant increase of the peel strength with pressure is probably due to a better penetration of the adhesive within the pores and cavities of the substrate surface (a better substrate/adhesive contact).

The following substrates were used to determine the influence of the substrate nature upon the peel strength: flexible PVC, rigid PVC (Royallite), Plexiglas, textolite, steel and aluminium. Hybrid assemblies were obtained: flexible PVC/rigid substrates, Al/steel and Al/Al and steel/steel assemblies. The obtained results are shown in table 2.

Two series of measurements were performed for the evaluation of the influence of the substrate nature on the peel strength. First, there were obtained assemblies of the solid substrates with plasticized PVC. The best results are obtained on rigid polymeric substrates and the highest value for the peel strength was recorded for flexible PVC/textolite assembly. The higher peel strengths of the polymeric substrates are probably due to a higher polarity of these substrates as compared to Al and steel.

In the second series of tests, there were obtained assemblies between metallic substrates. Table 2 clearly shows the best results for Al/steel assemblies.

The fracture of the adhesive assembly monitored by optical means revealed a mixed type mechanism: both in the adhesive layer and at the interface substrate/adhesive (fig. 8).

Samples of Al 2024 T<sub>3</sub>, rigid PVC, Plexiglas, textolite and steel were used to determine the shear strength of the pressure sensitive adhesive system based on hybrid acrylic adhesives.

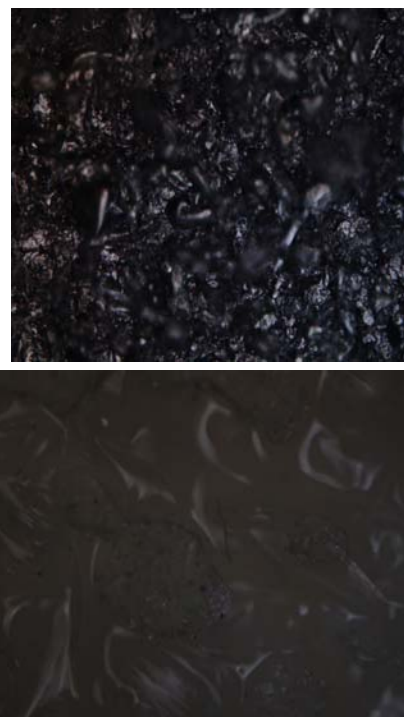


Fig. 8. Surface microphotographs after fracture of adhesive assemblies for Al 2024 T<sub>3</sub>/flexible PVC  
 a - alloy surface Al 2024 T<sub>3</sub>; b - flexible PVC surface

The surface covered with adhesive was 25.4x25.4 mm, and the assembly was obtained after solvent evaporation at different pressures and the shear strength was measured with INSTRON 3382 Universal Testing Machine.

The obtained results are shown in figure 9 and table 3. Data analysis from figure 9 and table 3 reveals the significant dependence of the shear strength on pressure and substrate nature.

The small difference between the values of the shear strength at 7.75 N/cm<sup>2</sup> and 7 days hardening time is probably due to the fact that the measurements were done exactly after 7 days, which is the minimum time to obtain the adhesive assemblies.

The fracture analysis of the adhesive assembly after shear test revealed a cohesive type mechanism. This fact is obvious from the microphotographs shown in fig. 10.

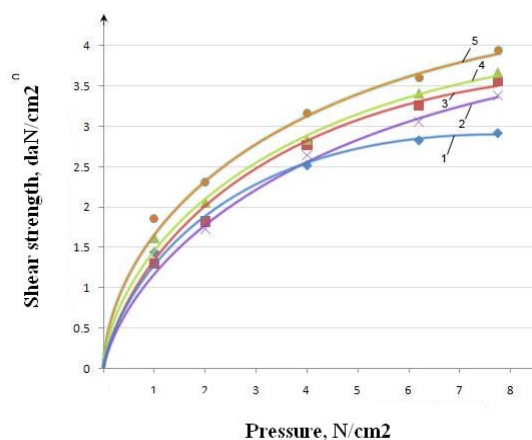


Fig. 9. Shear strength versus substrate nature and contact pressure for the adhesive assemblies based on hybrid acrylic adhesives  
 Surface covered with adhesive: 25.4x25.4 mm; contact time 7 days;  
 temperature: 25 °C; R.U. 50%; force rate 1.3 mm/min.  
 1- alloy Al 2024 T<sub>3</sub>/Al alloy; 2-steel/steel; 3-PVC/PVC (Royallite);  
 4-PMMA/PMMA; 5-textolite/textolite

**Table 3**

SHEAR STRENGTH VERSUS SUBSTRATE NATURE AFTER 7 DAYS CONTACT; CONTACT PRESSURE: 7.75 N/cm<sup>2</sup>; SURFACE COVERED WITH ADHESIVE: 25.4x25.4 mm, FORCE RATE 1,3 mm/min; TEMPERATURE: 25 °C; R.U. 50%

No.	Substrate	Shear strength, daN/cm <sup>2</sup>
1	Al alloy/Al alloy	2.92
2	Steel/steel	3.38
3	Royallite/Royallite	3.56
4	PMMA/PMMA	3.67
5	Textolite/Textolite	3.94

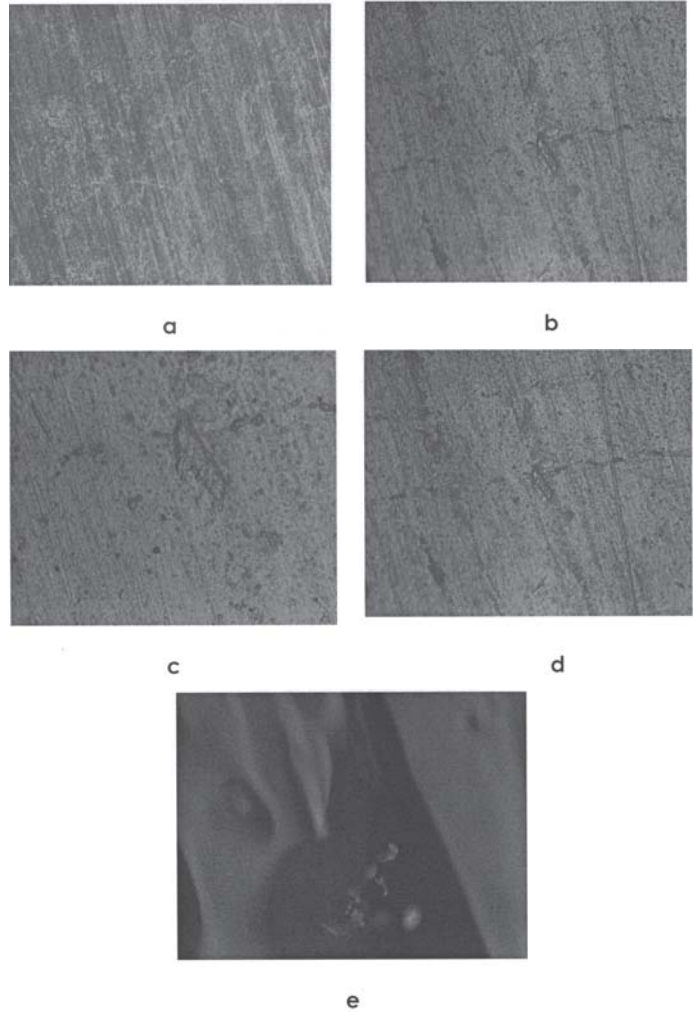


Fig. 10. Optical microphotographs for fracture surfaces at shear test a)-Al alloy/Al alloy; b)steel/steel; c) textolite/textolite; d)-PMMA/PMMA; e)-Royallite/Royallite

The tensile test was performed on cylindrical samples made out of oak tree and steel.

The minimum time to realize the pressure sensitive adhesive assemblies is 7 days. Therefore, the influence of the contact time upon the tensile strength of the adhesive assembly was evaluated after 7, 9, 14 and 16 days. The obtained results are shown in figure 11 and table 4.

Figure 11 shows the major influence of the contact time upon the tensile strength. The maximum tensile strengths for both types of substrates are obtained in 16 days contact time.

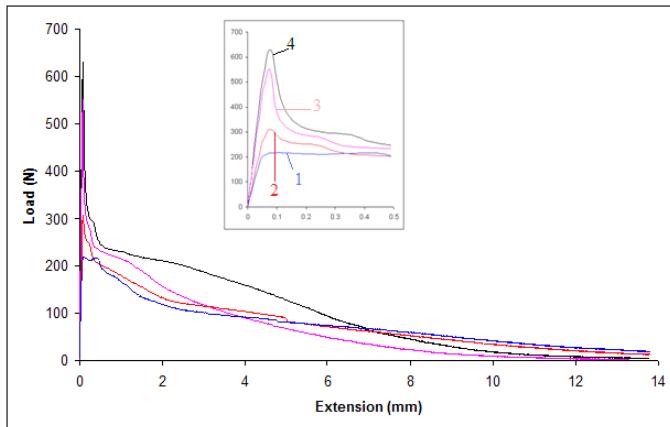


Fig. 11. Tensile strength versus time for oak tree assemblies:  
Temperatures: 25 °C; R.U. 50%; surface covered with adhesive: 12.56 cm<sup>2</sup>; contact pressure: 5.2 N/cm<sup>2</sup>; contact time: 1-7 days; 2-9 days; 3-14 days; 4-16 days

No.	Tensile strength for wood		Tensile strength for steel	
	N	daN/cm <sup>2</sup>	N	daN/cm <sup>2</sup>
1	210	1.67	180	1.43
2	300	2.39	290	2.31
3	540	4.30	340	2.71
4	630	5.02	560	4.46

**Table 4**

INFLUENCE OF CONTACT TIME UPON TENSILE STRENGTH OF THE ADHESIVE ASSEMBLIES BASED IN JUBRID ACRYLIC ADHESIVES; TEMPERATURE: 25 °C, R.U. 50%; SURFACE COVERED WITH ADHESIVE: 12.56 cm<sup>2</sup> FOR WOOD AND 9.6 cm<sup>2</sup> FOR STEEL; CONTACT PRESSURE: 5.2 N/cm<sup>2</sup>

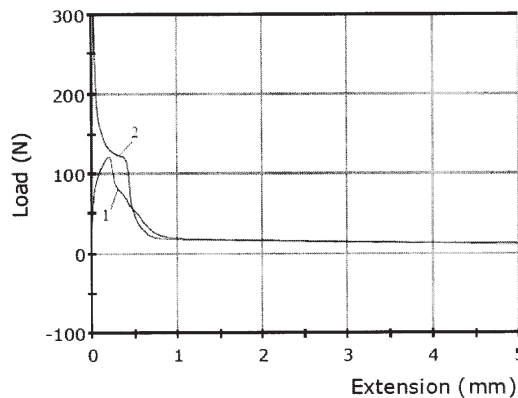


Fig. 12. Influence of contact pressure upon tensile strength of the steel assemblies  
 Temperature: 25 °C; R.U. 50%; tensile rate 2 mm/min; contact time 9 days; surface covered with adhesive: 9.6 cm<sup>2</sup>; tensile rate 2 mm/min.  
 1-p=2.1 N/cm<sup>2</sup>; 2-p=5.2 N/cm<sup>2</sup>

Contact pressure, N	Substrate: wood/wood			Substrat oțel/oțel		
	Contact pressure, N/cm <sup>2</sup>	Tensile strength		Contact pressure, N/cm <sup>2</sup>	Tensile strength	
		N	daN/cm <sup>2</sup>		N	daN/cm <sup>2</sup>
20	1.6	560	4.46	2.1	120	1.25
50	4.0	870	6.93	5.2	290	3.02
100	8.0	1160	9.24	10.4	580	6.04
150	12.0	1560	12.4	15.6	840	8.75
200	16.0	1630	13.00	20.8	1160	12.08

**Table 5**  
 INFLUENCE OF CONTACT PRESSURE UPON TENSILE STRENGTH FOR ADHESIVE ASSEMBLIES BASED ON WOOD AND STEEL SUBSTRATES; TEMPERATURE: 25 °C; R.U. 50%; TENSILE RATE 2 mm/min; CONTACT TIME 9 DAYS; SURFACE COVERED WITH ADHESIVE: 12.56 CM<sup>2</sup> FOR WOOD AND 9.6 cm<sup>2</sup> FOR STEEL

The influence of contact pressure upon the tensile strength is shown in figure 12 and table 5.

Figure 12 and table 5 show a significant influence of the contact pressure on the tensile strength both for wood/wood and steel/steel substrates.

### Conclusions

The studies regarding the adhesive performances of pressure sensitive adhesives based on hybrid acrylic adhesives led to the following conclusions:

- the peel strength, shear strength and tensile strength are dependent on contact time, pressure, force rate and substrate nature;
- the minimum contact time to realize the adhesive assemblies is 7 days, but the corresponding strengths are obtained at higher contact times (20 days or longer);
- the contact pressure is a major parameter that determines the adhesive strengths;
- the substrate nature is crucial for the obtaining of high strengths. The results on wood substrates are higher than those on steel;
- the fracture of adhesive assemblies could have various mechanisms: mixed (both in the adhesive layer and at the interface adhesive/substrate – peel of the assemblies based on AL 2024 T<sub>3</sub>/flexiblePVC) or within the adhesive layer (shear and tensile test).

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