A New Methodology in the Study of PVAc-Based Adhesive Formulations

A. Salvini,[1] L. M. Saija,[2] S. Finocchiaro,[2] G. Gianni,[1] C. Giannelli,[1] G. Tondi[1]

[1]Department of Organic Chemistry, University of Florence, Sesto Fiorentino, Florence 50019, Italy
[2]Cray Valley Italia s.r.l., via Finghè, Boretto, RE 42022 , Italy

ABSTRACT: The role of the main components of a PVAc-based wood adhesive formulation in the formation and performance of the adhesive joint was investigated. A new analytical methodology was applied to carry out the chemical separation and characterization of the adhesive components present in the bond line. By using extraction techniques on the wet and dry glues it was possible to observe the variation in the solubility of the adhesive components, for different glue formulations. The swollen-state NMR technique proved to be a very useful tool to characterize the insoluble parts present in the adhesive films. These findings, when put into relation to some specific properties of the adhesive joints, contribute to the understanding of the mechanisms involved in the adhesion process. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3841–3854, 2009

Key words: adhesives; dispersions; crosslinking; NMR; formulation

INTRODUCTION

Wood adhesives are polymeric materials capable of interacting both physically and chemically with the surface of wood so that the involved stresses are transferred between bonded parts without either rupture of the adhesive or detachment of the adhesive itself from the wood. Wood adhesives can be roughly separated into two distinct groups: those formulated from natural origin materials and those based on synthetic resins. The latter are further classified in two categories according to their behavior upon curing: thermosetting adhesives, such as amino resins (UF, MF), phenolic resins (PF), epoxy resins, and polyisocyanates, which crosslink upon cure, are insoluble, and do not soften on heating; thermoplastic adhesives, which generally show lower solvent resistance and water sensitivity and soften when exposed to heat. The major wood adhesive in this last group is polyvinylacetate (PVAc). Wood adhesives based on PVAc are economically important products with many desirable features. They are obtained by vinyl acetate emulsion polymerization in presence of polyvinyl alcohol (PVA) as protective colloid and are well known as "white glues." These adhesives set through evaporation and diffusion of the water into the wood and, at the same time, by coalescence of the polymer particles. Setting times are quite rapid at room temperature and dry resins are light in color and often transparent, resulting in an adhesive joint that is practically invisible. However, they tend to creep under static load and show a low moisture resistance. These drawbacks make them unsuitable for structural or exterior applications.

As reported in the surveyed literature,[1–8] several modifications have been employed to decrease creep and enhance water resistance of PVAc adhesive bonds. Among them, the use of specific crosslinking comonomers, such as N-methylolacrylamide (NMA) in the synthesis of poly vinyl acetate and the formulation of PVAc latexes with strongly chelating metal salts, such as Al and Cr derivatives, alone or in combination with thermosetting resins like UF, MF or reactive polyisocyanates, are the most common. However, these modifications may cause some side effect such as a lower shelf-life of glues or the yellowing of the adhesive joints upon heating or aging.

The crosslinking mechanism and the precise role of the main components of a PVAc-based adhesive formulation have not been fully investigated. In literature it clearly appears that only few raw hypotheses are formulated to explain the benefits stemming from them. Nevertheless, a better knowledge of chemical interactions, which develop in the adhesive joint, could be helpful for further optimisation.

This study focuses on a new analytical methodology for the characterization of PVAc water based adhesives. The aim was to better understand the

role of the different components of the formulation and their influence on the behavior of the adhesive joint. Combinations of analytical techniques have been selected and used for that purpose. In particular, a specific extractive procedure, both on wet and dry glues has been employed. The isolated fractions have been chemically characterized using FT-IR and NMR spectroscopy on liquid and solid phase. The swollen-state NMR has also been used to analyze the insoluble solid films. This last technique was employed by other authors[9–13] in the past to characterize rubber blends, crosslinked polymers, alkyd resins by means of swollen samples inserted in 10 mm NMR tubes. In the presented work, a special probe supplied by Varian, Nano NMR probe, was used. Such probe allows to analyze very small samples, (as 40 µL of a solution or 0.1–0.5 mg of a solid sample swollen with 40 µL of a suitable deuterated solvent) with a higher resolution compared to the traditional methods (simple swollen sample in 10 mm NMR tubes).

Elemental analyses were carried out to have a confirmation of any chemical transformation upon bond line formation. The wet and dry adhesives underwent physical-chemical characterization as well. Finally, the mechanical properties of the adhesive joints were evaluated with standard test methods.

MATERIALS AND METHODS

Materials

Distilled water, methanol (98%), toluene (99.7%), chloroform (99.4%), acetone (99.5%), ethyl acetate (99.5%), n-hexane (98%), acetic acid (99.5%), HCl (37%), Al(OH)$_3$, D$_2$O (99.9%), DMSO-d$_6$ (99.8%), CD$_3$OD (99.8%), 2,2'-azobisisobutyronitrile (AIBN), vinyl acetate were reagent grade and were used without further purification. PVA, N-methylolacrylamide (NMA), 2-(2-Butoxyethoxy)ethyl acetate (BDGA), t-Butyl hydroperoxide, sodium formaldehyde sulphoxylate, NaHCO$_3$ and AlCl$_3$ were supplied from Cray Valley Italia s.r.l and were used without further purification. The ^{1}H-, ^{13}C-NMR and FT-IR spectra of PVA and BDGA were recorded and reported in Tables I–III.

Instruments and analytical techniques

IR spectra were recorded on a FT-IR Perkin-Elmer Spectrum BX model, using the Spectrum v. 3.02.02 program. The solutions were analyzed using KBr or CaF$_2$ cells having 0.1 mm path.

^{1}H-NMR and ^{1}H-NMR COSY spectra of solutions were recorded on a Varian Mercury 400 and on a Varian VXR 200 at respectively 399.92 MHz and 199.985 MHz, using solvent residual peak as

TABLE I
^{1}H-NMR Spectral Data (δ, ppm, DMSO-d$_6$ as solvent)

	−CH$_2$−CH (OCOCH$_3$)−	−CH$_2$− CH(OH)−	−CH$_2$−CH$_2$ (OCOCH$_3$)−	−CH$_2$O−	−CH$_2$−CH(OH)	CH$_3$CO	−CHR −CH$_2$−	CH$_3$ −CH$_2$−CH$_2$−	CH$_3$−CH$_2$−
PVA	4.68 (m, 1H)	4.46 (m, 1H), 4.23 (m, 1H)			3.80 (m, 1H)	1.93 (m, 3H) (small amount)	1.40 (m, 2H)		
PVAc	4.75 (m, 1H)	–			–	1.95 (m, 3H), 1.91 (m, 3H)	1.72 (m, 2H)		
BDGA			4.07 (m, 3H)	3.45 (m, 10H)		1.98 (s, 3H)		1.35 (m, 4H)	
NMA-VAM[a] copolymer	4.87 (m, 1H)					1.97 (s, 3H)	1.75 (m, 2H) 1.51 (m, 2H)		0.85 (t, 3H, J_{HH} = 7.14 Hz)

[a] Other signals of NMA-VAM copolymer: 8.44 (NH, m, 1H); 5.50 (−NH−CH$_2$−OH, m, 1H); 4.54 (−NH−CH$_2$−OH, m, 2H) ppm.

TABLE II
^{13}C-NMR Spectral Data (δ, ppm, DMSO-d$_6$ as solvent)

	CH$_3$CO	—CH$_2$—CH$_2$(OAc)—	CH	—CH$_2$O—	—CH$_2$—CH(OAc)—	CH$_3$—CH$_2$—CH$_2$—	CH$_3$CO	CH$_3$—CH$_2$—	CH$_3$—CH$_2$—
PVA	170.2 (small amount)		68.2, 66.3		45.9		21.2 (small amount)		
PVAc	170.2		68.3, 67.4, 67.1, 66.7, 66.3		Overlapped with solvent signal		21.2		
BDGA	170.0	70.4		70.2, 69.9, 68.7, 63.5		31.7	20.8	19.2	14.0
NMA-VAM[a] copolymer	170.1		69.1			Overlapped with solvent signal	21.5		

[a] Other signals of NMA-VAM copolymer: 174.4 (OH—CH$_2$—NH—CO); 63.0 (—NH—CH$_2$—OH); 37.3 (—CH$_2$—CH(CO—NH—)—) ppm.

reference. ^{1}H-NMR spectra of solid samples swollen in DMSO-d$_6$ were recorded with a Varian Mercury Plus 400 spectrometer equipped with a Nano NMR probe, introducing 0.1–0.5 mg of the solid film and 40 μL of deuterated solvent into a nano probe sample tube. All spectra were recorded at 25°C, with a spinning speed of 2 KHz. The other experimental parameters are the same used in a standard ^{1}H-NMR experiment. ^{13}C-NMR spectra were collected at 100.57 MHz on a Varian Mercury 400 and at 50.286 MHz on a Varian VXR 200, by using solvent residual peak as reference. All ^{13}C spectra were acquired with a broadband decoupler.

Elemental analyses were performed with a Perkin-Elmer 2400 Series II CHNS/O analyser.

Solids content, pH, and viscosity were determined according to the international standards EN ISO 3251,[14] ISO 976,[15] and EN ISO 2555.[16]

Preparation of the standard polyvinyl acetate

Into a double-necked round bottom flask equipped with a magnetic stirrer and a reflux condenser, under nitrogen atmosphere, 1 mL of vinyl acetate was added to a solution of 12.1 mg of AIBN in 5 mL of ethyl acetate. The solution was stirred and heated at 60°C, for 6 h. n-Hexane (100 mL) was added at room temperature to the colorless reaction mixture and a white solid residue was obtained.

The solution was settled and the product was recovered and purified by solubilisation in chloroform and precipitation with n-hexane. The white solid obtained was then dried under vacuum up to a constant weight (700 mg). A yield of 75% was obtained. The ^{1}H-, ^{13}C-NMR, and FT-IR spectra of PVAc were recorded and reported in Tables I–III.

Synthesis of the polyvinyl acetate water dispersions

The PVAc water dispersions were synthesized by using a modification of the emulsion semibatch polymerization technique in a four-neck kettle equipped with mechanical stirrer, inlet for feeding streams and reflux condenser. The vinyl acetate was polymerised in presence of PVA (10%) as protective colloid and NaHCO$_3$ (22 mM) as buffer. t-Butyl hydroperoxide/sodium formaldehyde sulphoxylate (20 mM, 1 : 1, w/w) were used as redox radical initiator system. NMA (1%), when present as comonomer, was added at the same time of the vinyl acetate. The polymerization was carried out at a temperature between 80 and 90°C. The additional components such as 2-(2-Butoxyethoxy)ethyl acetate (BDGA, 5%) and the aluminum salt (AlCl$_3$, 0.5%), when present, were added at the end of the reaction at room temperature. Five samples

	OH (Stretching)	*CH* (Stretching)	*C=O,* (Stretching)	*CH* (Bending)	*C-O* (Stretching), *C-C* (Stretching), *C-O-C* (Stretching)
PVA	3339 (vs)	2941 (m), 2907 (m)			1092 (s)
PVAc		2967 (vw), 2924 (w)	1737 (vs)	1433 (w)	1373 (s), 1240 (vs), 1122 (w), 1022 (m)
BDGA		2959 (s), 2872 (s)	1742 (vs)	1457 (m)	1374 (s), 1243 (vs), 1118 (s), 1056 (s)
NMA-VAM copolymer	3340 (vs)	2945 (w)	1736 (vs)	1435 (w)	1375 (m), 1247 (vs), 1026 (vs)

C1–C5 with the composition reported in the Scheme 1 were prepared.

The prepared samples were submitted to physical-chemical characterization. Solids content, pH, and viscosity were measured and reported in Table IV.

Preparation of the films

Dry films were obtained from the samples C1–C5 maintaining thin coats (thickness 0.5 mm) on glass sheet or plastic surface at room temperature up to complete water evaporation.
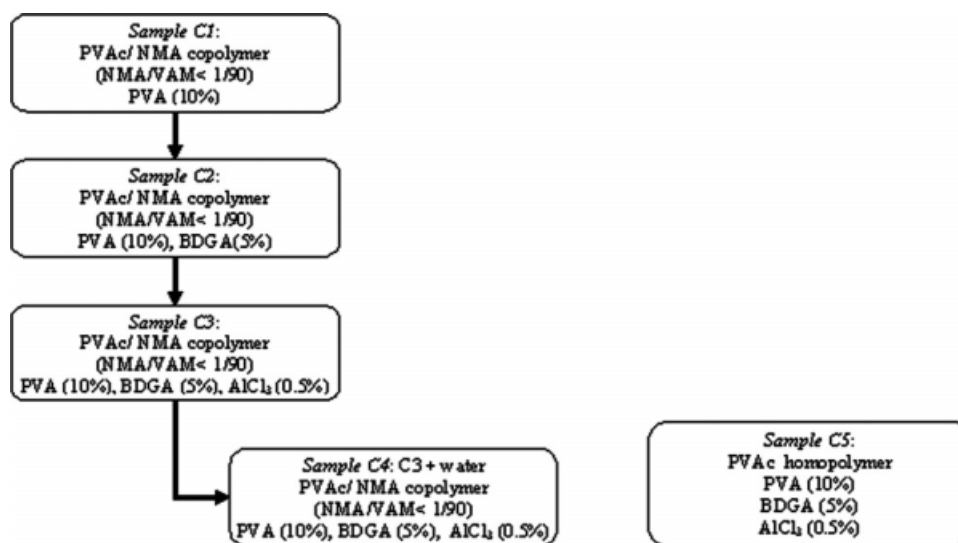
Extraction tests

Extractions were carried out on both liquid glues and dry film obtained thereof. Weighted samples (200 mg for liquid samples, 15 mg for the solid ones) were introduced into a round bottom flask equipped with a magnetic stirrer together with the solvent (10 or 2 mL, respectively) and maintained at room temperature for 14 h. Three solvents with different polarity (water or methanol or toluene) were used with three different fragments, respectively. Extractions with water were also effectuated at 85°C

for 6 h. The solid material present in the flask at the end of each test was recovered by filtration or centrifugation, washed with the same solvent, and dried under vacuum at room temperature. The different solutions derived from the extraction process were submitted to distillation at reduced pressure and room temperature, to remove the solvent. The obtained materials, dissolved in DMSO-d$_6$, were analyzed with ^{1}H-NMR spectroscopy.

The solid material, recovered as insoluble after each extraction text, was dried under vacuum at room temperature and the extractive procedure was also performed by using DMSO-d$_6$ (1 mL) as a solvent. After 6 h at room temperature the solutions were separated from the solid phase and analyzed using ^{1}H- and ^{13}C-NMR techniques. The insoluble residues were then analyzed with ^{1}H-NMR spectroscopy using the nano probe and DMSO-d$_6$ as swelling solvent.

Mechanical tests

The EN 205-D3,[17] the creep-test,[18] and the Watt 91[19] were measured, as reported in the respective international rules. Adhesive joints were obtained as described in the rule[17] by gluing two beech wood

Sample C1:
PVAc/ NMA copolymer
(NMA/VAM< 1/90)
PVA (10%)

Sample C2:
PVAc/ NMA copolymer
(NMA/VAM< 1/90)
PVA (10%), BDGA(5%)

Sample C3:
PVAc/ NMA copolymer
(NMA/VAM< 1/90)
PVA (10%), BDGA (5%), AlCl₃ (0.5%)

Sample C4: C3 + water
PVAc/ NMA copolymer
(NMA/VAM< 1/90)
PVA (10%), BDGA (5%), AlCl₃ (0.5%)

Sample C5:
PVAc homopolymer
PVA (10%)
BDGA (5%)
AlCl₃ (0.5%)

Scheme 1

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TABLE IV
Physical-chemical Characteristics of PVAc dispersions

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	C1	C2	C4	C5
pH	4.7 ± 0.1	4.7 ± 0.1	2.6 ± 0.1	2.8 ± 0.1
Dry residue[a] (%)	56.0 ± 0.1	57.9 ± 0.1	54.8 ± 0.1	51.1 ± 0.1
Viscosity[b] (mPa.s)	59,200 ± 600	69,400 ± 600	22,400 ± 400	10,400 ± 200

[a] $T = 80°C$.
[b] Brookfield RVT, spindle 7, 20 rpm, 23°C.

specimens using a pneumatic press. In particular density, moisture content, dimensions, thickness, and manufacture conditions are reported in the specific rule.

Synthesis of the polyvinyl acetate/NMA copolymer (NMA/VAM 1 : 2)

Vinyl acetate of 1 mL (0.932 g, 10.83 mmol) and 0.3 mL NMA (0.148 g, 1.47 mmol) were added, under nitrogen atmosphere, to a solution of AIBN (35 mg, 0.21 mmol) in 5 mL of methanol. The solution was stirred at 60°C for 6 h. After 24 h at room temperature a white solid insoluble residue (A, 154.3 mg, yield of 16.2 %) was separated.

The solution was concentrated under vacuum at room temperature, and a white solid was recovered (B, 881.6 mg, yield 82.2%). The solid was added to 5 mL of chloroform, stirred at room temperature for 6 h, filtered, and washed with the same solvent. The white solid obtained, soluble in methanol and DMSO, insoluble in chloroform, was dried under vacuum (C, 426.1 mg, yield 41.1%). The ^{1}H-NMR, ^{13}C-NMR, and FT-IR spectra of PVAc/NMA copolymer, namely C, were recorded and reported in Tables I–III. The NMA/VAM ratio in this copolymer fraction (C) was 1 : 2.

Reactivity of NMA-VAM copolymer (C)

NMA-VAM (50 mg) copolymer (C) and 1 mL of deuterated solvent (DMSO-d$_6$ or CD$_3$OD) were introduced into a NMR tube and the ^{1}H-NMR and ^{13}C-NMR spectra were recorded. Water solution of AlCl$_3$ of 0.2 mL (7%) was added to this solution and after 2 hours at room temperature the ^{1}H-NMR and ^{13}C-NMR spectra were recorded again.

The same procedure was performed using different reagents as HCl (6%, 0.2 mL) or CH$_3$COOH (0.2 mL) or Al(OH)$_3$/CH$_3$COOH solution (3,65 g/L of Al, 0.2 mL). After the addition of each reagent the ^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature.

RESULTS

Some different wood glue formulations based on modified PVAc polymers were characterized and compared with the purpose to explain the role of

their main components in the joint formation and in its final properties.

The examined blends were prepared the same way as reported in the experimental section. Apart from PVA, present in all formulations, the addition of a crosslinking monomer such as NMA during polymerization (samples C1, C2, C3, C4), the use of BDGA as film forming promoter (samples C2, C3, C4, C5) and AlCl$_3$ as external crosslinker (samples C3, C4, C5) were applied. In fact, AlCl$_3$ could act as crosslinking agent and/or hardener if a comonomer as NMA was present in the PVAc chain, whereas it could cause a viscosity increase in the presence of electron-donating groups of the polymer chains (for instance PVA or PVA grafted with PVAc fragments).

Sample C4 was obtained by adding water to C3 to reduce the viscosity in the range required by a commercial formulation. Nevertheless C3 was not analyzed, because its composition is equal to C4.

All these samples (except C3) were analyzed by using chemical, physical, and mechanical methodologies, as reported below.

Spectroscopic characterization

The pure single components of the adhesives were spectroscopically characterized to allow their identification in the formulated glues and in the extraction solutions. The FT-IR, ^{1}H-NMR, and ^{13}C-NMR data of the single components are reported in Tables I–III and in Figure 1 for ^{1}H-NMR spectra.

Specifically, in the case of PVAc the resonances present in the ^{1}H-NMR spectrum (DMSO-d$_6$) were assigned as reported below: signal at δ 1.72 ppm (m, 2H) is attributable to CH_2, signals at 1.91 and 1.95 ppm (m, 3H) are attributable to CH_3COO and the signal at 4.75 ppm (m, 1H) is attributable to CH ppm. The PVAc ^{13}C{^{1}H} NMR spectrum (DMSO-d$_6$) (Table II) shows resonances to δ 21.2 (CH$_3$COO), 66.3, 66.7, 67.1, 67.4, 68.3 (CH); 170.2 (CH$_3$COO) ppm. The CH$_2$ signal is overlapped with that of the solvent one.

The PVA alcoholic signals were attributed by recording also a ^{1}H-NMR spectrum after adding D$_2$O to DMSO-d$_6$ solution. In fact, the signals at 3.80, 4.23, 4.46 ppm were present using DMSO-d$_6$ as solvent while only a signal at 3.80 ppm was shown when D$_2$O was added. This signal is attributable to CH(OH) group
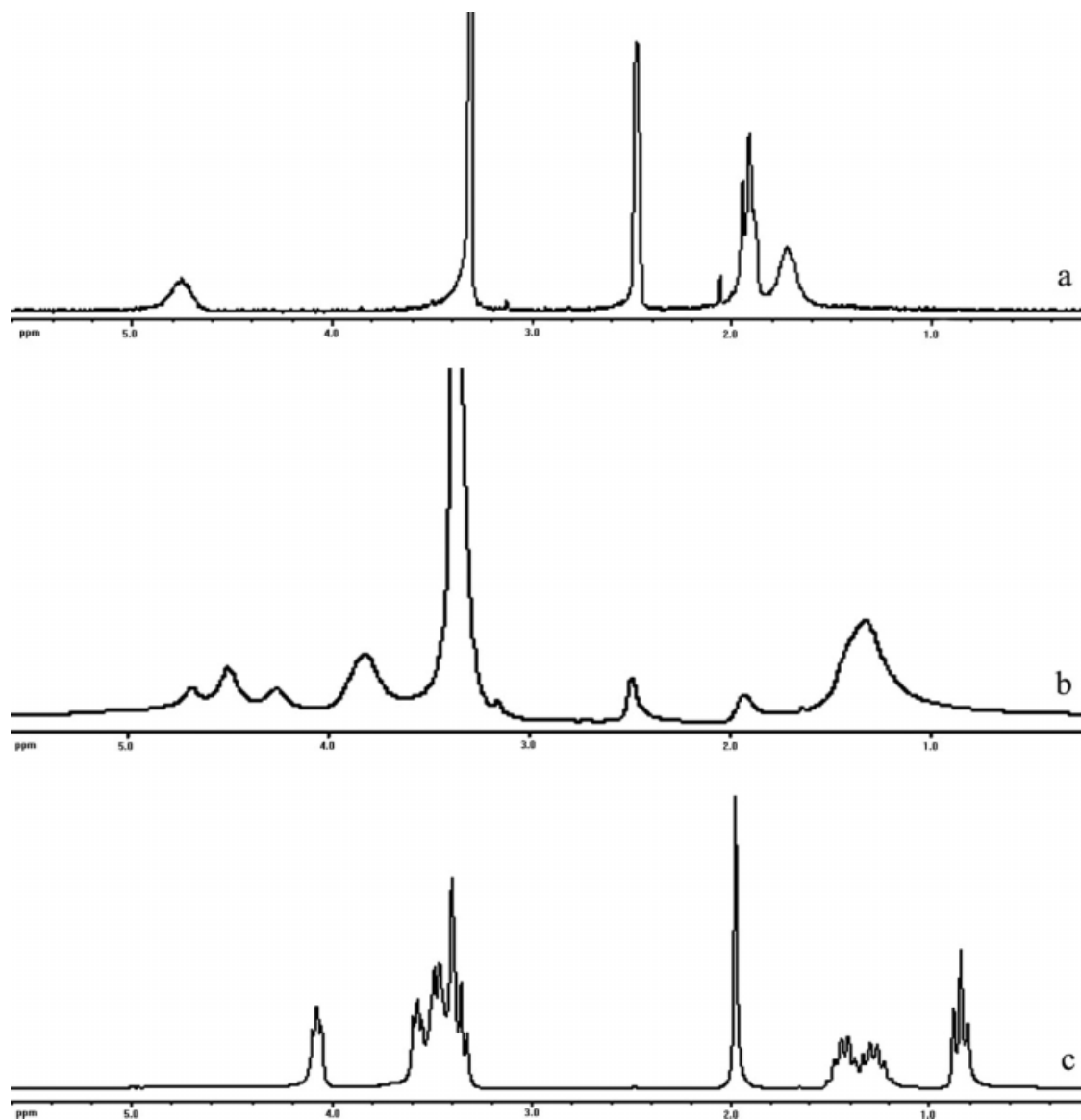
Figure 1 The ^{1}H-NMR spectrum (DMSO-d$_6$ as solvent) of: PVAc (trace **a**), PVA (trace **b**), BDGA (trace **c**).
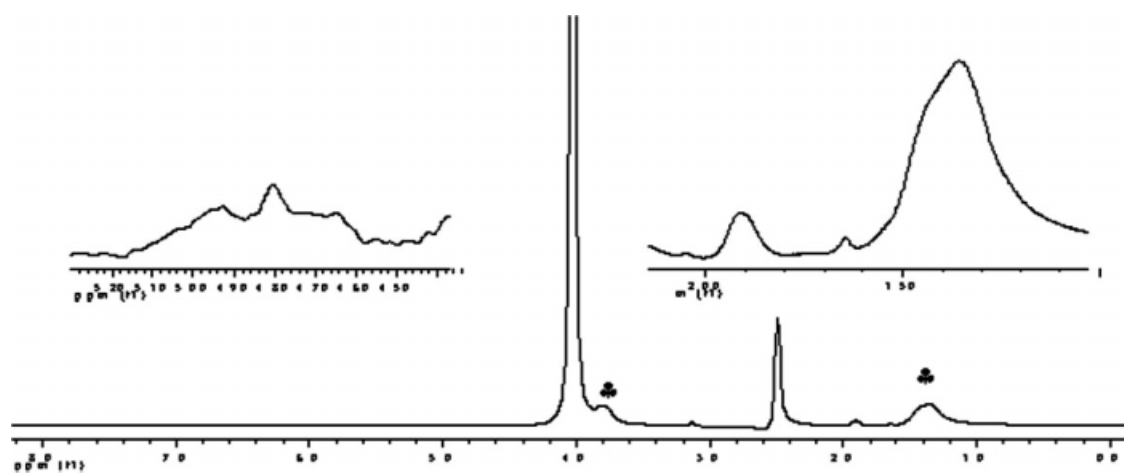
Figure 2 The ^{1}H-NMR spectrum after adding D$_2$O to DMSO-d6 solution of PVA. ♣ PVA.

TABLE V
Products recovered Using the Extractive Technique

		DMSO-d_6	H$_2$O, 25°C	H$_2$O, 85°C	Methanol	Toluene
C1	Extract from liquid product	PVAc PVA	–		PVAc	PVAc
	Residue from liquid product	–	–	–	PVAc PVA	PVAc PVA
	Extract from film	PVAc PVA	–		PVAc	PVAc
	Residue from film	–	–	–	PVAc PVA	PVAc PVA
C2	Extract from liquid product	PVAc BDGA PVA	PVAc BDGA PVA	PVAc BDGA PVA	PVAc BDGA	PVAc BDGA
	Residue from liquid product	–	PVAc	PVAc	PVAc PVA	PVAc PVA
	Extract from film	PVAc PVA BDGA	PVAc PVA BDGA	PVAc PVA BDGA	PVAc BDGA	PVAc BDGA
	Residue from film	–	PVAc	PVAc	PVAc PVA	PVAc PVA
C3	Extract from liquid product	PVAc BDGA	BDGA	BDGA	PVAc BDGA	PVAc BDGA
	Residue from liquid product	PVAc* PVA*	PVAc* PVA*	PVAc* PVA*	PVAc PVA	PVAc PVA
	Extract from film	PVAc BDGA	BDGA	BDGA	PVAc BDGA	PVAc BDGA
	Residue from film	PVAc* PVA*	PVAc* PVA*	PVAc* PVA*	PVAc PVA	PVAc PVA
C4	Extract from liquid product	PVAc BDGA	BDGA	BDGA	PVAc BDGA	PVAc BDGA
	Residue from liquid product	PVAc* PVA*	PVAc* PVA*	PVAc* PVA*	PVAc PVA	PVAc PVA
	Extract from film	PVAc BDGA	BDGA	BDGA	PVAc BDGA	PVAc BDGA
	Residue from film	PVAc* PVA*	PVAc* PVA*	PVAc* PVA*	PVAc PVA	PVAc PVA

* Identified using swollen state ^{1}H-NMR technique.

(Fig. 2). The disappearance of the other signals was in agreement with the H/D scramble between solvent and alcoholic group. The presence of signals at 21.1 and 170.2 ppm in the ^{13}C-NMR spectrum and at 1.93 and 4.68 ppm in ^{1}H-NMR is attributable to the residual acetate groups present in the PVA chain.

In the FT-IR spectra, recorded on the dry C1–C5 samples using a diamond cell, bands attributable to PVAc (2924, 1737, 1433, 1373, 1240, 1122, 1022, and 947 cm^{-1}) were observed while a band at 3340 suggests the presence of PVA. At this stage, it was not possible to observe the presence of other bands, linked to the other components of the formulations, due to their low concentration.

The NMR spectra on the soluble fractions, obtained by extraction of the liquid glues or the films fragments, were recorded by using standard techniques (DMSO-d_6 as solvent). The solid films were analyzed with the swollen-state NMR technique. The resonances present in the NMR spectra of soluble and insoluble components of samples C1–C5 were compared with the spectroscopic data of each single component. PVAc chains with a different solubility, some of them containing PVA fragments, were identified observing the ^{1}H-NMR spectra of extracts and residues (Table V). In fact, the signals at 1.72 (m, 2H), 1.95 (m, 3H), 1.91 (m, 3H), 4.75 (m, 1H) ppm, attributable to PVAc chains, were present both in the soluble fractions and insoluble residue, for all the solvents used in the extraction texts.

No signals attributable to the NMA copolymerized with vinyl acetate were observed in the spectra of C1–C4 samples due to the small amount of this comonomer in the formulations, and consequently no signals attributable to new bonds obtained from a crosslinking reaction could be observed in these spectra.

Extraction techniques

A screening of the solubility of various components in the different formulations was performed, and possible changes of the solubility, after film formation, were investigated. The extractions with solvents of various polarity were carried out both on the liquid glues and the dry films obtained from them. Methanol, toluene, dimethyl sulfoxide (DMSO-d_6), cold and warm water were used, as reported in the experimental. The soluble phases were separated from the solid residue by centrifugation or filtration techniques. The samples obtained after evaporation of the solvent were analyzed by NMR spectroscopy using DMSO-d_6 as solvent.

The presence of the signals attributable to PVAc [1.72 (m, 2H), 1.91 (m, 3H), 1.95 (m, 3H), 4.75 (m, 1H) ppm], PVA [1.40 (m, 2H), 3.80 (m, 1H), 4.23 (m, 1H), 4.46 (m, 1H) ppm], and BDGA [0.85 (t, 3H, J_{HH} = 7.14 Hz), 1.35 (m, 4H), 1.98 (s, 3H), 3.45 (m, 10H), 4.07 (m, 3H) ppm] in the spectra of soluble and insoluble fractions of each sample, permits to analyze the solubility of the same compound in the different formulations. The results are reported in Table V.

The comparison between the ^{1}H-NMR spectra of extractions and residues obtained from the wet and dry samples did not show any formation of new signals. The setting process does not cause any chemical transformation.

Through this procedure it was possible to observe that, in the case of samples C1 and C2, PVAc and PVA kept the same solubility in the wet glues and in the correspondent films.

Moreover, the presence of BDGA did not affect the solubility of PVAc and PVA. In fact, all the components of the samples C1 and C2 (wet and dry glues) are completely soluble in DMSO-d_6, whereas the separation of components with a different
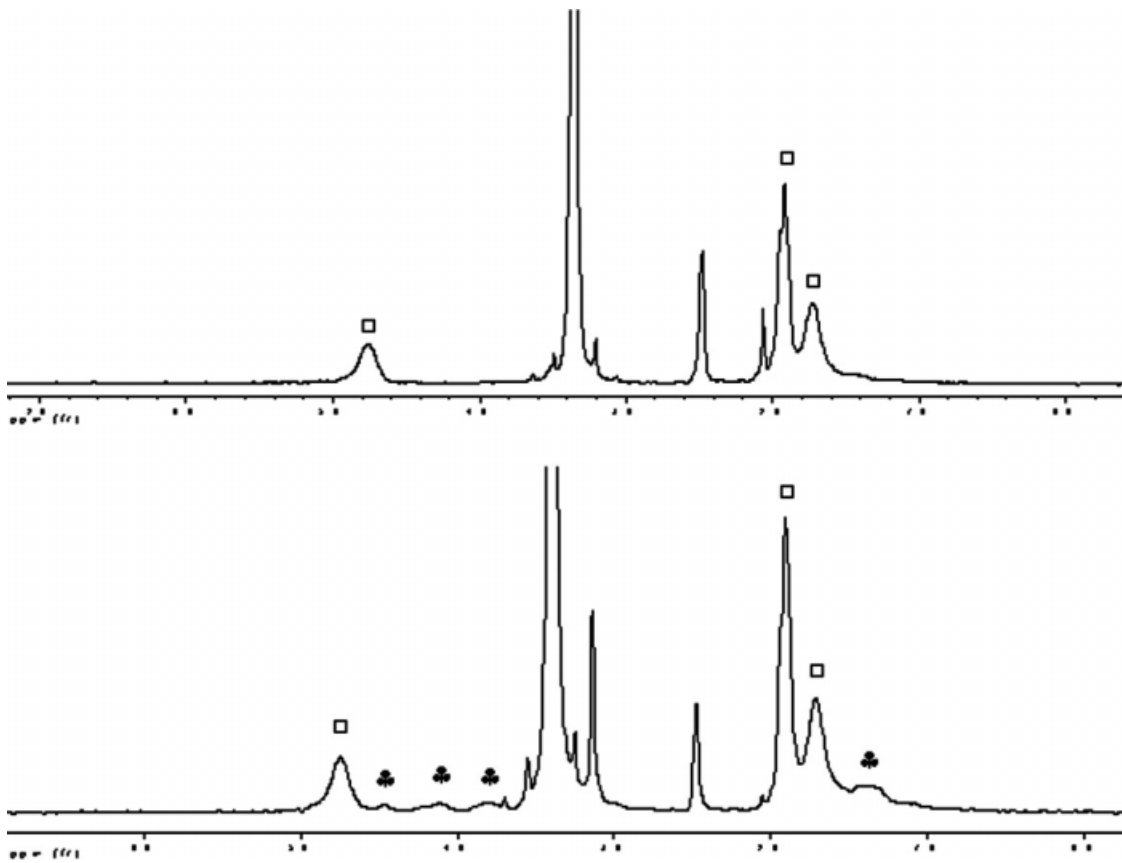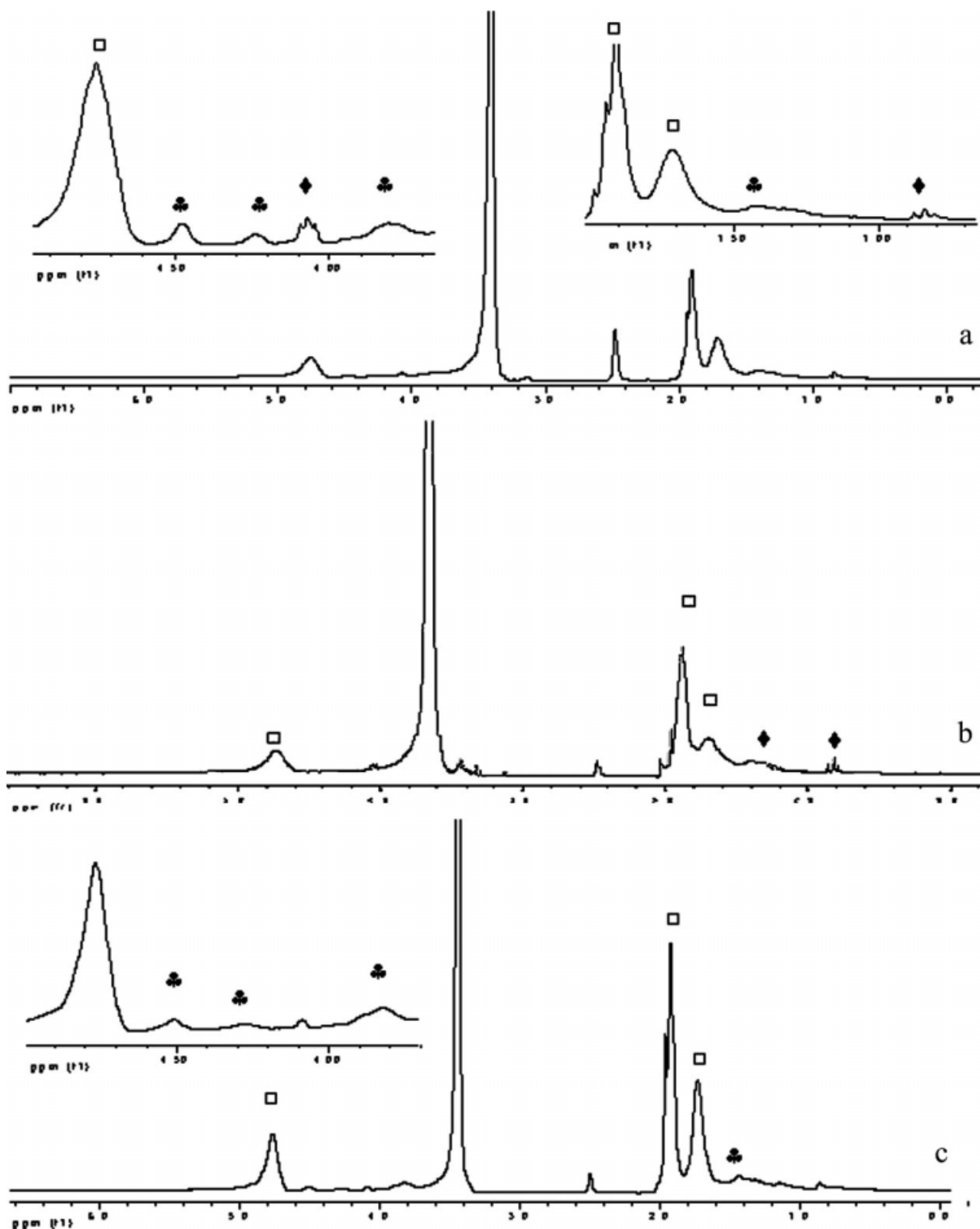
Figure 3 The ^{1}H-NMR spectrum (DMSO-d$_6$ as solvent) of: C1 film extract with methanol (trace **a**), C1 film residue from methanol extraction (trace **b**). □ PVAc, ♣ PVA.
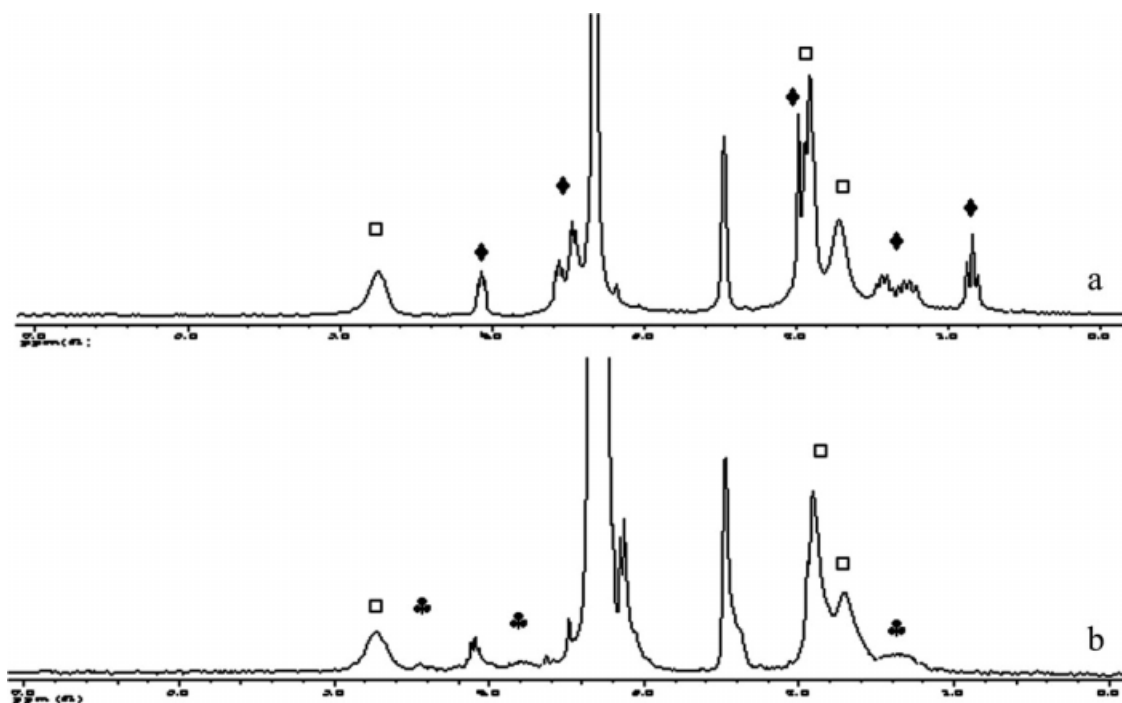
Figure 4 The ^{1}H-NMR spectrum (DMSO-d$_6$ as solvent) of: C2 film extract with methanol (trace **a**), C2 film residue from methanol extraction (trace **b**). □ PVAc, ◆ BDGA, ♣ PVA.

Figure 5 The effect of the presence of the AlCl$_3$ in the solubility of the PVA observed with extraction technique and ^{1}H-NMR spectroscopy: C2 film extract with DMSO-d$_6$ (trace a), C4 film extract with DMSO-d$_6$ (trace b), C4 film, solid residue, with DMSO-d$_6$, swollen-state ^{1}H-NMR technique (trace c). □ PVAc, ◆ BDGA, ♣ PVA.

solubility was observed in water, methanol, or toluene. In particular, signals attributable to PVAc were found both in the soluble and insoluble fractions. This result is in agreement with the presence of PVAc chains with a different solubility, some of

them containing PVA grafted fragments, as observed in the extractions of sample C1 with methanol (Fig. 3), toluene and water.

Finally, for the samples C1 and C2, PVA and BDGA were soluble in cold and warm water,

TABLE VI
Water Absorption and Soluble Fraction

	C1	C2	C4	C5
Soluble fraction after 24 h (%)	6 ± 1	11 ± 1	14 ± 1	20 ± 1
Water absorbed after 24 h (%)	59 ± 3	70 ± 2	50 ± 2	50 ±2
Soluble fraction after 7 days (%)	8 ± 1	13 ± 1	15 ± 1	22 ± 2
Water absorbed after 7 days (%)	62 ± 2	71 ± 3	50 ± 3	50 ± 3

whereas among the additives only BDGA was soluble in methanol (Fig. 4) and toluene.

When aluminum chloride was added to the formulation as in C4 or C5, only PVAc and BDGA were found still soluble in DMSO-d_6. On the contrary, the PVA and the PVAc containing PVA fragments (PVAc-g-PVA) changed their solubility and were found in the residues, as it was observed by swollen-state ^{1}H-NMR analysis on the C4 solid film swollen with DMSO-d_6 (Fig. 5).

Therefore, the presence of AlCl$_3$ changed the solubility of these components, which remained blocked into the adhesive joint. No change of solubility was observed for BDGA, which was always extracted. The lower solubility of C4 and C5 components can be attributed to the interaction between the aluminum and the polymer with formation of a kind of chelate bonds between the electron-donating groups of the polymer chains (PVA or PVA-g-PVAc fragments) and aluminum.

Water absorption of dry films

The water absorption was determined on polymer films (thickness ca. 1 mm) dried for 7 days in standard conditions (23°C/50% of relative humidity). Weighted samples were put in the water at 23°C for appropriate times (24 hours or 7 days). The amount of absorbed liquid was measured by weighting the same samples, after removing the water in excess from the surface (Table VI). In the same experiment it was also possible to quantify the water-soluble fractions by weighting the same samples after complete drying. From the obtained results reported in Table VI a relatively high solubility for all the films was observed. The absorption/solubility process is quite rapid, and equilibrium

TABLE VII
Test According to En 205-D3

	C1	C2	C4	C5
D3-1 (N/mm^2)	9.7 ± 0.8	13 ± 1	13.7 ± 0.6	14 ± 2
D3-3 (N/mm^2)	<0.05	<0.1	2.1 ± 0.5	0.5 ± 0.3
D3-4 (N/mm^2)	8.5 ± 0.2	4 ± 2	11 ± 2	9 ± 3
Classification D3	NO	NO	YES	NO

TABLE VIII
Creep Test

	C1	C2	C4	C5
MU700 (%)	100	0	0	0
Test passed	YES	NO	NO	NO

is almost reached in 24 h. The presence of BDGA in the formulation increases both the solubility and the water absorption of polymer films. Samples C4 and C5, containing aluminum chloride, have shown a lower solubility, after water immersion compared with samples C1 and C2, in agreement with the presence of an effective interaction between the aluminum and the polymer water-soluble chains present in the films. However, the observed different loss of weight, after immersion in water, for C4 and C5 suggest an important role of NMA in the water solubility reduction.

Mechanical tests

Standard tests were used to evaluate the mechanical performances of adhesive joints for nonstructural applications. The values of adhesive strength for thin bond-lines, obtained as reported in EN 205,[17] permit to classify an adhesive in agreement with the standard EN-204.[20] The results are reported in Table VII. Only sample C4, containing the crosslinking comonomer and the aluminum chloride solution satisfied all the conditions required in the EN205-D3 test for the EN-204-D3 classification (Table VII). On the contrary, the value of D3-3 for sample C5, which does not contain the crosslinking comonomer, which was very low.

All samples containing BDGA did not overcome creep test performed according to MU 700,[18] test for nonstructural adhesives (Table VIII), as BDGA is not completely released during the adhesive setting phase. On the contrary, according to the expectations a new sample prepared by adding aluminum chloride to the sample C1 showed good creep resistance.

The determination of tensile strength of lap joints at high temperature (80°C), Watt 91 (Wood Adhesive Temperature Test)[19] gives information on the heat resistance of nonstructural adhesive joints. The results are reported in Table IX. The results of the Watt 91 test were in line with the positive effect due to aluminum chloride and NMA and the negative effect due to BDGA.

TABLE IX
Watt 91

	C1	C2	C4	C5
WATT '91 (N/mm^2)	7.6 ± 0.8	5.9 ± 0.3	7.3 ± 0.6	6 ± 1
Test passed	YES	NO	YES	NO

TABLE X
Elemental Analyses at Room Temperature and at 80°C

	C1 RT	C1 80°C	C2 RT	C2 80°C	C4 RT	C4 80°C	C5 RT	C5 80°C
N %	0.06	0.09	0.06	0.07	0.03	0.08	0	0
C %	54.75	54.96	55.3	55.34	51.06	51.20	51.64	49.77
H %	7.47	7.70	7.70	7.80	7.28	7.69	7.31	7.79
Other %	37.72	37.25	36.94	36.79	41.63	41.03	41.05	42.44

Elemental analyses

When heated at 80°C adhesive films became yellow. This behavior could be an indication of some chemical reactions appearing at high temperature. Nevertheless, no important changes in the elemental composition were observed between films obtained at room temperature or at 80°C (Table X). The compositions observed from the samples C1–C5 were in agreement with the formulation components.

Synthesis and spectroscopic characterization of NMA-VAM copolymer (1 : 2)

To obtain additional information on the crosslinking mechanism involved in the adhesion process when modified PVAc is formulated with AlCl$_3$, a new NMA/VAM copolymer was synthesized. In this case higher NMA/VAM ratio has been used to make possible the observation, in the NMR spectra, of the characteristic signals of NMA comonomer and its transformation. The product of the reaction between NMA and VAM was a mixture of different copolymers containing various NMA/VAM ratios, each one with a different solubility. Using this feature, three different fractions were isolated. The fraction "A" was obtained at the end the synthesis as a white solid, insoluble in methanol. The remaining reaction mixture, soluble in methanol (namely "B"), was then separated in other two copolymer fractions, "C," insoluble in chloroform and "D," soluble in chloroform. All these fractions were characterized by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopies (Tables I–III) and their NMA/VAM ratios were calculated using the signals at 5.51 (m, 1H, NH—CH$_2$—OH, NMA), 4.52 (m, 2H, NH—CH$_2$—OH, NMA) and 4.80 (m, 1H, CH, VAM). The fractions with a NMA/VAM ratio >1 were insoluble in methanol and chloroform, whereas those having a NMA/VAM ratio >0.5 were insoluble in chloroform (Fig. 6).

Crosslinking reactivity

The copolymer fraction with a NMA/VAM ratio of 0.5 (C), was used to study the crosslinking reactivity of the modified PVAc in the adhesion process.
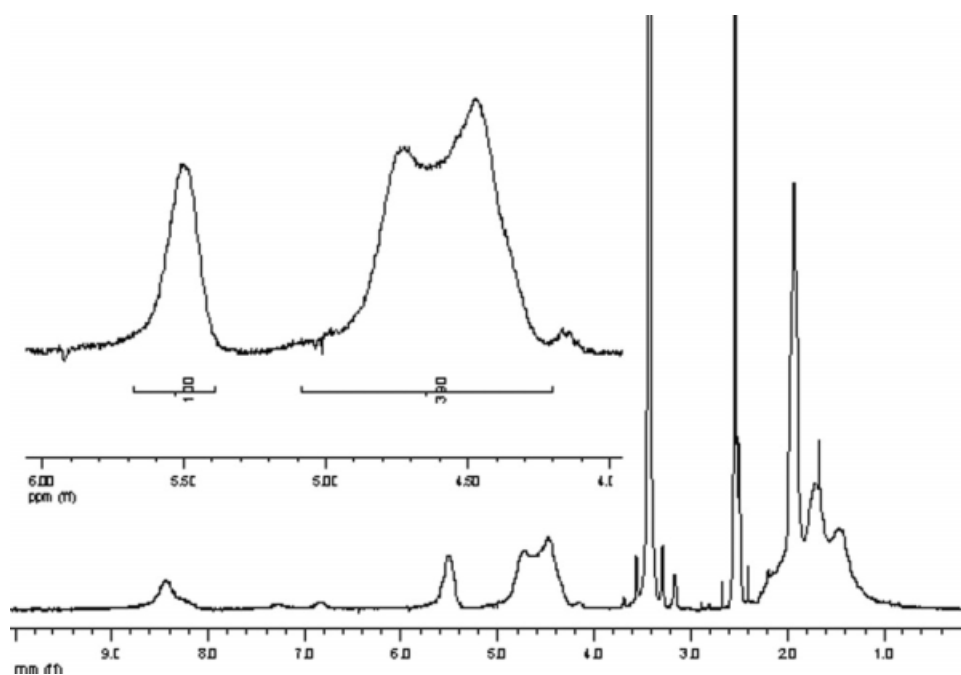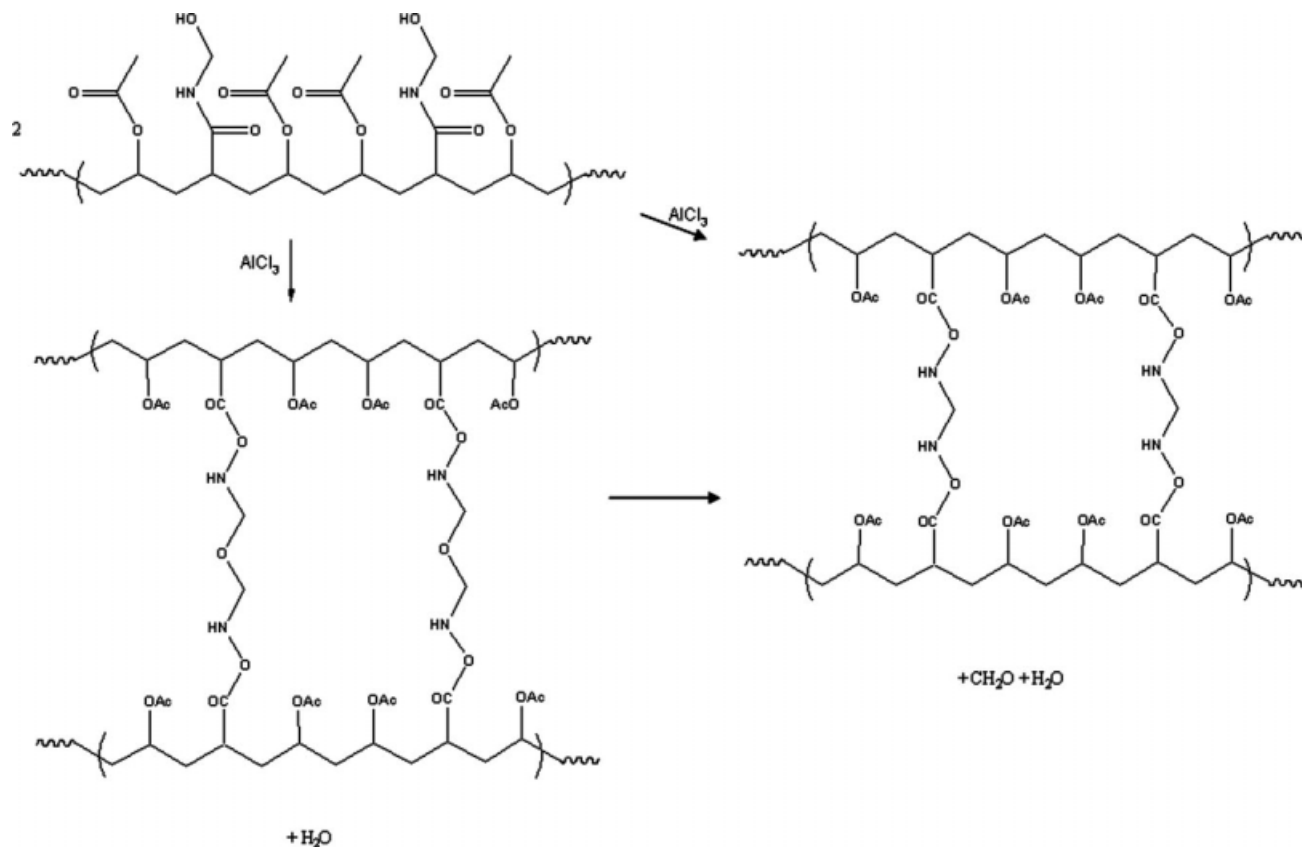

Figure 6 The ^{1}H-NMR spectrum (DMSO-d$_6$ as solvent) of NMA-VAM copolymer (fraction C).

Scheme 2

The reactivity of this copolymer was analyzed by NMR spectroscopy. The ^{1}H- and ^{13}C-NMR spectra were recorded before and after the addition of AlCl$_3$ to a copolymer solution with a deuterated solvent (DMSO-d6 or CD$_3$OD). This reactivity was then compared with the one showed in the presence of HCl or CH$_3$COOH or a Al(OH)$_3$/CH$_3$COOH solution, respectively. This way it is possible to verify the dual function of AlCl$_3$ as an acid catalyst or as a coordinating agent.

The reactivity in the presence of AlCl$_3$ was similar to the one observed after the addition of HCl.

In the ^{1}H-NMR spectrum the signal at 5.51 ppm (m, 1H, NH—CH$_2$—OH) disappeared, whereas a new signal at 9.47 ppm (CH$_2$O) was present.

These results could be in agreement with the formation of —CH$_2$—O—CH$_2$— o —NH—CH$_2$—NH— groups for the crosslinking reaction (Scheme 2).

To confirm if these changes in the ^{1}H-NMR spectrum were in agreement with a crosslinking reaction, the ^{13}C-NMR spectrum was recorded. In fact, the disappearance of the signal of —NH—CH$_2$—OH could have been also obtained for an acid catalyzed H/D scrambling with the solvent and the CH$_2$O formation could have been also formed from DMSO.[21]

In the ^{13}C-NMR spectra of the CD$_3$OD solution (Fig. 7) the higher intensity of the signal at 70.1 ppm

was in agreement with the formation of several —NH—CH$_2$—O—CH$_2$—NH— groups; this signal is placed on top of the signal at 69.1 ppm characteristic for CH in the VAM residue. The signal at 62.1 ppm attributable to NH—CH$_2$—OH was disappeared.

The other two low signals were present at 77.2 and 49.1 ppm in agreement with the formation of CH$_2$O and —NH—CH$_2$—NH— group.
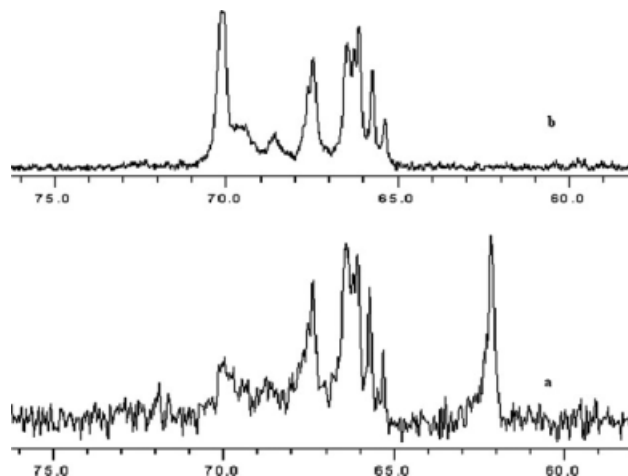
Figure 7 The ^{13}C-NMR spectrum (CD$_3$OD) as solvent) of NMA-VAM copolymer (fraction C) (trace a), NMA-VAM copolymer after AlCl$_3$ addition (trace b).

After 24 h a white insoluble solid was separated from the solution, in agreement with the formation of a cross-linked polymer.

No changes were observed in the NMR spectra when acetic acid was added to the copolymer.

To observe if the presence of an aluminum salt could produce also a positive effect for the coordination action, an acetic acid solution containing $Al(OH)_3$ was added. No changes were noticed in the ^{1}H-NMR spectrum, whereas in the ^{13}C-NMR spectrum only a weak increase of the signal at 71.0 ppm, characteristic of $NH-CH_2-O-CH_2-NH$, was observed.

The reactivity observed for the NMA-VAM copolymer was in agreement with melamine-formaldehyde and urea-formaldehyde crosslinking reactions.[22]

DISCUSSION

The novelty of this study is the combined use of extractive techniques and NMR analyses to investigate the role of main components in PVAc based glues with water resistant properties and to formulate some hypotheses on their interactions.

The selective extraction tests performed with different solvents (cold and warm water, methanol, toluene, and DMSO) on the liquid glues and the corresponding film fragments have allowed to follow the variation in the solubility of the various components of the formulations after film formation. Trough the subsequent spectroscopic characterization of the single phases so obtained, it has been possible to investigate the behavior of the diverse glues according to their formulations and to predict whether they were water and/or solvent proof.

The ^{1}H-NMR characterization of all glue components has led to observe the presence of the basic polymer or the used additives into the soluble or insoluble fractions obtained from water, toluene, and methanol, recording the spectra on the DMSO-d_6 solutions. Finally, for samples C4 and C5, containing aluminum chloride as hardening agent, the study of the components present in the solid films that are insoluble also in DMSO-d_6, has been carried out by using the swollen-state ^{1}H-NMR technique.

By combining the analytical results with the mechanical performance of the adhesive joints we can draw the following conclusions.

The presence of NMA, as a crosslinking agent in PVAc polymers clearly improves the water resistance of the adhesive joint, allowing to pass the D3 classification. The crosslinking reaction involves NMA methylol group and $AlCl_3$ as Lewis acid catalyst and happens in two separate steps, as shown above (Scheme 2). Nevertheless, the low amount of NMA used in these experiments does not permit to observe any signal attributable to the new bonds. To confirm the catalytic role of $AlCl_3$
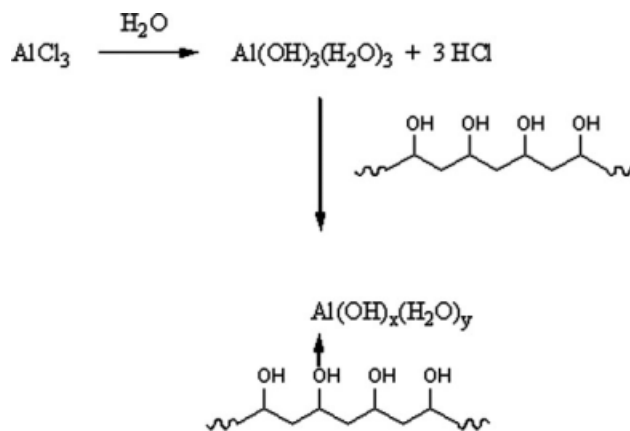
Scheme 3

in the crosslinking reaction, a new modified PVAc with a higher NMA/VAM ratio (0.5) was synthesized and its reactivity with $AlCl_3$ was analyzed by using NMR spectroscopies. The presence of CH_2O dissolved in the solution, and the formation of the new groups as $-NH-CH_2-NH-$ and $-NH-CH_2-O-CH_2-NH-$ were in agreement with a crosslinking reaction between the $-NH-CH_2-OH$ groups located in different copolymer chains. This behavior is confirmed by the formation of an insoluble white solid after 24 h.

The Lewis acid catalyst role was also confirmed by the comparison with the reactivity observed in the presence of HCl. On the contrary, when acetic acid was present the crosslinking reaction was not observed. On the other hand, if an aluminum compound as $Al(OH)_3$ was added to acetic acid, the formation of $-NH-CH_2-O-CH_2-NH-$ groups was noticed. Nevertheless, the rate of the reaction is very low and an insoluble polymer was not obtained.

The presence of an acid catalyst as $AlCl_3$ or HCl is then very important in the crosslinking reaction and the coordination to aluminum result to be important when the pH is higher, as in the presence of acetic acid.

In addition to its catalytic function, the aluminum salt is also necessary to block the PVA chains and the PVAc containing grafted PVA in the adhesive joint, improving the water and moisture stability of the joint itself. This performance is achieved also when a self crosslinking comonomer for example NMA) is not included in the formulation. This behavior is in agreement with the formation of a sort of chelate bonds between the electron-donating groups of the polymer and Al (Scheme 3). However, new signals are not observed in the recorded spectra probably because of the low amount of the groups involved in the coordination.

BDGA has only the function to promote film formation at low temperature. Therefore, its presence compromises the mechanical stability of the joint, as shown by the low creep resistance values.

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