# Tannery row – The story of some natural and synthetic wood adhesives

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**Abstract** Tannin adhesives are a relatively old but limited speciality which has become again topical with the very marked environment-friendly outlook of wood science at the beginning of the new century. Although the lecture will start by intermingling the technical experience of the author in this field mainly with some humorous stories on the early and not so early beginnings of this speciality, this will only be a brief introduction to more recent scientific/technical developments on mainly synthetic thermosetting adhesives, although natural adhesives will not be forgotten. The lecture will also relate in a very brief form, and without being limiting, some of the author's developments in synthetic (and some natural) resins wood adhesives, and in other fields of wood science and wood technology which might have or have had an impact on the advancement of this field.

## Introduction

I could have entitled this lecture "*Semper Novi Ex Africa*" – there is always something new coming out of Africa – to paraphrase one of my better known Roman cornationals. It appealed to me as my career in wood science did indeed start and mature in that most beloved continent. I decided against it, because the ancient roman quote has a somewhat negative, sarcastic undertone that would neither agree with what has been achieved there, nor with my nature or what I want to say in this lecture. I have rather chosen the present title, "*Tannery Row*", as most in theme with a lecture taking place in California, the country of John Steinbeck's "*Cannery row*". His characters lovingly remind me of some of the similar, "salt of the earth" characters who spiced my early career in tannin and tannin adhesives. I must point out right now that although this lecture is mainly and foremost about science and technology, the description during the oral presentation of any of these characters/episodes is brought foreward with the same love and affection John Steinbeck clearly had for his personages: great characters are great because they always bring a good point to bear. Secondly, as

no man is an island, as much as I may have contributed to what is presented here, I owe gratitude to a multitude of other people and their work. They are indeed too many that I can hope to mention them all here. However, I intend to deliver this lecture on the clear understanding that it will be a clear mark of recognition of their work as much as of mine. Thirdly, I was told that an Academy Lecture is supposed to be a summary of a scientist's life work. Fortunately, my research in wood science has been so varied, that as a result, I have had some difficulty to chose significant examples when summarizing it. Presented here are then what the author thinks, rightly or perhaps very wrongly, some of the interesting contributions he was involved in. The list is by no means exhaustive, and some results which are not quoted here might even be considered of greater interest by some of those colleagues mentioned above: in any such case I of course wish to thank them for it! Last but not least, I hope to yet have ahead of me many years to still contribute in the most varied way to this fascinating field, this lecture being in my mind a summary of what has been achieved just and only up to now. I hope, too, that some kind soul will ask me again to deliver one of these lectures in about 20 years from now, as there are likely to be many more items of interest to add. To make space for science and technology I will briefly outline here only one of the strange, and sometimes funny stories which I have actually had the pleasure to relate during the oral presentation of this lecture. And this one I must mention, because it is the only way in which I can mention Winston Ntschona (1972–1973) in a scientific paper and put his name in the references, too. It is not given to many scientists to have had for two years a laboratory assistant who went on eventually, about 10 years later, to win a Tony Award (the world theatre's Oscar), received in New York! His assistance was indeed my pleasure when I was still a very young factory chemist in Port Elizabeth, South Africa, and a struggling part-time theatre actor was assigned to me as an assistant to do my testing during the development phase of tannin adhesives. I remember him acting and enthralling the other analysts in the lab, and to sometimes have given him a lift to rehearsal when the volume of work to develop tannin adhesives was such that he was late for practice of what was the real love of his life: acting!

It is not given to many wood adhesives that the most famous person to have somehow contributed to their development was a world famous theatre actor! A strange thought comes to mind: is this dramatic science or comical chemistry? The reader can form his own opinion. There is, however, a clear message, I believe, to be learned from this story for all younger up-and-coming scientists!

## Tannin adhesives

There is no doubt that to many people, rightly or wrongly I am still the "Tannin Adhesives" man. I have really loved these natural adhesives, as their development was my birth to both wood and adhesives to the point that I am still involved with them almost exactly 30 years later (I met both in January 1971). I have often resented this denomination, as any good actor that has been typecast. It has been good typecasting, but typecasting nonetheless. For me, instead, any adhesive, all adhesives, are a fascinating experience. I started my career with tannin adhesives when commercial tannin adhesives did not yet exist (except in a single factory using its own formulation, Westralian Plywoods in Perth, Australia), and by the time (in 1976) I left the company where we developed and commercialized them, we were selling about 5000 tons/year of resin solids. There have been many people before me who have contributed to the field, some to a considerable extent,

and some even taking a lot of merit which can be clearly demonstrated did not belong to them at all, some of them even making a fat living on the success of other people. However, doing research on tannins, and to develop a tannin adhesive one can make a living from, are two very different things, and the latter is exactly what has been my main contribution. When I started and ever since, I have not had the advantage of the guidance of a senior adhesive formulator to tell me what one has to do to obtain certain effects: no one around me had any real adhesive formulating experience, and outsiders that did, tried instead to replicate unsuccessfully trite synthetic resins technology. I had to work it out by myself, sometimes logically, sometimes by trial and error, sometimes totally empirically, but always learning, and simply for one reason: my end of the month salary strictly depended on it! Apart from the obvious stress this generated, there was also the inherent satisfaction of achieving unthought-of goals in such a precarious situation, and having to deduce things, often to reinvent the wheel all by myself, proved tough training invaluable later when tackling synthetic adhesives. This perhaps allowed me insights that cannot easily be gained if someone experienced offers you the solution on a platter without you having to suffer for it.

What is then my contribution to tannin adhesives (and I talk here only of those which can be clearly documented)? I will only list and refer briefly to them, as extensive reviews on the subject already exist (Pizzi 1980, 1983a, 1994), but I will also mention people who, contrary to other major contributors which are clearly mentioned in references, also contributed to a major, sometimes even determinant extent, but who, for a variety of reasons, have also never been mentioned in the relevant references. (1) The development, refinement and industrialization of non-fortified, but chemically modified, tannin adhesives for particleboard, for which R. Deterry (1968) and R. Kroon (1971) must share greatly in the merit (Pizzi and Ryder 1976; Pizzi 1978, 1981a, 1994; Pizzi and Stephanou 1992). (2) The development and industrialization of the technology of fast pressing tannin adhesives for particleboard, for some of which R. Barray and Lajouesse (1973), must share greatly in the merit (Pizzi 1979a). (3) The development and initial industrialization of the tannin-urea-formaldehyde formulations both for plywood and for corrugated cardboard (Custers et al. 1979; Pizzi 1978, 1979; Pizzi and Scharfetter 1978). (4) The development, industrialization and standardization of tannin-resorcinol-formaldehyde cold-setting glulam and fingerjoint adhesives (Pizzi and Roux 1978a, b; Pizzi 1979; Pizzi and Daling 1980): these are today mentioned in at least three international standards (Australia, South Africa, Zimbabwe). (5) The development and full scale industrialization of tannin-based "honeymoon", separate application fast-set adhesives (Van der Westhuizen et al. 1978; Pizzi et al. 1980; Pizzi 1983; Pizzi and Cameron 1984, 1989) (full industrialization – production – having ensued since January 1981). (6) The clarification of the mechanism of metal ions accelerated plywood adhesives, the full development of the formulation and their full scale industrialization, while the merit for the initial development of the formulation is due to R. Kroon (1976) (Pizzi 1979a, b, c, 1983; Pizzi and van der Spuy 1980; Rossouw et al. 1980). (7) The succesful formulation development and industrialization in Chile of *Pinus radiata* tannin adhesives for particleboard and for glulam (Pizzi 1982; Pizzi et al. 1993c; von Leyser and Pizzi 1990; Pizzi and Stephanou 1993b, 1994f; Pizzi et al. 1980, 1994c), any previous industrialization efforts having finished in disaster. (8) The development of isocyanates/tannin copolymers as adhesives for difficult woods to bond and other applications (Pizzi 1981b, 1982, 1993, 1994). (9) The development of very low formaldehyde emission tannin adhesives for particleboard and of all

sorts of special hardeners for them (Pizzi et al. 1994c, 1996a, 1997c, 1998a, b; Pichelin et al. 1999; Trosa and Pizzi 1998a, b, 2000). (10) The development of the technology for high moisture tolerance OSB using tannin and other adhesives (the greatest merit of which, as gives me pleasure to say, belongs to one of my students, F. Pichelin, but also to some others) (Pichelin et al. 1998, 2000a, b, c; Heinrich 1996). (11) The discovery and development of the induced tannin autocondensation adhesives (the merit of which must also go to W. Roll and Klacuczar) (Pizzi 1994; Meikleham et al. 1994, 1995; Roll et al. 1995, 1997; Pizzi et al. 1995a, b; Pizzi and Meikleham 1995; Garcia and Pizzi 1997a, b). (12) The development of one industrially experimented system to considerably increase pine tannin (and not just carbohydrates) extraction yields (Sealy-Fisher and Pizzi 1992). (13) The extensive study of radical reaction contributions to the chemistry of real tannins (and the lack of applicability of models where the colloidal state of the tannin is not taken into account) and the importance of the tannin colloidal state (Pizzi et al. 1995b; Merlin and Pizzi 1996; Masson et al. 1996a, b, 1997; Noferi et al. 1997; Garcia et al. 1997) (Fig. 1). (14) The first molecular mechanics studies on tannins (Pizzi et al. 1986a) (not considering some 1985 work of E. Hillis which unfortunately was done using a flat – hence invalid – heterocyclic ring structure), so early in fact that people do not even know it has appeared in print a long time ago (my first thesis is in molecular mechanics of proteins (Damiani et al. 1970)). (15) The development of tannin based rigid foams (Meikleham and Pizzi 1994) and (16) the use of tannins as superplasticizers for cement (Kaspar and Pizzi 1996) and (17) the development of an easy $^{13}$C NMR method for the determination of flavonoid tannins average molecular masses,
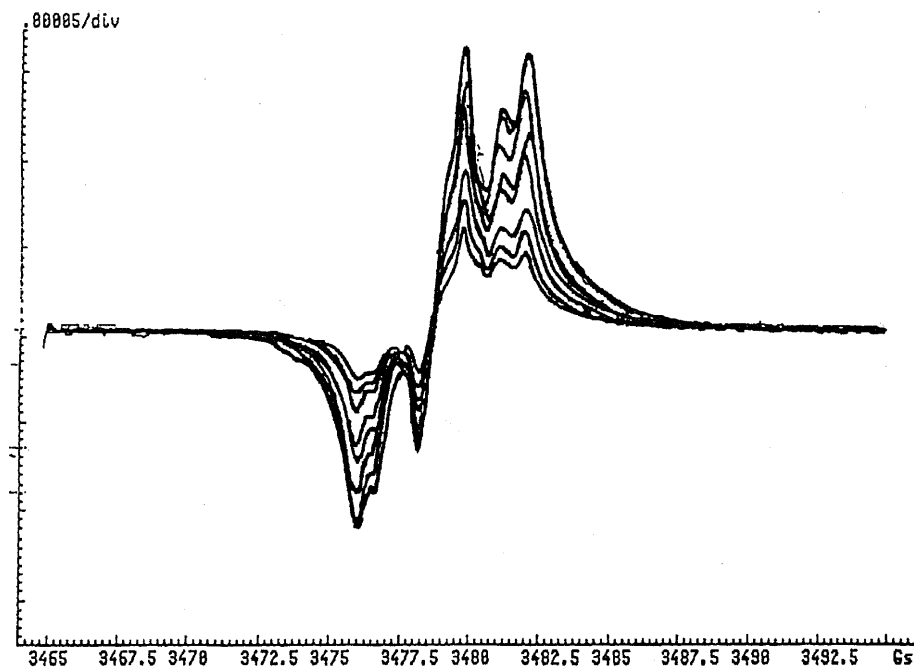


**Fig. 1.** ESR spectra intensity and peak distribution variation with time of phenoxyl radicals of a flavonoid tannins showing radicals on tannins A rings (closer to the centre of symmetry and on the B-rings (away from the centre of symmetry) (from Masson et al. 1996a)

average degree of polymerization and polydispersity (Thompson and Pizzi 1995). There are many others, but long lists becoming exceedingly monotonous, I will stop here.

The above are the main achievements in tannin adhesives to which I have contributed (and not indifferently). I will now list and explain briefly my other contributions in other fields of wood science, and not only adhesives, and the reader will be able to judge for himself if I have been justly or unjustly typecast as the "Tannin Adhesives" man (a typecasting, I must point out, that does not displease me at all).

## PF adhesives

Spilling over into the synthetic phenol-formaldehyde (PF) resins field, coming from natural phenolics, such as tannins, was an obvious extension and progression of my interests: a "*must*" more than just a chance. Now, while it is relatively easy technically to discover and develop new things in a very new field in which very few people are active, such as was the case with tannin adhesives, the story is rather different in the field of the oldest man-made polymers around, namely synthetic phenolic resins. Here one can look for years, and find sweet nothing of new, as testified by many of the publications in this field which limit themselves to present as new regurgitated material already discovered a long time ago (a good example of this being Grenier-Loustalot et al. 1996, but there are many others) and perhaps already forgotten (but often still well documented!). To really make some impact in this field, one cannot help needing a very rare quality: luck! And lucky I was! And just that!

The first unusual finding was the unforeseen trend of the gel time vs. pH curve for PF resols: this curve was effectively checked for the last time in its entirety by Sprung in 1938, and everyone afterwards copied it as it really made a lot of sense (Megson 1958). But Sprung had checked the curve only up to pH 9, the continuation at higher pH being indicated by a segmented rather than continuous line, because the interest was keener in earlier days on acid-setting PF novolaks (not for wood). The curve had a very different trend than foreseen (Fig. 2), but this was established only in 1993. The reason for this resides in those elusive entities called quinone methides (Pizzi and Stephanou 1993c, 1994a, b; Lenghaus et al. 2000). The second unusual finding was that of the $\alpha$-set esters accelerators. The main problem that has held back PF resins vis-à-vis melamine resins in wood is that they are much slower to cure, and here was a simple and inexpensive solution to this problem. What is mind-boggling is that these accelerators were discovered as far back as 1952 and are extensively used in binding fields other than wood. I am not the discoverer of the $\alpha$-set esters accelerators, but I was lucky to hear about them in another field, try them and make them work for wood adhesives through a very different approach, identify the two or three which are suitable for wood adhesives (most of the others are not) and partly explain their mechanism of action (although this later aspect is still controversial) (Pizzi 1994; Pizzi and Stephanou 1993c, 1994a, b, e; Pizzi et al. 1997a). The third lucky discovery in the field of PF resins was the preparation of PUFs. Others, mainly Tomita and Hse (Tomita and Hse 1994; Tomita and Matsuzaki 1985; Tomita et al. 1994) had talked of PUFs, but mainly prepared in acid environment, hence acid-setting so as to harden as UFs. In this context my work is then not original at all, except that my PUFs are made and hardened in alkaline environment, thus behave as pure PFs, but contain high amounts of urea, and have accelerated hardening (Fig. 3). (Pizzi et al. 1993a; Pizzi 1994; Zhao et al 1999;
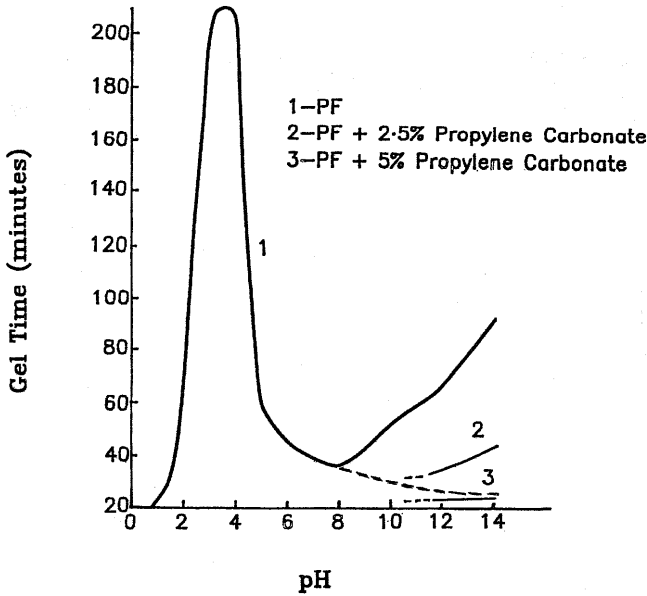
**Fig. 2.** Gel time curve of PF resin as a function of pH and effect of esters accelerators. Note the slowing down of the gel time over a certain pH (variable) (curve 1), the incorrectly theory-forecasted curve (segmented curve), and the gel time acceleration effect of different percentages of an ester in the same pH region (curves 2 and 3) (from Pizzi and Stephanou 1993)



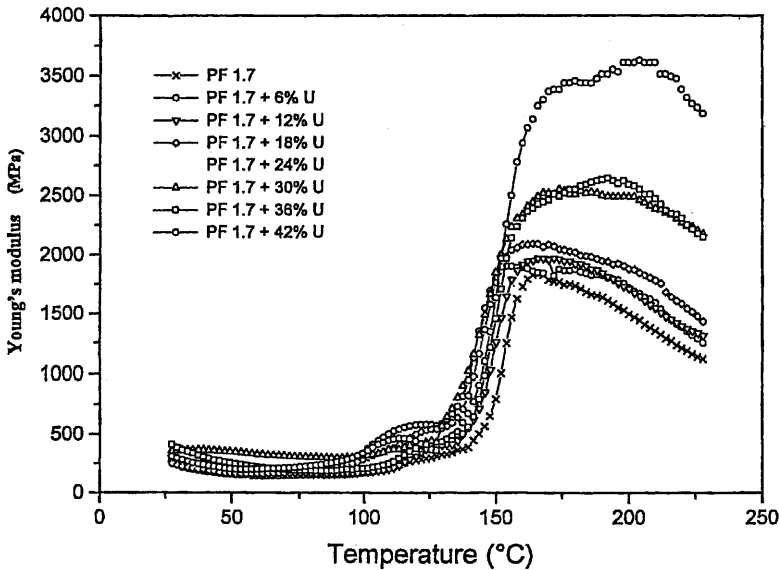**Fig. 3.** Schematic representation of the molecular doubling effect of the reaction of urea with PF resols under alkaline resin preparation conditions (more complete scheme available in Zhao et al. 1999) and thermomechanical analysis graph showing the increasing maximum values of the modulus with increasing amounts of urea co-condensed with the PF resol (from Pizzi 1994; Pizzi et al. 1993; Zhao et al. 1999)

Zhao et al. 2000b). It is of interest, however, that the chairman of some panel products producers association is on record to have stated at some international conference that today, the majority of PF resins producers coreact up to 5% urea in their PF resins (to be precise, it can be easily detected by NMR and its proportion has been surely and steadily increasing little by little during the last few years); notwithstanding that Tomitta, Hse and myself are very happy that what we have devised is used in industry, no mention was made of where industry picked up this non-patented technology! There are other findings to which I have contributed in PFs, the two main ones being (i) to define the mechanism of metallic catalysis (both acceleration and retardation) in acid pH and to isolate some of the ring complexes formed (Pizzi 1979c, d, e; 1983d) (Fig. 4) and (ii) the surface catalysis, marked decrease in curing activation energy, and the consequent acceleration effect a lignocellulosic interface has on PF (and all the other thermosetting) wood adhesives (Pizzi et al. 1994a). But the next field of activity, and one of particular interest to me is beckoning.

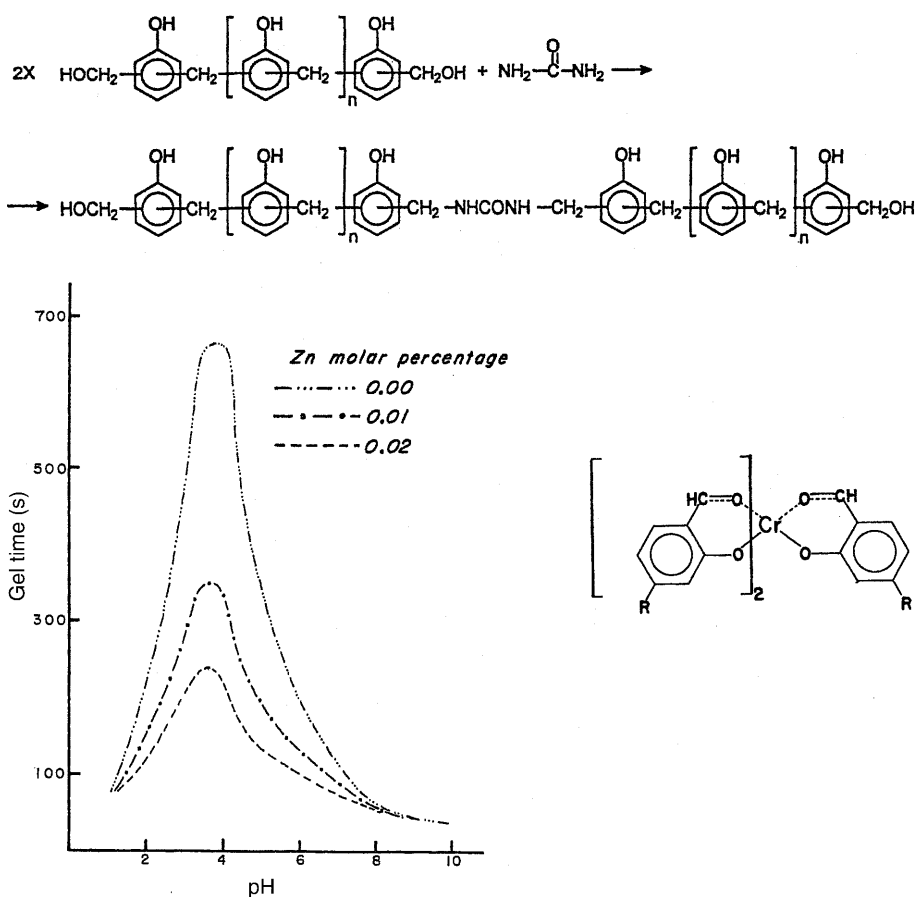**Fig. 4.** Schematic representation of gel time curve as a function of pH for PF and TF resins accelerated under acid/neutral conditions with $Zn^{2+}$, and multiring structure of the isolated $Cr^{3+}$/resorcinol/formaldehyde and Chromium/phenol/formaldehyde stable intermediate complexes found in the case of retarders presenting the same mechanism of the accelerator (from Pizzi 1979c, d, e, 1983; Pizzi and van der Spuy 1980)

## PRF cold-set adhesives

Phenol-resorcinol-formaldehyde (PRF) structural, exterior-grade cold-set adhesives are among the resins of highest technological content in the field of wood adhesives. They are very expensive, too, because resorcinol is very expensive, and their past history since their development has boiled down to trying to decrease their resorcinol content while maintaining the same level of performance. My first encounter in this field was with the TRF, hence a tannin adhesive; they are still in commercial use in South Africa and Australia and clearly mentioned in the respective national standards. When I switched to the synthetic PRFs, the first result was the honeymoon adhesive based completely on PRFs. The honeymoon concept was born in North America towards 1974, but this system was far too expensive to be economical as it was based on a chemical produced in one world site only and at a price of about 80 thousand US $ per ton (then) and hence it never became commercial, the project soon having been discontinued. By 1979, however, we had perfected the whole range of PRF honeymoon adhesives and these became commercial successfully in early 1981, followed not more than 8 months later by the even cheaper PRF/tannin extract honeymoon systems with the same technical advantages but using only half the resorcinol and hence available at only 60% the price of traditional PRF resins (Pizzi et al. 1980; Pizzi and Cameron 1984, 1989) (Fig. 5). I would like to point out that all these honeymoon adhesives can bond timber at very high moisture content, and not only some relatively recent variation on the theme (Greenweld 1997) as some people would like to make believe. The honeymoon adhesives did not constitute a resin development but rather a system improvement, halving overnight the requirements of resorcinol in finger-jointing and glulam beams. I have five other published developments in this field which are not commercial (at least not yet), but which nevertheless still have considerable potential, namely the lignin-resorcinol-formaldehyde cold-sets (van der Klashorst et al. 1985; Truter et al. 1994), the
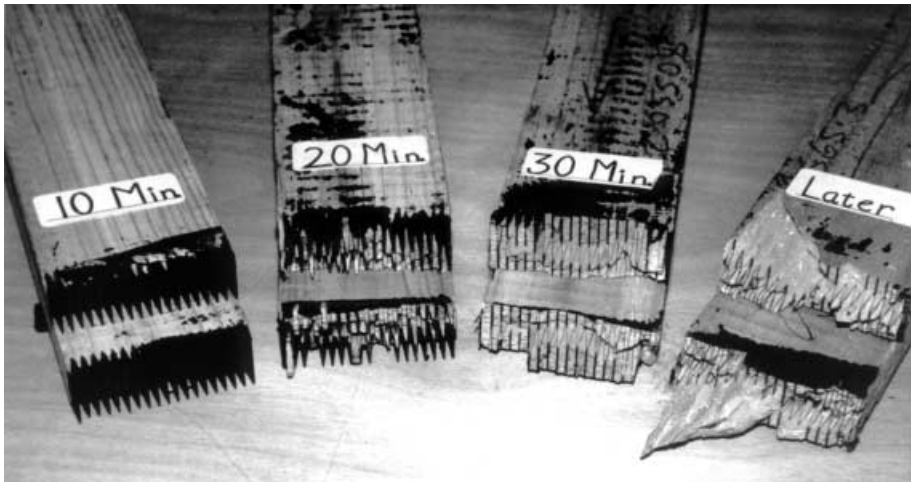


**Fig. 5.** Industrially produced honeymoon adhesives bonded fingerjoints tested in bending 10 min, 20 min, 30 min and 1 h after bonding of the joints at 20 °C. Note the progressive rapid increase of wood failure indicating the coming up to standard of the joint strength. The adhesive used here is a low cost PRF/tannin type (see Pizzi et al. 1980; Pizzi and Cameron 1984, 1989)

"blue glue" (Pizzi and Vermeulen 1987; Scopelitis and Pizzi 1993a; Pizzi and Cameron 1989; Pizzi 1994), the RUF resins (Scopelitis and Pizzi 1993b), the non-resorcinol alkaline cold-sets (Pizzi et al. 1988) and the self-neutralizing acid setting PFs (Pizzi et al. 1986b), containing no resorcinol at all, these latter being based on a further development of self neutralizing hidden catalysts, such as the morpholine/p-toluene sulphonic acid used in paper-impregnating melamine resins. I will describe in more detail only the front runner, and the reader can look at the others in the relevant references. Of these five the "blue glue" is the most useful as it can be used as a traditional PRF or as a honeymoon component. In both cases the percentage of resorcinol needed is still half of that of any other PRF, arriving at a low value of only 4–5% resorcinol on liquid resin at parity of performance: for comparison, today's best traditional PRFs contain between 16 and 18% resorcinol on the same basis. What is the "blue glue"? It is a system to molecularly double, even branch, a PRF and thus spare half the resorcinol that would otherwise be used (Fig. 6). It is a chromatic side reaction of the cheapest "brancher" used, urea, that confers to the adhesive, and only in the liquid resin, the characteristic ink-blue colour. Contrary to the honeymoon adhesives, the "blue glue" is a true resin advance and not just a system improvement.

## UF and MUF adhesives

UF and MUF resins have not been in the distant past my main field of operation, although I have used a lot of them at industrial level for a long time. I came to be interested in these resins at formulator level almost by chance, about twelve years ago, with my interest being captured mainly by the melamine resins: and what a discovery this was! I dare say that today melamine resins are one of my favourite fields of research. Why such an enthusiasm?

$$\text{resorcinol} -CH_2-[-\text{phenol}-CH_2-]_n-\text{resorcinol}$$

$$\text{resorcinol} -CH_2-[-\text{phenol}-CH_2-]_n-\text{resorcinol}$$

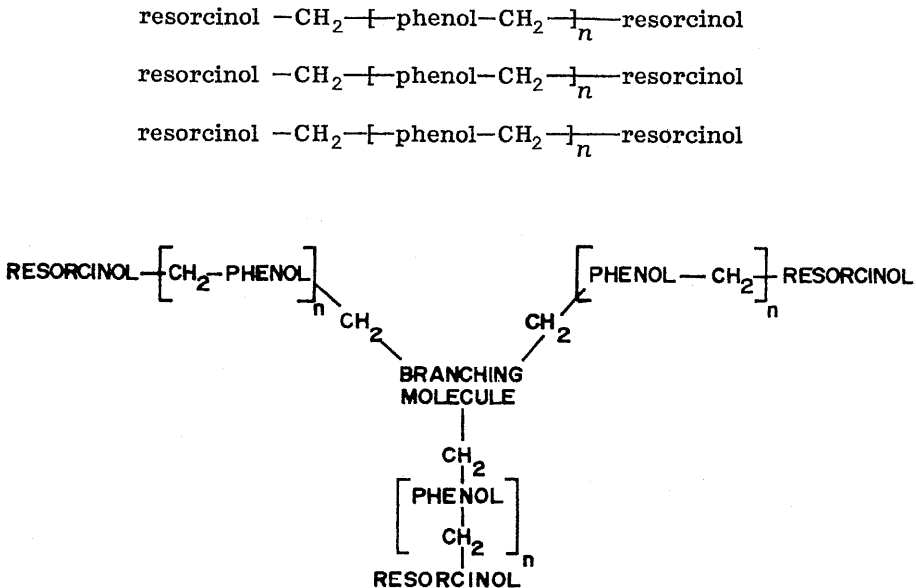$$\text{resorcinol} -CH_2-[-\text{phenol}-CH_2-]_n-\text{resorcinol}$$



**Fig. 6.** Schematic representation of the "blue-glue" branching system illustrating the decrease in the proportion of resorcinol in PRF cold-set adhesive for glulam and fingerjoints (best reference Scopelitis and Pizzi 1993)

Contrary to any of the other resins used in wood adhesives, the literature on melamine resins and, even more important, on MUF resin adhesives, is rather scarce, or better, very scarce. There are some good historical reasons for this, but these are beyond the scope of this presentation. Whatever the reasons, we have here a major class of adhesives, in Europe perhaps the dominant class of exterior adhesives, on which not even a fraction is known of what is known on other resins. In short, in almost any direction one looks, the chance is very high of finding something new which is also of significance: melamine resins are then a very ripe field for new discoveries both at the fundamental and at the application level. My first papers in the field of MUF adhesives, while no great flight of fancy, were nonetheless the first ones in which workable industrial formulations were developed, their behaviour somewhat explained and the formulations published (Mercer and Pizzi 1994). It is not that good industrial formulations did not exist before, they did, but none was published. After this rather easy success a series of interesting findings followed: (i) the determination that MUF hardening occurs mainly (but not totally) through the formation of bridges between melamine residues, a discovery independently shared with Prof. Higuchi (and his paper actually appeared first) (Higuchi et al. 1994; Pizzi and Panamgama 1995). (ii) The equations developed to correlate the liquid NMR results of PF but mainly MUF, MF and UF resins with the strength of the resins, in their hardened state, hence the IB strength and formaldehyde emission of boards bonded with them (Ferg et al. 1994; Mercer and Pizzi 1996a, b; Panamgama and Pizzi 1995, 1996). It was interesting that a similar work on MUF resins, although not as extensive, and with a slightly different focus, was also carried out independently by another industrial research group (Aarts et al. 1995). (iii) The work on the correlation of formulation and manufacturing parameters on properties and performance in PMUF resins with the characteristic feature that in most industrial PMUF adhesives phenol remains mainly as a useless pendant group in the hardened amino-plastic network (conclusion arrived at independently by Prof. Higuchi (Higuchi et al. 1994 – and again his publication appeared first), what reaction order is necessary to obtain the best benefit from the added phenol and demonstrating that equivalent MUFs have generally better performance of the equivalent PMUF, thus that PMUF are not really necessary (Cremonini et al. 1996b; Prestifilippo and Pizzi 1996) (Fig. 7). (iv) The concept of preparing MF and MUF resins at a formaldehyde molar ratio well below 1, and to just make up the difference by addition of hexamine in the glue mix to make up the intended, higher molar ratio: this was based on the stability of the benzylamine bridges formed resulting in much lower formaldehyde emission for the higher strength induced but in a higher molar ratio (Pizzi et al. 1996b). (v) The concept of coreacting heavily, but still partially hydrolyzed polyamides (nylon) with urea in the preparation of better water resistance UF resins (Wang and Pizzi 1997) worked well but for the difficulty to hydrolize waste nylon fibre partially, but consistently. (vi) X-ray diffraction studies of UF resins hardened alone and on a wood substrate showing the change of conformation and of the level of cristallinity in the two cases (Levendis et al. 1992; Ferg et al. 1994).

The publication of these new developments generated some interest, but all were far from the impact generated by the next development whose results appeared in print in 1996 (Prestifilippo et al. 1996; Cremonini and Pizzi 1997, 1999): the upgrading to full exterior capability of UF resins by addition to their glue mix of small amounts of melamine salts of organic acids (i.e. melamine acetate) (Fig. 8) (Table 1). Considerable interest was generated by a system that gave
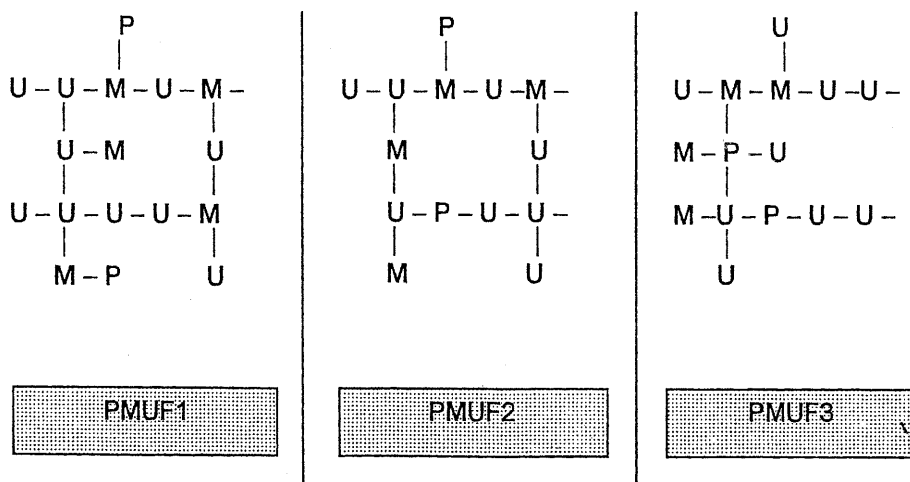
**Fig. 7.** Schematic representation of the dependence from the type of formulation used of the fate of phenol in a PMUF resin. (1) Phenol only present as unlinked free phenol/phenol derivatives but mainly as pendant group neither participating in resin cross-linking nor contributing to its performance and its water resistance. (2) An intermediate case. (3) A case in which phenol is co-condensed and participating in the cross-linked network (see Cremonini et al. 1996b; Prestifilippo and Pizzi 1996; Higuchi et al. 1994)
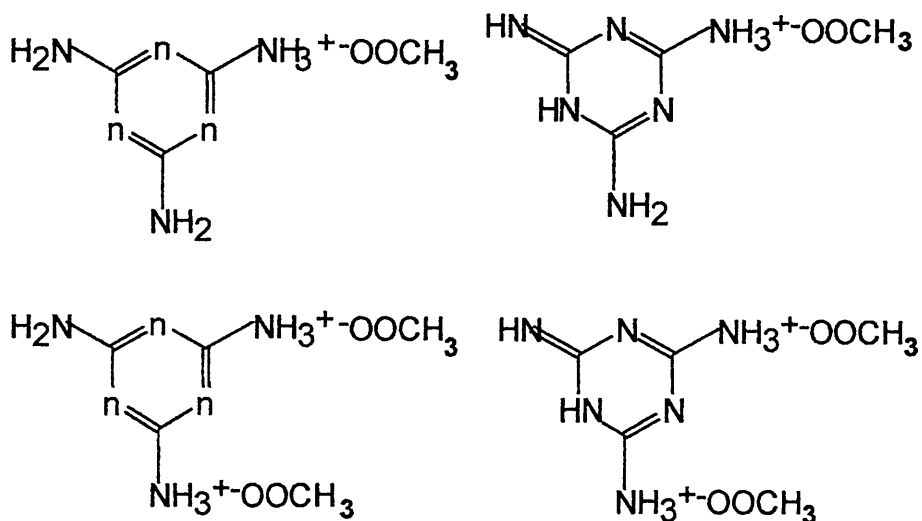


**Fig. 8.** Formulas of different chemical species constituting impure melamine acetates salts used as additives of UF resins to prepare MUF wood panels adhesives of high performance and low melamine content (from Prestifilippo et al. 1996; Cremonini and Pizzi 1997, 1999)

plywood a performance equivalent to that bonded with a 40:60 M:U MUF with just the equivalent of a 10:90 M:U weight ratio, especially as this appeared in print during the period in which the price of melamine had just risen dramatically. Many companies have shown interest in this system, but as melamine acetate is

**Table 1.** Tensile strength results of beech plywood panels 12.7 mm thickness, 5 plys, bonded with addition of low amounts of melamine as melamine monoacetate, compared with commercial MUF resins, tested according to European Norm EN 314, treatment 5

| Melamine monoacetate on liquid UF (%) | Melamine on UF solids (%) | Average tensile strength (EN 314) (N/mm$^2$) | Wood failure (%) |
|---|---|---|---|
| 10 | 10.7 | 1.65 | 10 |
| 15 | 16.1 | 1.96 | 10 |
| MUF, M:U 30:70 control | 43 | 1.33 | 10 |
| MUF, M:U 50:50 control | 100 | 2.76 | 40 |
| EN 314, treatment 5, full exterior | | >1.0 | – |

not yet (there was a company interested in manufacturing it) available commercially, the system is not yet used commercially. There is, however, an exception: a relatively small adhesive producer, who will remain nameless, servicing a captive market of five particleboard mills, where people think they get normal melamine content resin, not being aware that instead they get resins of much lower melamine content but spiked with the melamine salts: an interesting, although not very honest example of how well the system works!

There are, however, better systems in the pipeline, and these are well on the way to be used industrially. Additives have been found which are relatively simple, inexpensive and used in small amounts in the glue mix, and which allow a premanufactured MUF resin of M:U weight ratio 10:90 to perform in particleboard as to-day MUF resins of M:U weight ratio 50:50 do in wet tests: both a decrease of melamine content, while maintaining performance as well as maintenance of the same level of melamine in the resin, while practically doubling internal bond strength both wet and dry are possible (Pizzi et al. 1996–1999; Mouratidis et al. 2000) (Table 2). I urge you to listen to the presentation of Mouratidis et al. (2000), where some of the performances induced by these materials are described (without disclosing their nature).

There is more: an additive, of very low cost, already available in thousands of tons for other purposes, and of no toxicity which, added to any standard MUF resin as those commercial anywhere in the world today, allows equal performance but with an effective decrease of 33% of the percentage of MUF resin solids used on wood for particleboard and other panel products: again, it is just added to the

**Table 2.** Internal bond strength of laboratory particleboard bonded with a MUF resin added of a type of strength increasing additive (FAIR TC96-1604, 1996–1999)

| | MUF 1:1.2 | | |
|---|---|---|---|
| | M = 23% liquid Control 12% resin load | M = 23% liquid +2% additive 12% resin load | M = 9% liquid +2% additive 12% resin load |
| I.B. dry (V20) (MPa) | 1.01 | 1.32 | 0.96 |
| I.B. 2 h boil redried (MPa) | 0.18 | 0.32 | 0.18 |
| I.B. 2 h boil, tested wet (V100) (MPa) | 0.14 | 0.22 | 0.14 |

glue mix, and it is the easiest one of all to use! I urge you to listen to my own presentation on MUF resins where its effect is documented and discussed (Pizzi 2000) (Fig. 9) (Table 3). It also works for UF and PF resins, but in the case of these resins, it only allows decreases of between 15 and 20% in resin percentages, at equal performance of the particleboard: still a very impressive result, allowing for instance a further easy and instant decrease of formaldehyde emission from UF bonded panels. It works best for MUF adhesive resins however, for reasons which we have already worked out (Zhao et al. 2000a; Pizzi et al. 2000). As stated in the beginning: one can beat the performance of PF resins easily with MUF adhesives by using any of these additives in conjunction with one of today's high performance resins (a M:U 50:50). There are quite a few dimensions and possibilities: what disclosed it is not just useful to decrease melamine!

Last but not least on MUF resins: while the honeymoon Greenweld system for glulam and fingerjointing from New Zealand which is based on separate application of a MUF resin on one profile surface, with resorcinol and an additive being added on the other profile surface, is patented (Greenweld 1997), and reputed (correctly, as the PRF honeymoon systems are, too) to bond high
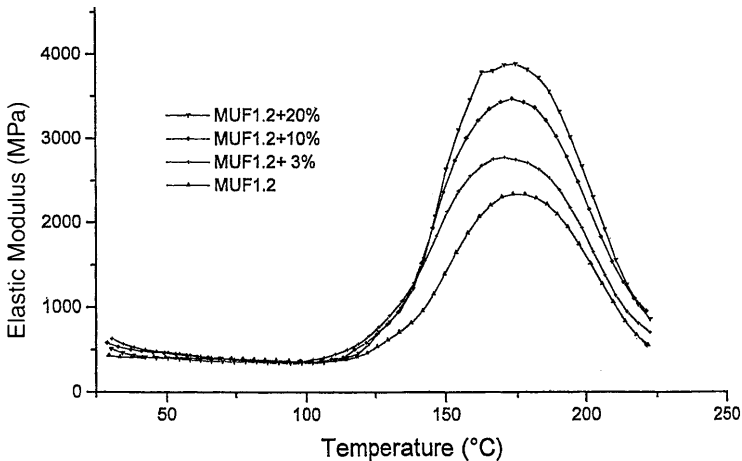


**Fig. 9.** Thermomechanical analysis graph showing the increasing maximum values of the modulus of a MUF bonded joint with increasing amounts of effectiveness upgrading additive. Compare results with board results in Tables 2 and 3 (from Zhao et al. 2000a)

**Table 3.** Internal bond strength of laboratory particleboard bonded with a MUF resin added of a type of strength increasing additive (Zhao et al. 2000)

|  | MUF 1:1.1 | | |
|---|---|---|---|
|  | Control 10% resin load | +10% additive 10% resin load | 10% additive 8% resin load |
| I.B. dry (V20) (MPa) | 1.01 | 1.34 | 1.03 |
| I.B. 2 h boil redried (MPa) | 0.39 | 0.38 | 0.37 |
| I.B. 2 h boil, tested wet (V100) (MPa) | 0.16 | 0.16 | 0.16 |
| Formaldehyde emiss., perforator (mg/100 g) | 3.2 | 2.9 | 2.4 |

moisture content timber, the same has been achieved without needing any resorcinol, nor additives, by just having a honeymoon MUF resin system and using a properly engineered high performance MUF resin (Properzi et al. 2000). With a properly engineered MUF resin, even resins of lower amounts of melamine present a comparable performance (Properzi et al. 2000): and they come free of charge as the system is not patented!

UF resins are interesting, too, but are as well-researched and almost as old as phenolics, hence a much tougher research area in which to find something really new. The only advantage on phenolics that UF resins have had in recent times has been the intense reformulating they have had to undergo as a consequence of the drastic decrease in formaldehyde emission dictated by enforced government regulations. While this was experienced as a disaster in the industry, for logical commercial reasons, it did introduce instead a new breath of life in the research on these resins, by then stagnating, with a number of excellent technological discoveries. I cannot pretend to have contributed much to the UF field having been mainly an exterior wood adhesives fan, but a couple of interesting things I have contributed too. The first was the quite recent finding (Lu and Pizzi 1998) that, contrary to what was the case with old style resins, with modern low molar ratio UF resins, there are advantages in somewhat hot-stacking the boards after pressing, resin degradation and recovery of residual curing being part of an equilibrium, the differential rate at which the two opposite reactions proceed maximizing the latter at a temperature higher than ambient. An interesting result that allows increases in internal bond strength of up to 15% more without changing anything, or, conversely, a decrease of 15% UF content in the board at parity of performance, or even a faster press time for the same strength and resin content as used to-day (or a combination of all three!). This, and the relevant modelling equation which derived from this has now been shown to be valid also for MUF resins hot-stacking (Zhao and Pizzi 2000) (Fig. 10). The other contri-
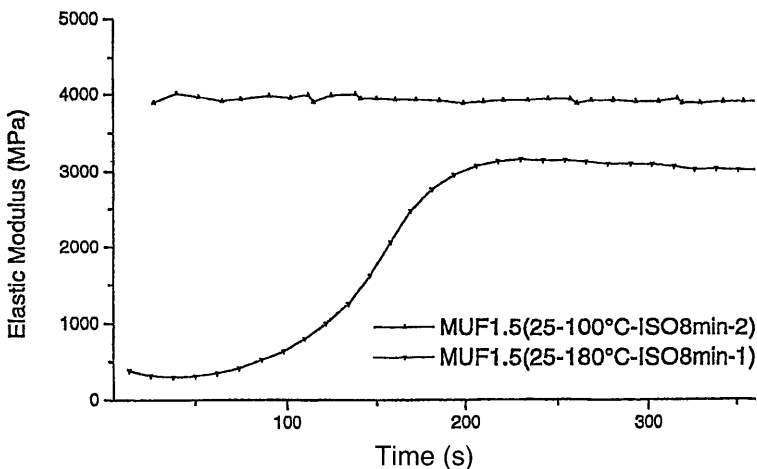


**Fig. 10.** Thermomechanical analysis of a joint glued with a modern MUF adhesive showing the advantage of hot post stacking for modern, low molar ratio aminoplastic adhesives bonded panels. Note the max modulus achieved during isothermal heating (180 °C for 8 min) (lower curve) and max modulus achieved after cooling and reheating at 100 °C for 8 min (higher curve): the difference in modulus is the potential gain due to hot-post-stacking (from Lu and Pizzi 1998; Zhao and Pizzi 2000)

bution of interest was the findings by molecular mechanics of the interface that the inherent sensitivity to water of UF-bonded wood is not just due to structural characteristics of the UF resin, but also to the affinity of water for some ligno-cellulosic substrate materials being higher than those of an already hardened UF resin: an adhesion rather than just a hydrolysis problem sharing responsibility for the well known lack of water resistance of UF resins (Pizzi 1990a, b; Pizzi 1994).

There were other findings of interest in UF resins, but none as much as the ones reported above. The only other one worth to be briefly mentioned was the investigation of the conditions in which urons proportions are maximized, how uron-urea-formaldehyde resins can give better internal bond strength results than UFs, and the mechanisms of opening/closing of uron rings as a function of pH and their influence on formaldehyde emission (Soulard et al. 1999).

## Isocyanates

Or Diisocyanates, as I love to call them. It would pain any objective adhesives specialist that there is a constant war between these adhesives and the more traditional wood adhesives, when instead both have much to be gained from by joining forces. My contribution to isocyanates (and to other resins) has been to push strongly in this direction, even at the industrial level, namely the use of di-isocyanates as both copolymerizing agents of traditional adhesives, as upgrading additives of other wood adhesives and of other adhesives as the eliminators/minimizers of the residual toxicity problem of hardened isocyanates. My very pleasant adventure with these resins started in 1981 with the laboratory development of mixed pine tannin/di-isocyanate adhesive systems (and isocyanates/other resins systems such as MF and PF but always in the context of tannin adhesives) (Pizzi 1982a). It continued only in 1990 in Chile with the then dire need of having to make work industrially the pine tannin/isocyanate formulation – which worked well and was commercial in that country for about 8 years, up to 1998 (Pizzi et al. 1993c). Even more rewarding, however, was the work leading to isocyanate/PF copolymers for plywood and particleboard (Pizzi and Walton 1992; Pizzi et al. 1993b, 1995c; Pizzi 1994), just mixed in the glue mix and copoly-merized in situ in the board during pressing. There are two unusual stories to relate on this subject: the first took place in Chile in 1990: the plywood mill, where the adhesive started commercially, had a considerable supply of a beautiful veneer which was almost unbondable with PF resins (Tepa, *Laurelia philippiana*). Even the bonding results obtained by commissioning three of the world's leading ad-hesive companies to formulate suitably upgraded PF resins failed miserably. We used then the PF/isocyanate glue mix (with a rather poor PF) in the full knowl-edge that the PF alone would not work, and that pMDI alone cannot be used alone on plywood as it does not bond. The mix worked and worked splendidly: there are three years worth of production of exterior grade tepa plywood in the USA and in Korea bonded with this resin. At that time it was correctly believed that a phenol and an isocyanate cannot coreact in water solution: this is correct and just good chemistry. But because the isocyanate/PF adhesive worked so well, we were astonished, and also somewhat naive: the Chilean company asked a famous overseas pMDI producer (which will remain nameless) to send a technical team to see what was happening in this plywood factory and to offer advice or at least an explanation. A team of four polyurethane experts arrived, walked into the factory, looked at the excellent plywood which was being produced, looked at the staff glue-mixing, namely pouring pMDI in a 50% water-borne PF resin, just said "this cannot exist, hence it does not exist" and walked out. And that was it! They were

good specialists, but the plywood bonded with something that according to them did not exist was very good too. And very real. It became then clear that some new, unknown reaction was occurring and I was the lucky one to have to work it out and proved it (for the unbelievers, we isolated and identified the compounds formed one by one, by $^{13}$C NMR too-Pizzi and Walton 1992) and to expand this to its use for aminoplastic and tannin adhesives, too (Pizzi et al. 1993b, c; Pizzi 1994; Pizzi et al. 1995c) (Figs. 11, 12, 13). The NMR in Fig. 12 obtained by the reaction of monomeric MDI (not pMDI) with saligenin (o-hydroxybenzyl alcohol) clearly show the existence of the carbamate groups of urethane bridges in the 160 ppm region, only the peaks around 153–156 ppm belonging to the aromatic carbons linked to the phenolic hydoxyls. We (the company: I was the poor guy that had to battle with the patents examiners, no glamour there) took a patent on the system (USA patent 5,407,980, Pizzi et al. 1995c). Almost 10 years later I was contacted through a third party by a big international adhesives company that wanted to know where this system was commercial as they were very keen to evaluate/use it: what they had not realized was that about two years before they had bought 51% of the Chilean company and that the patent and technology were already "in house"! It is a strange story, but the effectiveness of the isocyanate/PF, isocyanate/UF, isocyanate/melamine resins, isocyanate/tannins, and of isocyanate/methylolated lignin, especially in difficult-to-glue situations is now well documented, even at industrial level: so, who lost? The traditional adhesives were upgraded to do a job they could not do alone, the isocyanates became suddenly very usable as plywood adhesives which they could never do alone, and due to the mix being in water, no potentially toxic residual isocyanate groups can survive in such a hardened glue line. They all won! I rest my case! And I had fun doing it.

Isocyanate/UF and isocyanate/melamine resins were also tried (Pizzi 1982; Pizzi et al. 1993b) with different interests: isocyanate/melamine resins, although
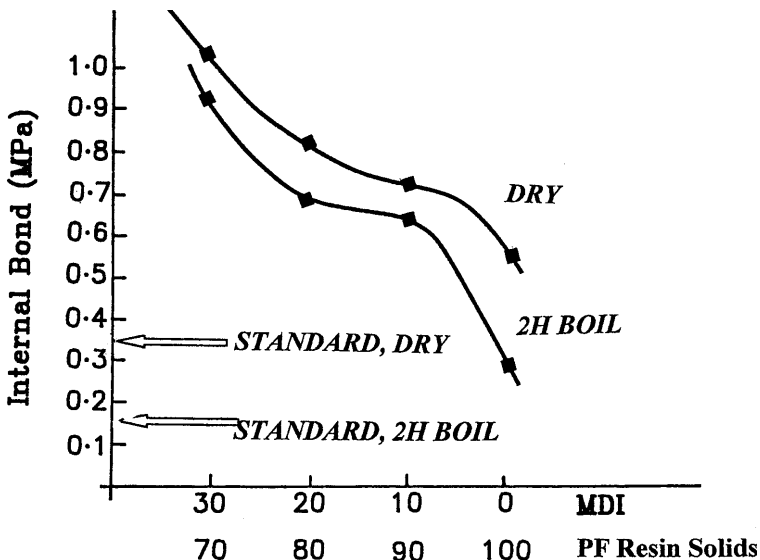


**Fig. 11.** Internal bond strength dry and after 2 h boiling of particleboard panels bonded with phenolic/isocyanate adhesive formulation versus relative proportions of PF and pMDI
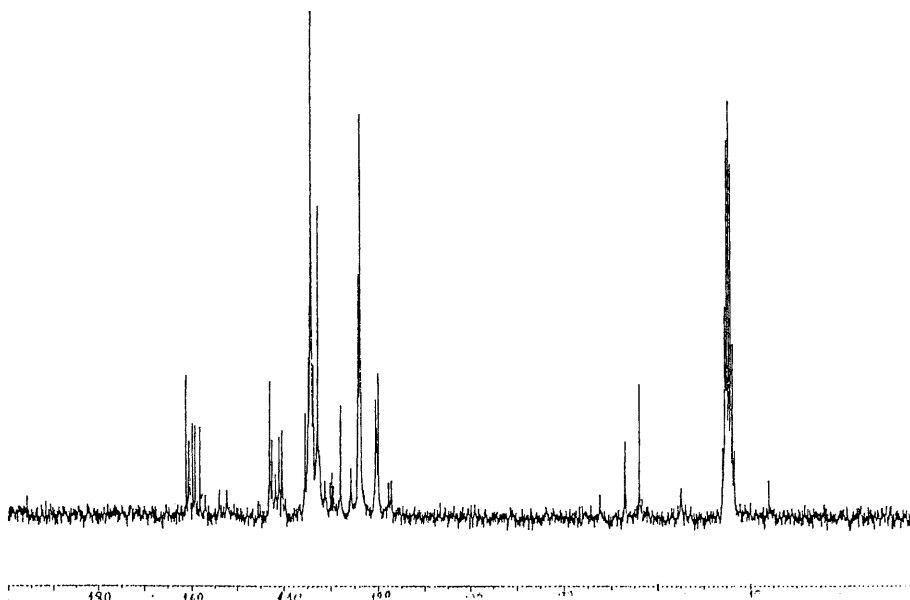
**Fig. 12.** $^{13}$C NMR spectrum of reaction product of monomeric MDI with o-hydroxybenzyl alcohol (saligenin) (from Pizzi and Walton 1992)
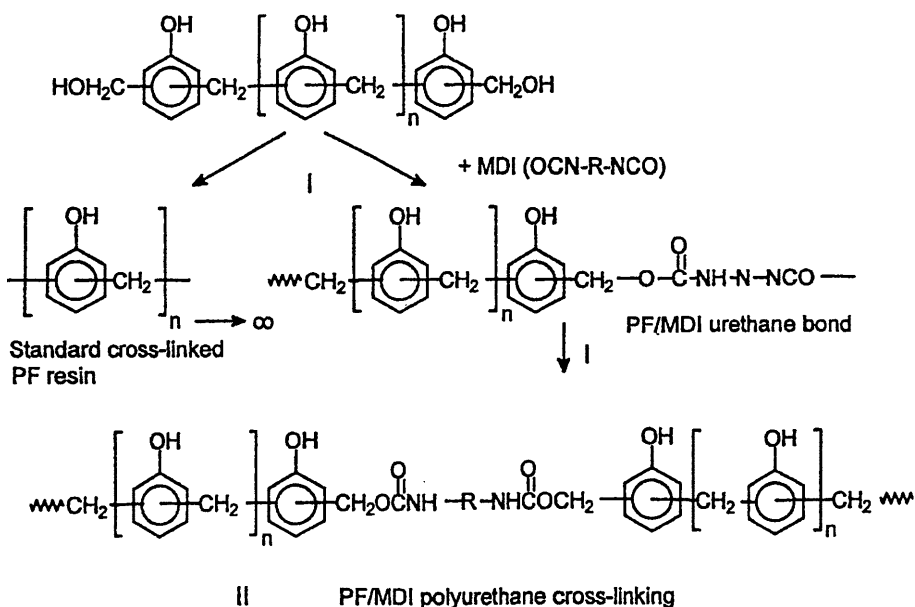


**Fig. 13.** Reaction scheme of the most common reactions (not all) occurring in pMDI/PF glue-mix curing

much more of interest today with the very high cost of melamine, had little interest for us at that time when melamine was relatively cheap and isocyanate relatively expensive. Isocyanates/UFs were of more interest and worked rather

well, although the amount of isocyanate used (40% on total resin solids) to make them really exterior grade adhesives, passing the relevant standards, made them economically unattractive at that time. We were looking at eliminating melamine in MUFs, and melamine was very much cheaper than it is now! They are perhaps of more interest now than then, if the isocyanate is used in small, economically viable amounts to just upgrade the water resistance of UFs without pretending to pass PF-level exterior standards. This technology must not be confused with the Netherlands patent (Tinkelenberg et al. 1982), in which a UF of U:F molar ratio of 1:≪1 is mixed with pMDI, a technology that was kept in reserve to counteract the now unlikely event that the formaldehyde emission regulations became so limiting that aminoplastic resins might not be able to meet them anymore. Our technology, contrary to theirs, used UF resins of U:F molar rations of 1:>1. As regards recent doubts (Wolcott 1999) about t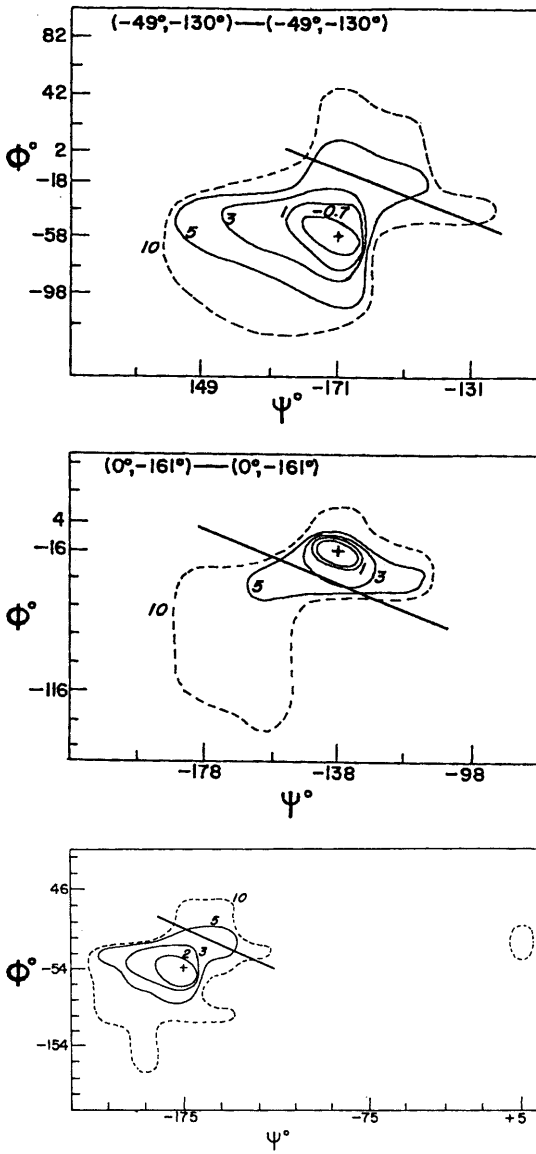he reaction of the methylol groups of US with the isocyanate group to rather form interpenetrating networks, I would like to point out that at molecular level, in any copolymer of this nature both situations coexist, and coexist to a variable extent. This has always been known in most fields of polymer chemistry: that the final network is formed by a classical polyurea/biuret network obtained by the reaction of isocyanate with water, interpenetrating with a classical UF network cross-linked through methylene bridges, interpenetrating with the urethane network formed by coreaction of UF methylols with isocyanate groups. This is clearly discussed and stated, and relative proportions of the three given in the case of PFs, UFs and MFs in Pizzi et al. (1993b, c) and Pizzi and Walton (1992). The fact that the amount of urethanes bridges formation is lower for UF than for PF resins is also defined by the difference in kinetic constants (Pizzi and Walton 1992). The fact that only two DMA tan $\delta$ peaks are noticed (and this is valid also for the resins where the copolymers were isolated and identified – Pizzi and Walton 1992) is due to the superposition of the two reactions of isocyanate with water and with the methylols, the kinetics of the two reactions and their reaction constants not being very far from each other (Pizzi and Walton 1992). In the same literature it is also clearly stated, however, that cross-linking by copolymerization also takes place, and to a very noticeable extent, as shown by the formation of the urethane bridges. Let's face it, even if all of the isocyanate were transformed to polyureas and biuret by exclusively reacting with water instead of some of it forming urethane bridges with the methylol groups of the formaldehyde-based resins, one would have to some extent the reaction of for instance the PF resin with urea as detailed in Fig. 3 of formation of PUF resins, hence one would still have copolymerization. The same can be said for aminoplastic methylols, at worst and quite evidently reacting with polyureas and biuret formed by the reaction with water of diisocyanates. What is even more interesting is that the authors in question (Wolcott et al. 1999) show thermograms and tan $\delta$ graphs which clearly illustrate instead that some copolymerization does indeed occur (Pizzi et al. 2000).

Another interesting development in this field was that of the two components isocyanate/PF(or TF)/methylolated alkali lignin adhesives with lignin constituting up to 65% proportion of resin solids (Stephanou and Pizzi 1993a, b) which with the aid of accelerators according to two different principles (Stephanou and Pizzi 1993b; Batubenga et al. 1995) achieved excellent exterior grade performance at fast particleboard pressing times comparable with modern industrial practice: this is still a development that might be of topical interest in the future as the cost of such a mix is low. More conceptually interesting was the finding that not only (a) addition of pMDI accelerates considerably the gelling and curing of lignin, as

indeed it does also for synthetic PF resins, but that (b) at least methylolated alkali lignin is as fast or faster gelling than PF resins, the poorer performance of lignin resins being due to the relative scarcity in the number of suitable lignin reactive sites, hence due to a too low density of cross-linking of the final network, rather than being due, as thought for many years before, to too slow a gel time and poorer reactivity of methylolated lignin reactive sites (Pizzi 1994; Stephanou and Pizzi 1993a, b).

## Adhesion, polymer chemistry, structure of wood constituents, of resin oligomers, and at the interface, and others

While adhesive proper are my main interest, it is evident that dealing with adhesives will eventually lead anyone, at one level or another, to get interested also in adhesion. Adhesion is a very complex and difficult field which can be approached in several different ways. Not knowing much about the more classical approaches to this field other than that they are built by complex mathematics but mostly on empirical basis and parameters far removed from reality, I felt rather uncomfortable with such approaches. As specific adhesion is based on a visco-elastic energy dissipation term and on the thermodynamic work of adhesion, which is related to the sum of secondary forces interactions at the interface, I chose to approach the field from the side of my initial youth speciality, namely molecular mechanics, simply because I knew the technique well (not many people are aware that my first thesis was with one of the early, rather well known research groups in molecular mechanics applied to proteins structure, and that its aim was to demonstrate that Flory, at that time very famous but not yet Nobel prize in chemistry, was wrong on some small structural detail of myoglobin, because the potential functions coefficients he had developed were not as advanced as ours – both of which Flory graciously recognized) (Damiani et al. 1970). This technique is ideal to interpret interfacial physico–chemical phenomena starting from basic, first principles, this approach being extensively used in many fields of science and technology today considerably more advanced than what is properly known to-day as the adhesion field (Pizzi 1999). First however, before tackling the interface, I had to build up all my systems on some of the substrates and of adhesive oligomers to be used. In wood my first structural studies were on crystalline cellulose I and II (Pizzi and Eaton 1984a, 1985a, b; 1987a, b): this is a rather rarefied, somewhat theoretical "ivory tower" field, mainly populated by highly self-protective scientists who "stonewall" severely as soon as they perceive someone new trying to get in (anyone trying to get in should have his head read-they should rather be trying to get out!). As this very closed scientific community did not know why I was doing this work, which surely was not for joining them, I had my problems – nevertheless the results obtained were rather good. It is a pleasure to relate, however, that other than endlessly debating details of crystalline forms of cellulose whose structures can be supported by X-ray diffractions studies (and rather badly if one has to judge by the half a century of details controversies having rife in this field), no one has ever tackled the much more difficult task to define the mix of possible structures of amorphous cellulose by such a theoretical approach: that is, except a very extensive study by the undersigned (Pizzi and Eaton 1985a, b, 1988; Pienaar et al. 1989). It is still the only study of the kind in existence (Fig. 14a, b), and it gives me considerable pleasure that this work and the structures that were defined were used by someone in pharmaceutical/medical science I have never even met (Alvira et al. 1987, 1990, 1991), as the basis to demonstrate and build up a

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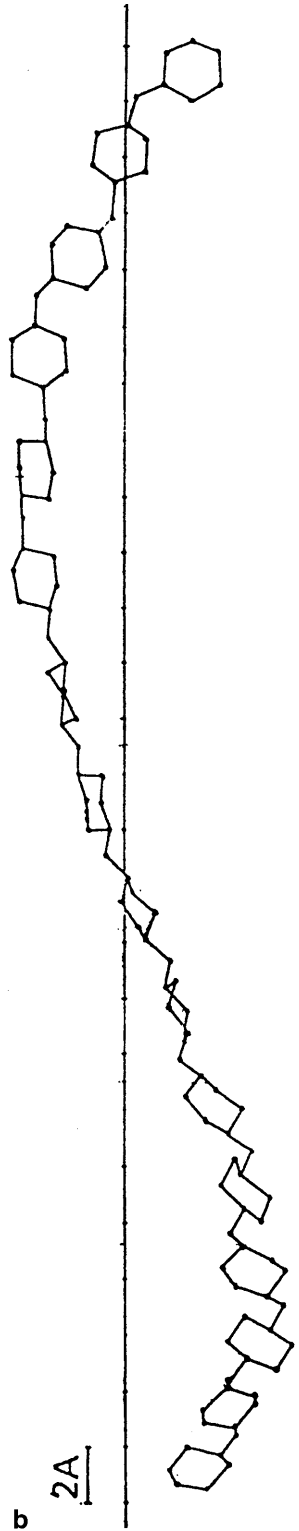
**Fig. 14a, b. a** Energy maps of the most energetically stable conformations of the β-glucosidic linkage connecting two homogeneous most stable cellobiose conformations of amorphous cellulose, namely (−49°, −130°)–(−49°, −130°) and (0°, −161°)–(0°, −161°) and of the heterogeneous most stable cellobiose conformations (−49°, −130°)–(0°, −161°). **b** Model of one strand of amorphous cellulose obtained by extrapolation of the (−49°, −130°)–(−49°, −130°) amorphous cellotetraose conformation showing that the conformation forms a helix. *Note*: This is not the appearance of amorphous cellulose where all the 5 cellobiose most stable helix conformations and connecting β-glucosidic linkages contribute and alternate statistically (Pizzi and Eaton 1984a, 1985a, b)

mathematical theory explaining the separation on amorphous cellulose columns of enantiomers of the amino-acid alanine: in reality a problem of differential, preferential adhesion!

There was no "stonewalling" when the molecular mechanics results of the interfacial interactions, thus real theoretical adhesion studies at molecular level between a number of PF and UF resins oligomers and cellulose, were published (Pizzi 1990a, b, 1994; Pizzi and Eaton 1987c; Pizzi and Maboka 1993; Pizzi and de Sousa 1992), wood preservatives on cellulose (Pizzi 1990c, d) and later even ternary systems with two interfaces (a finish over a primer on cellulose) (Pizzi et al. 1997b; Probst et al. 1997; Pizzi and Probst 1998), simply because there was no one else in this field. Many results of these studies were confirmed by applied results, too, on adhesives and other adhesion systems (Pizzi and De Sousa 1992; Pizzi 1994, 1999). The results were also in line and contributed to confirm and accelerate some important applied and industrial trends, such as the shift to the use of ortho orienting catalysts in PF wood adhesives, and the already mentioned sensitivity of hardened UF oligomers to be displaced by water from the cellulose "surface", and that the tridimensional conformation of UF, PF and other resins oligomers is different in presence or absence of the substrate (Fig. 15a, b). It is molecular mechanics which also allowed the construction of the cellulose water absorption isotherm from molecular level data, to identify on crystalline and amorphous celluloses the relevant sites, to describe mathematically the interference of adsorbed water molecules at the molecular level and to correlate macroscopic effects with molecular parameters (Pizzi et al. 1987d, e).

On top of the industrial confirmation that the molecular mechanics approach to adhesion at the molecular level worked, and worked also for the particularly complex case of wood adhesion, the approach led to the solution of a controversy that seemed impossible to solve by more traditional approaches in the field of generalized specific adhesion theory, this in all fields not just wood (Pizzi 1997b, 1999), namely what the real relationship is between the thermodynamic work of adhesion $W$ and the value of intrinsic fracture energy $G_0$.

$$W \leq G_0 \leq W^2$$

I have had recently the pleasure to see specialist research groups on adhesion (not in wood science), who would have philosophised no more than two years ago on the inutility of molecular mechanics, starting to adopt, among other techniques, also molecular mechanics in the fear of being left behind. I think my job is done here!

There are two other interesting series of contributions in this field: one having made quite an impact reasonably recently, while the other has been ignored on the basis of the accepted principle that if one does not mention something, then it
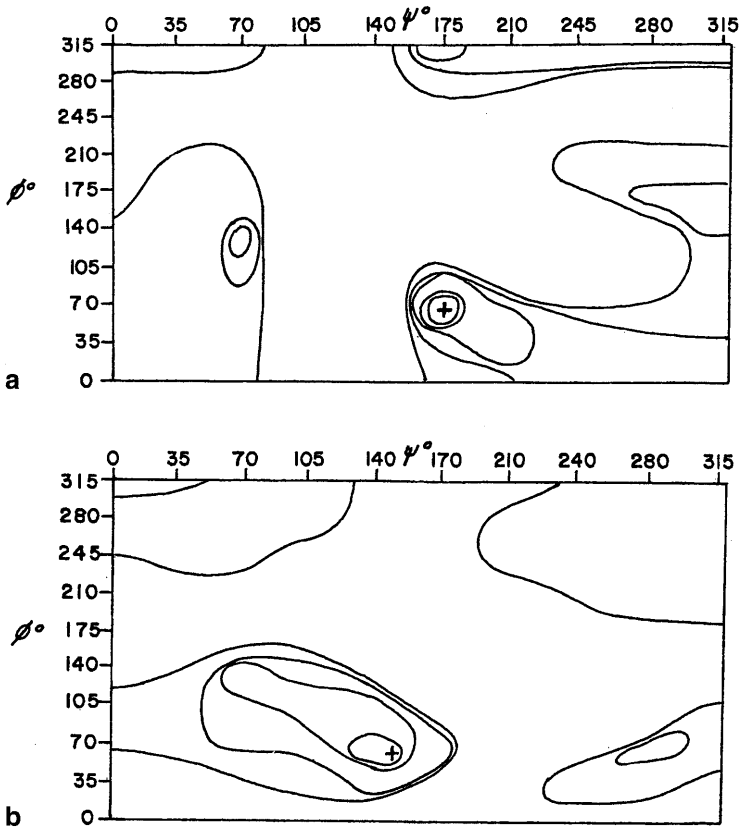
**Fig. 15a, b.** Total energy maps of the favourite conformation of methylene-bis-urea (UF dimer) on **a** only one of the sorption sites on the Cellulose I crystallite (on other sites different conformations can and do occur), and **b** when alone. Note the difference of the conformation indicating the influence exercised by the substrate structure on the adhesive structure

does not exist: this latter one is the first serious molecular mechanics study on the structure of flavonoid oligomers and condensed tannins, showing some very interesting results, and has appeared in print such a long time ago that in fact people do not even know it exists, notwithstanding the fact that it was published in a very well known polymer journal (Pizzi et al. 1986a). It is rather funny to see people in other fields who, while still contributing other worthwhile knowledge, scramble today for position on the bandwagon of molecular mechanics studies of flavonoid monomers and dimers, may be some trimers (Hatano et al. 2000), clearly without being aware that some part of the same work has been done already before and done with better constrained force field programs (Fig. 16a, b, c), some of it to support high temperature NMR work by another research group,

▶

**Fig. 16a–d. a** Most favoured conformation of one rotamer of catechin-$(4\alpha \rightarrow 8)$-epicatechin biflavonoid, and relevant energy map indicating the existence of **b** two possible rotamers for same dimer and timer derived from it; **c** of two possible dimer rotamers and four possible trimer rotamers in fisetinidol-$(4 \rightarrow 6)$-fisetinidin bi- and triflavonoids; **d** most favoured conformation of $4 \rightarrow 8$-linked catechin tetraflavonoid, showing all B-rings pointing outward from helix axis (Pizzi et al. 1986)

a

b

c

d
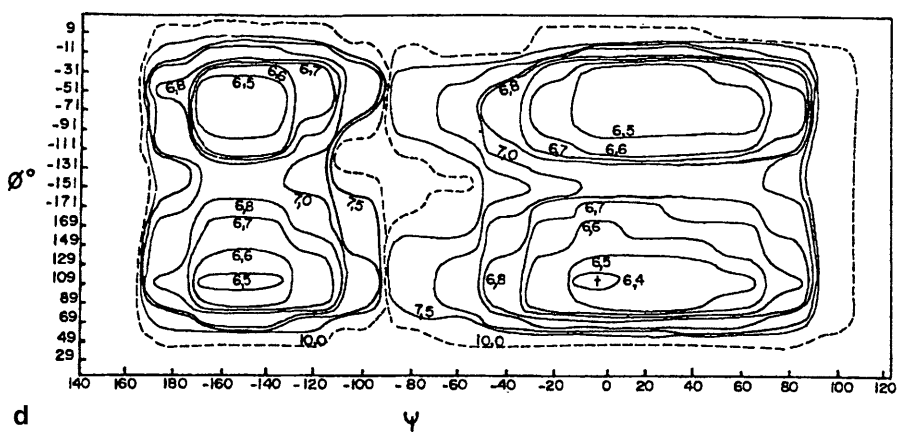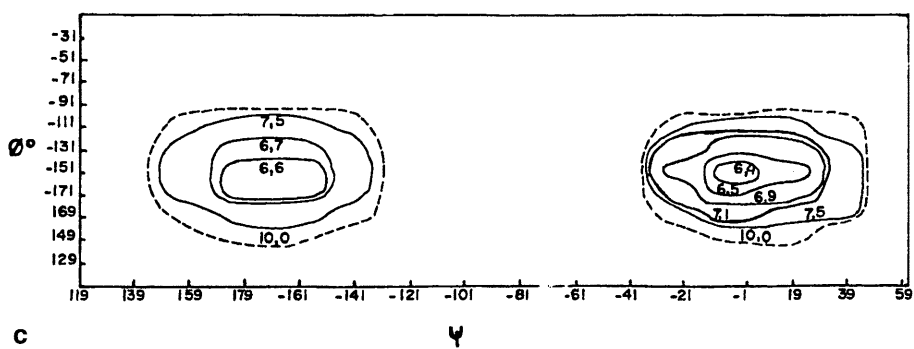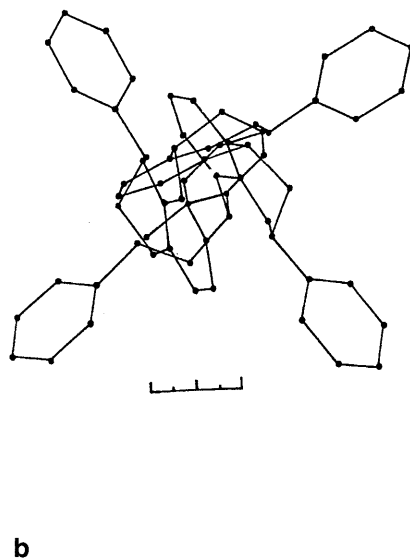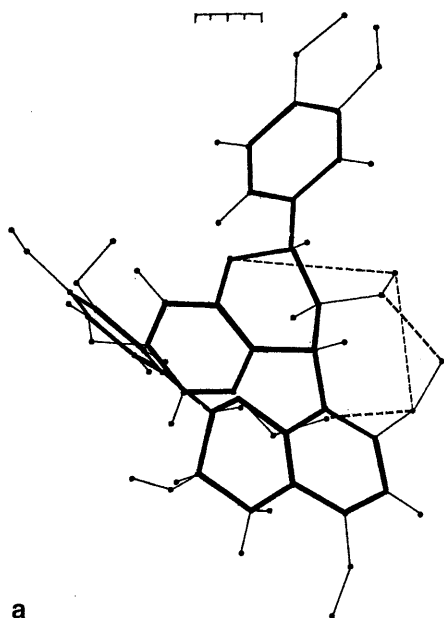
in which the existence of different rotamers was demonstrated. It also led to some interesting theory of the association between tannins and proteins and tannins and carbohydrates in the so called "resurrection" mechanism of some small arbust (*Myrotamnus flabellifolia*) (Pizzi and Cameron 1986).

The first case instead is that of the use of thermomechanical analysis methods to follow the hardening in situ in a wood joint of any of the adhesive resins we have seen (Pizzi 1997a; Pizzi et al. 1999a, b; Garcia and Pizzi 1998c; Lu and Pizzi 1998; Kamoun et al. 1998): this has stirred some interest as it allows to cut to a considerable extent the scanning, lengthy comparative work on different adhesives which used to be done exclusively on lab boards (Fig. 17). The method has also allowed to obtain equations correlating max modulus (or minimal deflection) of the thermomechanically tested joint with the internal bond strength of boards made under standard conditions by using the same adhesive (Laigle et al. 1998; Zhao et al. 1999; Kamoun and Pizzi 2000). It has allowed to detect, for the first time, the initial formation of entanglement networks in the cure of polycondensation resins placed under the peculiar conditions prevalent in a wood joint during hot curing (Garcia and Pizzi 1998c). It has allowed furthermore the discovery of a phenomenological equation describing the actual state of a molecular network of any type (Pizzi 1997b; Pizzi et al. 1997b, 1998c), be it a cross-linked or an entanglement network, correlating thermomechanical minimum deflection $f$ (hence modulus too) of a bonded joint with the energy of interaction $E$ at the interface and within the body of the two materials in contact, thus, under constant reproducible conditions the energy of interaction at the interface which could only be calculated before by extremely long calculations and by theoretical means. This through the number of degrees of freedom $m$ of segments between network's
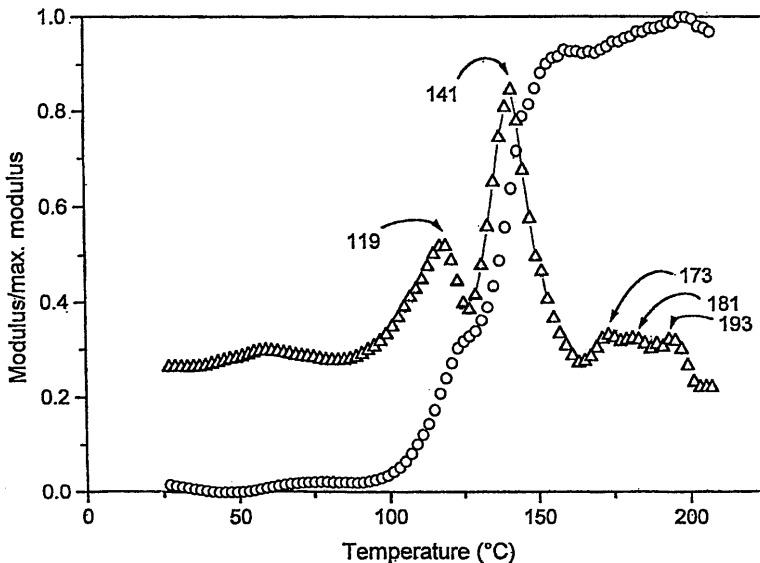


**Fig. 17.** Curves of increase in modulus as a function of temperature during the in situ curing of a PF resin in a beech wood joint, and its first derivate. Note the presence of two peaks in the latter, the first indicating first the formation of an entanglement network under the peculiar conditions the resin finds itself on the wood, before proceeding to a cross-linked tridimensional network (from Garcia and Pizzi 1998c)

nodes and a coefficient of branching $\alpha$ (Flory's in polycondensates, a different one for other polymers), (Pizzi 1997b; Probst et al. 1997; Pizzi et al. 1997b, 1998c; Pizzi and Probst 1998)

$$f = -\frac{km}{\alpha E}$$

and has also allowed the explanation of systems at two interfaces, such as substrate/primer/varnish (Fig. 18). The follow-up of the same study yielded a second equation correlating degree of conversion at gel $p_{gel}$, with Flory's branching coefficient $\alpha$ and reactant sites ratio $r$ and with Carother's average functionality of the system $f$

$$p_{gel} = 1/f + 1/2\sqrt{\alpha/r}$$

in the domain of polycondensation's gel theory (a combination of the two older but simpler theories), all the adhesives we have talked about up to now are polycondensation products and/or harden by polycondensation reactions, that gave much higher precision in the calculation of the degree of conversion at gel than any of the highly complex theories, methods and equations which came after Flory's 1942 theory.

Of further interest was the accurate description of time-temperature-transformation (TTT) and constant-heating-transformation (CHT) curing diagrams for UF, PF, PRF, MUF and tannin resins, and on an interactive substrate,
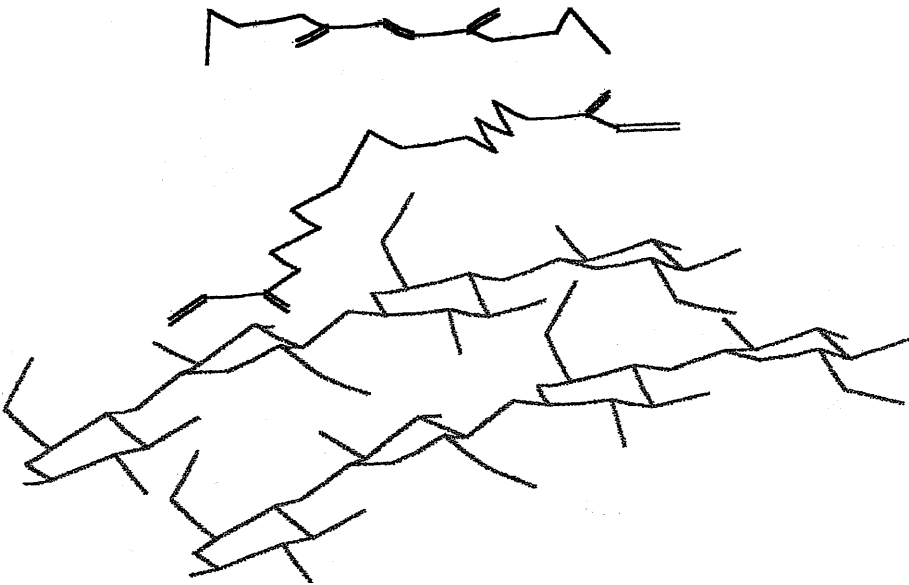


**Fig. 18.** Tridimensional view obtained by molecular mechanics calculations of the minimum energy conformations at the interfaces of a ternary system composed of a polyester (alkyd) varnish (the top molecule) on a specialised primer placed on the surface of a schematic elementary cellulose I crystallite (from Pizzi 1999; Pizzi et al. 1997; Probst et al. 1997)

Fig. 19a–c. a Schematic classical TTT and CHT curing diagrams of epoxy resins on glass fiber substrate. **b** Schematic TTT curing diagram of PRF, MUF, UF, PF wood adhesives on wood as an interacting substrate. **c** Schematic CHT curing diagram of PRF, MUF, UF, PF wood adhesives on wood as an interacting substrate

namely wood (Pizzi et al. 1999a, b; Garnier and Pizzi 2000; Properzi et al. 2000b). Up to that time only epoxy resins on glass TTT and CHT diagrams had been constructed and these by very lengthy methods. It became sorely necessary to do it for the resins commonly used as wood adhesives, and to do it on a lignocellulosic substrate, when people started to reason for wood adhesives on the basis of the epoxies/glass as if nothing more appropriate existed. The influence of the substrate and the use of water based resins yielded TTT and CHT diagrams rather different from the epoxies/glass, one showing that the latter could not be transferred to the case of wood adhesives without causing major deductive errors (Pizzi et al. 1999a, b; Garnier and Pizzi 2000; Properzi et al. 2000b). We also devised a very much faster method for the construction of TTT and CHT diagrams by the use of thermomechanical analysis (Fig. 19a, b, c).

As regards physico-chemical analysis of adhesives and polycondensation resins, a line of research which affected all of them, namely UFs, PFs, MFs, and MUFs, and gave interesting results, was the development of methods to correlate the strength and level of crystallinity of a cured resin with the relative proportions of the different chemical groups present on the liquid resin before curing, this latter one obtained by $^{13}$C NMR. This line of investigation arrived at the point of obtaining regression equations correlating easily obtained NMR parameters (peaks ratios) of the liquid resin with the internal bond strength and formaldehyde emission of particleboard bonded with the same resin under standard conditions (Ferg et al. 1994; Levendis et al. 1992; Panamgama and Pizzi 1995, 1996; Mercer and Pizzi 1994, 1996a, b). It also confirmed by X-ray diffraction (Levendis et al. 1992) the molecular mechanics, finding that the conformation of a polycondensation resin is different when in presence of the substrate than when alone (Pizzi 1990a, b, 1994; Pizzi and Eaton 1987c) Fig. 15a, b). It is from this same line of research that the development of an easy $^{13}$C NMR method ensued for the determination of flavonoid tannins average molecular masses, average degree of polymerization and their polydispersity (Thompson and Pizzi 1995).

The last unusual investigation in which I participated, and which I am going to talk about is really an odd one, but again it stems from trying to correlate molecular mechanics calculations of the state of matter at molecular level with macroscopic, well measurable effects. By dislocating relatively to each other the chain sheets of cellulose I crystallites, one can calculate from the molecular level, correlate and reproduce the voltage curve of the piezo-electric effect of wood obtained by Russian and Japanese researchers for small clear timber samples (Pizzi and Eaton 1984b). This can be and was successfully applied to develop a piezo-electric response method for the identification at macroscopic level of visible and hidden defects of wood planks even longer than 5 m (Knuffel and Pizzi 1986).

## Wood preservation

As they told me that an IAWS Academy Lecture should present a summary of the salient contributions of a researcher's whole working life, notwithstanding the

**a**

Temperature (°C)

$T_{g\infty}$

$T_{g0}$

Degradation

Devitrification

Gelled rubber

Gelled glass

Gelation curve

Vitrification Curve

Liquid

Non gelled glass

In time

**b**

Temperature (°C)

System
$T_{g0} = 0\,°C$
due to solvent

$T_{g\infty}$

Substrate degradation

Degradation

Solvent remobilisation from substrate

Devitrification

Resin to $T_{g\infty}$

NON GELLED RUBBER

'GELLED RUBBER'

Pseudo gel curve

Gelled glass

Gelation curve

Vitrification Curve

Liquid

To time = ∞

Non gelled glass

In time

**c**

Temperature (°C)

$T_{g0} = 0\,°C$
due to solvent

Degradation

Devitrification curve

NON GELLED RUBBER

GELLED RUBBER

Gelled glass

Pseudo gel curve

Vitrification Curve

Gelation curve

Liquid

To time = ∞

Non gelled glass (frozen solvent)

In time

unashamedly adhesives-oriented title, this presentation would not be complete without speaking, unfortunately only too briefly, of wood preservation. It has often occurred to me that some universities have kindly asked me to do a presentation on wood preservation without realizing that the "preservation" man and the "adhesives" man wore the same hat, and vice versa! This is just to illustrate how far apart these two specialities are from each other. I got into wood preservation by complete chance, at the very beginning of 1980, when a public service rearrangement landed the institute I worked for with the national preservation project, 15,000 samples in three testing grounds, and no graduate personnel having had followed the project for the preceding twenty years: this is what I call "desperation alley"! At that time wood preservation had been dominated for decades by the microbiological approach (and quite correctly, this surely being the most important approach to this science): we had to go the chemistry and treatment process route, simply because this is all we could contribute: it was lucky we did! The two routes have been experiencing a considerable revival ever since and are still very "fashionable". It is enough here to just list and reference what I consider our (many other people participated) main achievements in this field: (1) a pretty extensive series of studies clarifying the chemistry of CCA, CCB and other inorganic wood preservatives, and of their interaction chemistry and kinetics with wood and wood constituents (Kubel and Pizzi 1982a, b; Pizzi 1981c, d, 1982b, c, d, 1983e, 1990c, d; Pizzi et al. 1984a, b; Pizzi and Kubel 1982, 1983; Pizzi and Vogel 1982). There was already very important work done on this by Dahlgren and Hartford (1972), but our work went much further, defining chemical compounds formed, series of reactions occurring, and quantifying their kinetics at the level of both wood and its constituents. Even structural molecular mechanics studies of the preservative/wood constituents interactions were done on this (Pizzi 1990c, d). It must be pointed out that several other research groups have also contributed considerably to this work since, but this work still constitutes a good basis of the chemical knowledge on CCA (and I hope my colleagues in this field will forgive me for this perhaps rather biased opinion). The consequences of the reactions and interactions clarified in (1) lead to a number of rather important applied/industrial consequences, namely (2) the first system to minimize/eliminate CCA sludging during industrial treatment, this having caused considerable financial losses, incredible pollution and often appalling level of timber treatment. Our system, and other researchers' variations on the same subject are still used extensively in industry. Our main paper on this has the signal honour to be the only "foreign" one quoted in the American preservation standard (I can thank Hartford for this) (Pizzi et al. 1984a). (3) The banning of CCA type B. Very few people know that South Africa was the first country to ban the use of CCA type B on the basis of it being a chemically unbalanced, dangerous and polluting formulation as the excess of arsenic in it had no hope to get/stay fixed in the timber. It is even less known that it was me who made the final decision to have it banned. Three months later New Zealand followed suit, and five months later Sweden did too. (4) The finding that high temperature drying of CCA treated timber leads to some differences in the reactions occurring with consequent losses in effectiveness due to both insolubilization and further leaching (Conradie and Pizzi 1987) (Fig. 20). (5) The development and codification of the equations to calculate with ease the CCA fixation time under different conditions (Pizzi 1981d).

$$\text{time} = 0.462/k_{\text{ads}} + 2.303/k_{\text{red}}$$
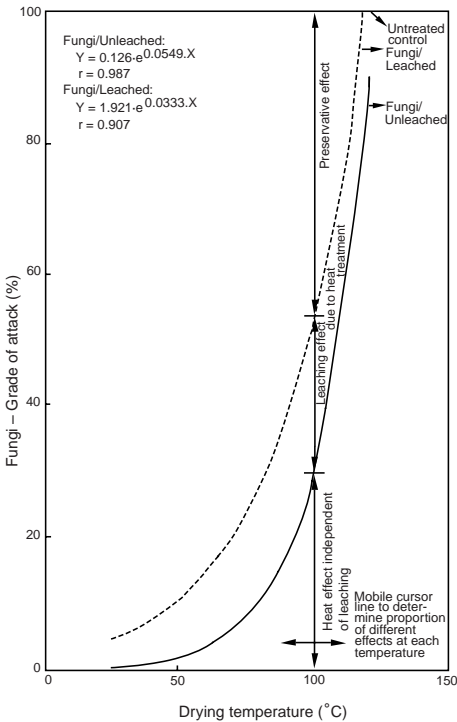
**Fig. 20.** Relationship between drying temperature and average grade of fungal attack of CCA treated timber before and after leaching after 8 months exposure in accelerated fungal tests (from Conradie and Pizzi 1987)

where $k_{ads}$ and $k_{red}$, respectively, are the rate constants of CCA adsorption and of $Cr^{VI}$ reduction.

There is some chairman of some wood treaters' association on record to have said sometime during the last two years that nothing exists in this line. Unfortunately it is just my fault, as the work was published in a fairly obscure Austrian journal (still abstracted by the Forestry Abstracts though) (Pizzi 1981d; Pizzi et al. 1984). Some more modern data could definitely benefit this equation, especially for the second term: there is a challenge for some bright young researcher! (6) The development of the low toxicity wood preservative systems based on the fixation on the wood of unsaturated soaps of copper: the copper linoleates (in reality copper sunflower oil soaps) for which more than 30 years field trial results exist (Pizzi 1993a, b), and the copper rosinates (Pizzi 1993a, b). (7) The very much more recent development of the non-toxic, class 3 and class 4 wood preservatives, based on protein borates (mainly albumin borates and soy protein and soy flour borates) (Thevenon et al. 1997, 1998a, b, c), which are now well on the way to official certification for industrial use in France. (8) The elucidation of the chemical reactions involved in the so-called thermally retified wood (Tjieerdsma et al. 1998), and the identification of which is the catalyst of the system. Unfortunately, also the identification, in small amounts to be sure, of the presence of toxic phenanthrene and anthracene structures induced by the wood thermal degradation caused by this process which gives to the timber thus treated its characteristic colour and odour (Kamdem et al. 2000), the disproving that at least

for some of these processes the claimed resistance to microorganisms biological attack is not valid (Kamdem et al. 1999), and the ascertainment that the very real improvement in dimensional stabilization is due to the stress release consequence of extensive cell wall degradation (Kamdem et al. 2000). (9) The first indications that wood treatment with carboxylic acids anhydrides, in particular acetic anhydride, does not only improve the timber dimensional stability by exclusively bulking it (as believed up to then) at cellular level by acetylation, but that other reactions and rearrangements leading to a proportion of further wood constituents cross-linking occur and also contribute to the improved dimensional stability obtained (Pizzi et al. 1994b; Boonstra et al. 1996, 1997). (10) The development and application of suitable and effective fire retardants for mining timber (as no publications exist on this, it must be noted that a good part of the merit is shared with W.E. Conradie, H. Vermaak and A. Jansen). This was an interesting subject as underground mining fires are exclusively due to timber and caused 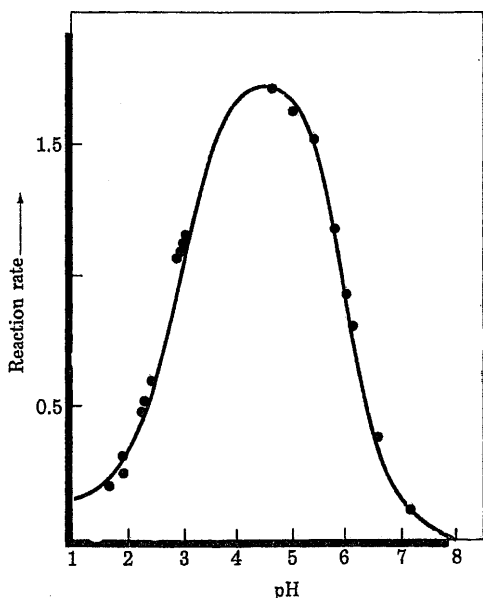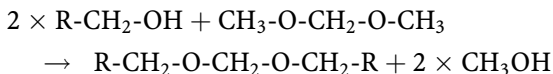revenue losses in lost production and damages running into billions of dollars. The major problems were the severe limitations on expenses for the fire retardants/loads which were possible for the many thousands of cubic metres of timber that are used in deep gold mines. The results were indeed excellent, with very simple inexpensive materials used (no new extraordinary knowledge, but rather a new industry was created): in 1980 no mining timber was treated in South Africa, while by 1995 already 25 thousand tons of fire retardant salts were produced and applied (at approx. 4% salts on dry timber), and major underground fires were drastically cut to less than 10% by the application of this simple but very appropriate technology: in 1986 we even got a local industrial prize for this development.

### Imines/acetals for resins chemistry

It would not be fair in this lecture to avoid to express at least one controversial opinion on something, so here it goes:

$$O{=}CH_2 + {:}NH_2CONH_2 \rightleftharpoons {}^-O\text{-}CH_2\text{-}N^+H_2CONH_2 + HOCH_2NHCONH_2$$

$$H_2C{=}NCONH_2 \rightleftharpoons H_2C{=}N^+HCONH_2 + HOH_2C\text{-}NHCONH_2$$

Fahrenhorst (1955) has foreseen the formation and existence of the azomethin group, without, however, presenting any proof, nor even searching for its existence. The series of reaction shown above comes straight out of a book detailing the formation of imines and the relation of reactivity as a function of pH is just the inverse of the classical gel time vs. pH curve of UF resins (Fig. 21). The final azomethin group is easily detected by ^{13}C NMR, being in reality the C=O group substituted. Furthermore, the curve of the rate of reaction of an aldehyde/ketone with an amine or amide to form imines or imides is shown in Fig. 21 and presents the same trend as the gel time curve of UF and MUF resins. In reality, as shocking as this might initially appear, advancement and hardening of aminoplastic resins through azomethin groups is the same accepted mechanism leading to the equivalent quinone methides in PF resins. UF resins NMR spectra and hexamine decomposition spectra, where the azomethin groups of the spectra are clearly indicated, as any ^{13}C NMR spectral tables, indicate clearly that the imines =C=N-transmits in the same region as what is accepted today as being the substituted ureas C=O shifts, have already been presented (Soulard et al. 1999;

**Fig. 21.** Reaction rate as a function of pH of an amine with a carbonyl compound closely mimicking the trend of the reactivity of melamine and urea with formaldehyde (McMurry 1992)
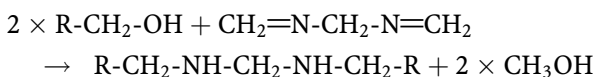
Pichelin et al. 1999). There is really no reason to prefer the latter to the former explanation, the clinching NMR evidence being the same for the two theories, the classical and the azomethin group one.

Equally unusual is the evidence for transacetalization reactions as the mechanism through which a good part of formaldehyde-based polycondensations also proceed. All these reactions, for UF, MF, MUF and PF resins for wood adhesives proceed in water where formaldehyde is not present as HCHO, but is rather present as methylene glycol $HOCH_2OH$. In some resins some small amount of methanol is produced in the system by the Cannizzaro reaction. The longer the reaction time and the higher the reaction temperature, the higher the amount of methanol which is present. Furthermore, MF resins, particularly PF resins and sometime also MUF resins, these latter ones much more rarely depending from the type of formulation used, are produced using methanol-stabilized formalin with a 9–12% content of methanol stabilizer. Formaldehyde is then present in the system as methylene glycol and as a series of ethers derived from methylene glycols such as $CH_3-O-CH_2-O-CH_3$, $CH_3OCH_2OH$, $CH_3-O-CH_2-O-CH_2-OH$, $CH_3-O-CH_2-O-CH_2-O-CH_3$ etc. In the case of methylol groups on the resin ($R-CH_2-OH$), these can easily react with the ethers which are abundantly present to form not only methylene ether bridges, but also $R-CH_2-O-CH_2-O-CH_2-R$ bridges. Many of the badly identified NMR signals in this region are nothing else than these types of bridges obtained by transesterification reactions. Resins often are distinguished by considerable differences in this NMR shift region, this not only differentiating the resins for potential emission for the known equilibrium $HO-CH_2-OH \rightleftharpoons$ ethers, but also forming longer, hence more flexible joints between phenolic and melamine nuclei, with better distribution of stress in the joint and hence better resin performance as regards mechanical
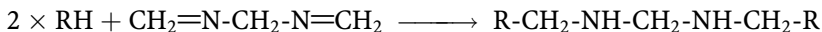
resistance of the joint (for example, better internal bond strength in a particleboard).

$$2 \times \text{R-CH}_2\text{-OH} + \text{CH}_3\text{-O-CH}_2\text{-O-CH}_3$$
$$\rightarrow \text{R-CH}_2\text{-O-CH}_2\text{-O-CH}_2\text{-R} + 2 \times \text{CH}_3\text{OH}$$

It is not that such a mechanism substitutes the classical methylene and methylene ether bridges ones, it is just an additional one, but when present in noticeable proportions, it does affect, generally positively, the performance of the adhesive. The same effect can be obtained by the same type of atoms configuration by substituting N for O. Thus, small amounts of immines/polyimines such as $\text{CH}_2{=}\text{N-CH}_2\text{-N}{=}\text{CH}_2$ obtained by hexamine decomposition and its acid anion stabilization, or equally well by the addition of small amounts of amonia or ammonium salts to formaldehyde (Pichelin et al. 1999), again will improve considerably the internal bond strength performance of both aminoplastic and phenolic resins (Pizzi et al. EU FAIR TC 96-1604, 1996–1999) according to, among other things, a similar mechanism.

$$2 \times \text{R-CH}_2\text{-OH} + \text{CH}_2{=}\text{N-CH}_2\text{-N}{=}\text{CH}_2$$
$$\rightarrow \text{R-CH}_2\text{-NH-CH}_2\text{-NH-CH}_2\text{-R} + 2 \times \text{CH}_3\text{OH}$$

and equally

$$2 \times \text{RH} + \text{CH}_2{=}\text{N-CH}_2\text{-N}{=}\text{CH}_2 \longrightarrow \text{R-CH}_2\text{-NH-CH}_2\text{-NH-CH}_2\text{-R}$$

## Conclusions

In this review I have cited in the references 160 of my present 265 papers in internationally referred journals and another 14 references (patents, book chapters etc.) out of a total of more than 500, so only a limited part of the subjects I have had the luck and the pleasure to address. It could not be otherwise in order to hold this review to a manageable size.

To conclude, while coming back to the literary field, after a John Steinbeck start, what is written above reminds me of the novel of Guy de Maupassant "A life: mine!" I thank you all to have had the patience to listen to it.

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