

# Thermomechanical analysis of the tannins of *Acacia Nilotica* spp. *Nilotica* as a rapid tool for the evaluation of wood-based adhesives

Z. Osman

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**Abstract** In this article, autocondensation reactions of *Acacia nilotica* spp. *nilotica* (Ann) tannin extracts solutions have been studied at several pH values by thermomechanical analyzer (TMA). TMA has been chosen for this study as it has been shown to give results more rapidly and more precisely than panels. It also tends to exaggerate the differences in results which render it an excellent tool for comparison. Therefore, autocondensation reactions were studied and compared with its polycondensation reactions upon addition of different hardeners such as paraformaldehyde, urea, and PMDI at same pH values. The aim was to evaluate the tannin's reactivity and therefore its suitability for the production of commercially and technically viable tannin adhesives for wood products. The results of autocondensation showed that the maximum Young's modulus values (3300 and 3600 MPa) were obtained at pH 4. However, these values have been achieved at high temperature (160 and 208 °C). Results of copolymerization reaction of the tannins with different hardeners revealed that some of these co-reactants were found to depress tannins autocondensations, while others appear to enhance the formation of the final networking. Polycondensation of the Ann tannins with 8% paraformaldehyde and 10% PMDI gave the maximum Young's modulus values at lower temperature (91–101 °C) and acidic pH5. However, the addition of 20 and 30% PMDI achieved the best Young's modulus values 2300 and 3300 MPa, respectively, at pH 4. Furthermore, the obtained values were comparable to those obtained by the addition of urea and the self condensation reactions. This is very important for

particleboard production from economical and technical point of view. It has been noticed that the addition of hardeners lowered the temperature of hardening, and the obtained values were more consistent with the pH acidity. The study concluded that the tannins of Ann were very reactive, and therefore, it could be a potential precursor for particleboard adhesives. The results also indicated that the tannins can be used alone, and it would possibly produce zero emission environmentally friendly particleboard.

**Keywords** Tannins · Autocondensation · Copolymerization · *Acacia nilotica* spp. *nilotica* · Thermomechanical analysis

## Introduction

Tannins are natural phenolic structures present in numerous wood species particularly in the southern hemisphere [1]. They are mostly accumulated in their barks, although, in some instances, they may be found in the leaves and the fruits. Their traditional use in leather manufacturing has been extended to other applications one of which is the formulation of wood adhesives, a domain which is steadily gaining importance because of its ecological and environmental relevance [2].

Extensive research, particularly by Pizzi and coworkers [1, 3], has optimized formulations for wood adhesives in which tannins alone and/or, together with appropriate crosslinking agents, provide materials displaying properties comparable to those of conventional phenol- and urea-formaldehyde counterparts. Some of these formulations represent the major steps forward in the very important wood processing industry (particle boards, etc.) because they minimize formaldehyde emissions, thus solving a

Z. Osman (✉)  
National Center for Research, Institute of Technological  
Research, P.O. Box 2404, Khartoum, Sudan  
e-mail: zeinabosm@yahoo.com

serious ecological problem associated with the use of conventional wood adhesives indoors, while calling upon the exploitation of a readily available renewable resource.

The autocondensation of the tannin without the addition of any aldehyde has already gained a lot of attention [4]. This reaction is based on the autocondensation of the tannin due to the opening of the link O1–C2 of the tannins of gallo catechin type (ring A of type Phloroglucinol and ring B of type pyrogallol) which drives then to autocondensation between C2 and the free sites in C6 or C8 on the unit of gallo catechin [5].

Extensive studies on the radical mechanisms of tannin's autocondensation reaction induced by bases and Lewis acid has already been described [5–9]. Hardening of tannins without the addition of any aldehyde has also been examined by Pizzi and coworkers [10]. The results revealed that in spite of the differences in polyflavonoid tannin's structure and reactivity, effective wood particleboard bonding could be obtained. Nevertheless, these autocondensation reactions yielded bonds of interior grade qualities. The reaction of hexamine with tannins in aqueous solutions was analyzed by Pizzi [11, 12], who showed that hexamine is not a formaldehyde-yielding hardener, and thus, it leads to cured products with low formaldehyde emissions.

Extensive research study on the reaction of the tannins and hexamine has been reported [13, 14]. Results have shown that Mimosa and Pine tannins have cured with hexamine, and produced particleboard have thermal and mechanical properties adequate for using in some industrial applications. Most of these studies focused on the inducing of tannins autocondensation reaction using hardeners which did not release formaldehyde. Ballerini and coworkers [15] reported that zero emission panels can be produced by reacting tannins and glyoxal.

For the analysis of the autocondensation reactions, tannin and its copolymerization with coreactants, it must be considered that different pH (acidic, basic) can influence in chemical pathways. Pena and others [16] have proved that autocondensation reactions occur in mimosa tannin solutions at alkaline pH. It has been noted too that autocondensation reactions can occur at room temperature resulting in an increase of viscosity. A fact must be considered in adhesive formulation because an important parameter as the pot-life could seriously be modified. Furthermore in all of the reported studies with different tannins' structures, it has been noticed that autocondensation and copolymerization were favored at alkaline pH as the effect of lower pH (acidic) was very small.

In this study, autocondensation reactions and copolymerization reactions have been thermomechanically studied at different acidic pH values to determine the effect of pH coupled with the tannin's structure on the chemical pathway.

## Materials and methods

### Preparation of tannin's extracts

Preparation of tannins' extracts were carried out according to a reported method [17]. A solution of 40% concentration was prepared from the spray dried powder of Ann tannins.

### Preparation of thermomechanical samples

Ann tannins alone and in mixture with different hardeners were tested dynamically by a thermomechanical analysis (TMA) using plies of total dimensions of  $21 \times 6 \times 0.6$  mm, and relative humidity of 8–12% were bonded with the resin layer of 40  $\mu\text{m}$ . The samples were tested isothermally at constant heating rate of  $10^\circ\text{Cmin}^{-1}$ , from 40 to 250  $^\circ\text{C}$  with a Mitter TMA 40 apparatus in three-point bending on a span of 18 mm and an alternating force cycle of 0.4 N on the specimen to measure the modulus of elasticity, the minimum value of deflection, and the degree of freedom of the tested adhesives.

Calculation of the average number of degree of freedom ( $M$ ):

The average number of degrees of freedom was calculated according to a previously reported study by Pizzi et al. [18] and Probst et al. [19], namely

$$E = km/(\alpha f)$$

where  $k$  is a constant dependant upon the testing condition (sample's dimensions), and the value used for this study was 16. Here  $m$  is the average number of degrees of freedom between the crosslinking nodes of a hardened network, and  $E$  is the sum of energy of interaction at the interface of the polymer and the wood; then  $f$  is the deflection caused by the TMA;  $\alpha$  is Flory's coefficient of branching for polycondensates.

### Studied systems

The following formulations were prepared and thermodynamically studied at different at different pH values (4, 5 and 7). All hardeners were added the oven dry weight of the tannins.

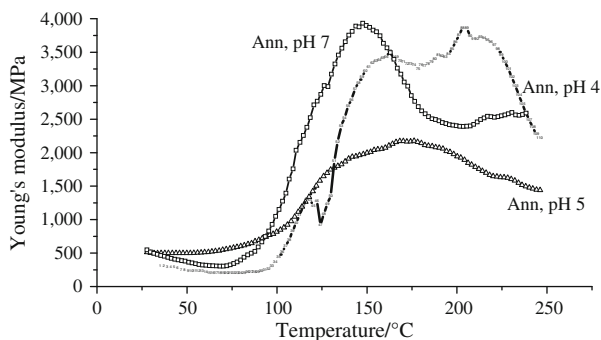
1. Tannin of Ann alone.
2. Tannin of Ann + 8% paraformaldehyde.
3. Tannin of Ann + 5% paraformaldehyde + 5% urea.
4. Tannin of Ann + 5% paraformaldehyde + 10% PMDI.
5. Tannin of Ann + 5% paraformaldehyde + 20% PMDI.
6. Tannin of Ann + 5% paraformaldehyde + 30% PMDI.

## Results and discussions

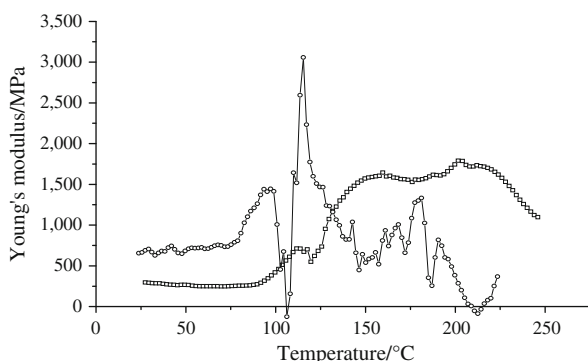
### Autocondensation of Ann tannins

Obtained TMA curves at different pH (4, 5, and 7) (Fig. 1) showed an increase in Young's modulus values as a function of temperature. The autocondensation reaction produced a succession of plateaus which converted to peaks by plotting the first derivative as shown in Fig. 2.

Table 1 summarized the values of Young's modulus, minimal deflection ( $f$ ), and degrees of freedom ( $m$ ). At pH 4, the curve of first derivative showed the presence of three principal peaks. The first peak at relatively lower temperature 118 °C indicating the formation of the entanglement network and gave a value of Young's modulus of 1676 MPa. The Formation of this entanglement network may be due to the reaction of the same phenolic nuclei, when the molecular mass of the polymer ( $M$ ) reached the critical molecular mass ( $MC$ ) [20]. It has already been proven that as fast as this relation is attained, the more the tannin is reactive. This could be interpreted by the low value of ( $m$ ) which indicated the degree of crosslinking and tightness of the polymer network.



**Fig. 1** Young's modulus as a function of temperature for autocondensation of Ann tannins at different pHs



**Fig. 2** Young's modulus curve and its first derivative for Ann tannins at pH 4

Unlike other studied tannins which are commercially used (Pine, Mimosa, Quebracho, and chestnut tannins), the tannin of Ann contained high ratios of prodelphinidin [21]: hence, a very reactive A-ring of phloroglucinol and of B-ring of catechol and pyrogallol. These rings are becoming very reactive at higher temperature [22] and gave rise to another two peaks at (160 and 208 °C). The values of degrees of freedom and the minimum relative deflection, 1.4 and 15.6, respectively, were small, indicating again the tightness of the network formed.

It was observed that when the pH acidity decreases, tannin's autocondensation was depressed [16], giving rise to lower values for Young's modulus and comparatively higher values for ( $f$ ) and ( $m$ ). It must be noted that the autocondensation reaction occurred at lower temperature when compared with those achieved at pH4. Notably, these results were in contrary to a study reported by Garcia et al. [20] where the effect of the lower pH (4.5) produced was very small on the tannin's autocondensation. It seems that the types of tannins and percentages of prodelphinidin and procyanidin have their impact on these reactions, a phenomenon that should further be investigated.

It has already been reported that autocondensation of a faster tannins as Pine produces a less-crosslinked network. This could be interpreted with the high values of deflection and degrees of freedom [23]. Furthermore, the Ann tannins though of prodelphinidin–procyanidin type expected to be more reactive than the Pine tannins, gave excellent results at acidic pH and without the addition of any catalyst [18, 19].

### Polycondensation reaction of tannins with 8% paraformaldehyde

Being of phenolic nature, the tannins behave similar to the phenol when they reacted with the formaldehyde. According to previous studies, the reaction is always very rapid in an alkaline media, bridges methylene on the reactive positions of the A-ring which leads to the formation of polymer network [24]. Unexpectedly, the high reactivity of the tannins of Ann has been again observed at a lower pH (acidic).

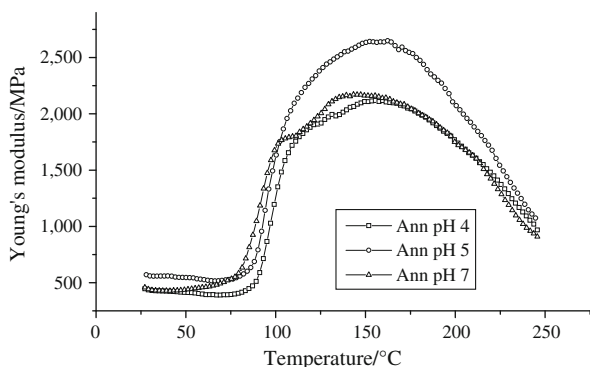
The reactivity of the tannin of Ann with 8% of para formaldehyde varies according to the pH values (Fig. 3). At pH 4, the value of the Young's modulus was relatively low (2150 MPa) when compared with the one achieved at pH 5 (2800 MPa). The unexpected results obtained at pH 4 were due to the fact that the autocondensation reaction which leads to an increase in the viscosity of the tannins depresses its reaction with the paraformaldehyde [25].

Therefore, the best values for Young's modulus,  $m$  and  $f$  were obtained at pH 5. Furthermore, the reaction was begun at a lower temperature (94 °C) when compared with the autocondensation reaction.

**Table 1** Temperature (°C), values of Young's modulus, relative deflection, and the number of the degrees of freedom for the formulations containing Ann and different hardeners

Formulations	Temperature/°C (Maximum values of Young modulus/MPa)	Relative deflection/ $\mu\text{m}^*$	Average degrees of freedom in number*	
Ann alone, pH 4	118 (1676)	15.6	1.4	
	160 (3300)			
	208 (3660)			
Ann alone, pH 5	111 (1300)	27.2	2.8	
	133 (1100)			
Ann alone, pH 7	119 (2200)	16.1	1.4	
	162 (1500)			
Ann +8% paraformaldehyde				
	pH 4	97 (2150)	16.5	1.5
	pH 5	94 (2800)	12.6	1.0
	pH 7	91 (2000)	17.6	1.6
Ann +5% paraformaldehyde +5% urea				
	pH 4	94 (2300)	15.4	1.3
	pH 5	91 (1900)	18.6	1.7
	pH 7	85 (1750)	20.2	1.9
Ann +5% paraformaldehyde +10% PMDI				
	pH 4	105 (2250)	15.7	1.4
	pH 5	101 (2690)	13.2	1.1
	pH 7	87 (2100)	16.8	1.5
Ann +5% paraformaldehyde +20% PMDI				
	pH 4	99 (2300)	15.4	1.3
	pH 5	101 (2300)	15.4	1.3
	pH 7	88 (1710)	20.7	2.0
Ann +5 paraformaldehyde +30% PMDI				
	pH 4	99 (3300)	10.7	0.7
	pH 5	102 (2750)	12.9	1.1
	pH 7	85 (2800)	12.6	1.0

\*The relative deflection ( $f$ ) and the average degree of freedom in number ( $m$ ) were calculated from the maximum values of Young modulus, ( $\infty = 0.135$ )

**Fig. 3** Young's modulus as a function of temperature for Ann tannins and 8% paraformaldehyde at different pH values

Neutral pH 7 was found to lower the temperature of hardening and in most cases the Young's modulus values achieved were either better than or comparable to those obtained by pH 5.

It could be deduced that the reaction of the tannins with paraformaldehyde would be more favorable at alkaline pH [26, 27], and this will be studied in a future study.

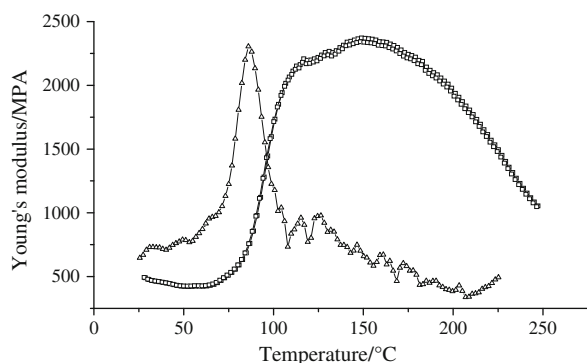
At acidic pH where the tannins alone are very reactive, the addition of paraformaldehyde seems to yield slightly less improvement to the final network. This is due to the rapid autocondensation reaction which leads to the formation of less-reticulated network [23]. It may be also due to the high tannin's reactivity with formaldehyde that leads to the formation of a premature and immobilized polymer network. In any case, the speed of reaction of the systems

tannin paraformaldehyde depends directly on the value of the pH. Ann being of phloroglucinol type, its reactivity with the paraformaldehyde is very high, and its usage as glues may need to be handled with special attention to pH values [28, 29]. Furthermore, the achieved results were still better than those obtained with the other types of tannins [16, 24].

#### Polycondensation reaction with 5% paraformaldehyde and 5% urea

The addition of urea to tannins/paraformaldehyde hardening system was already known and studied. Urea was found to favor this system in all studied cases with different types of tannins [23]. It also functions very effectively as formaldehyde scavenger and tannin's stabilizer [30]. However, in the case of Ann tannins, the obtained results were unexpectedly inferior to those obtained by the paraformaldehyde alone. The best value of the Young's modulus (2300 MPa) was achieved only at pH 4, and at a relatively low temperature of 94 °C. This could be attributed to the fact that the Ann tannins were fast reacting tannins; therefore, the addition of urea does not improve the crosslinking which has been reported in the case of slower reacting tannins. Nevertheless, the degradation of the hardened polymer network (Fig. 4) begun early at a lower temperature of 100 °C.

At pH 5 and 7, (Table 2) the values of Young's modulus and the deflection were 1900 and 1750 MPa and 18.6 and 20.2, respectively, lower than those obtained at pH 4. Therefore, in general, the addition of urea to tannin\paraformaldehyde did not ameliorate the system, in contrary it produces small values of Young's modulus than those achieved by the tannin's autocondensation or by its reaction with paraformaldehyde. This means that the urea as a hardener depressed the effect of tannin's autocondensation as well as its copolymerization with the paraformaldehyde.



**Fig. 4** Young's modulus and its first derivative as a function of temperature for the tannins of Ann at pH 4 +5% urea +5% paraformaldehyde

It is worth noting that the addition of urea to tannins/paraformaldehyde system was known to yield better results at lower pH values in the case of Pine and modified Quebracho tannins. However, these values of Young's modulus,  $f$  and  $m$  were still lower than the ones achieved by the Ann tannins [23].

#### Copolymerization reaction with the diisocyanate

The addition of the polymeric 4,4'-diphenylmethanediisocyanate polymer, PMDI, to the tannins/paraformaldehyde system was already known and has been commercially used for several years [31]. It is used in a small amount to improve the glue's qualities. It is mainly used with the basic adhesives such as tannins [32, 33], and principally with the phenol formaldehyde [34] and phenol urea formaldehyde [35].

The addition of 10% of PMDI and of 5% of paraformaldehyde to the tannin of Ann, in aqueous solution, improves the glue quality. The hardening reaction of the system tannins/PMDI/formaldehyde generally produced high Young's modulus values (Fig. 5). The best results are obtained at pH 5 (2690 MPa,  $m = 1.1$  and  $f = 13.2$ ). It has been observed that the increase of the pH of the tannins lowered the temperature of hardening. Furthermore, at pH 7, the hardening begins at 78 °C but the value of Young's modulus was small than the one obtained by pH 4 and 5. This may due to the formation of polyureas between the tannins and PMDI which leads to the development of a less tight premature copolymer.

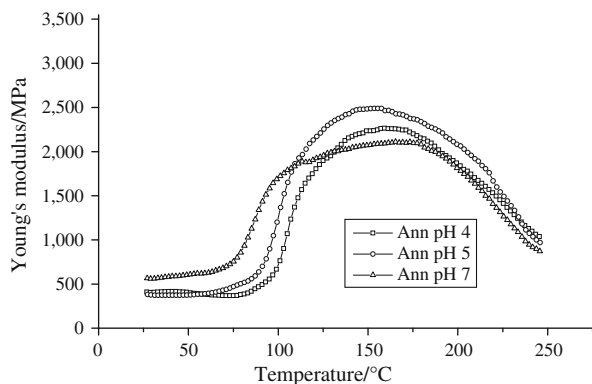
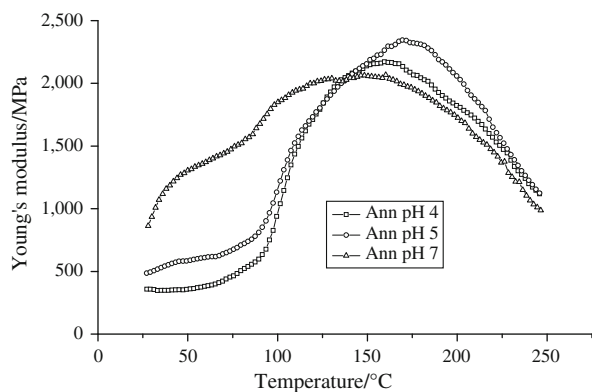
When the amount has increased to 20%, the system gave almost similar results to those obtained by the addition of only 10% PMDI (Fig. 6). It did not bring any improvement when compared with this system. This is very important from technical and economical point of view.

However, when the percentage of PMDI was increased up to 30% the obtained results were very interesting at the three pH values (Fig. 7). The value of Young's modulus obtained at pH 4 was the highest (3300 MPa) in comparison with the one achieved at pH 5 and 7 where Young's modulus values were 2750 and 2800 MPa, respectively.

It has been observed that a small amount of PMDI (10%) added to the systems tannins/paraformaldehyde can improve the quality of the adhesive by increasing the level of crosslinking of the hardened copolymer network. This could be interpreted by the low values of  $m$  (1.1–1.5). In general, the copolymerization between the tannins/paraformaldehyde and the PMDI was favorable at pH 4 and 5, as at these pHs, the Young's modulus values produced were higher than those obtained at pH 7. Nevertheless, at pH 7, copolymerization was very marked, and the entanglement networks were appeared earlier and at lower temperatures (85–88 °C) [36].

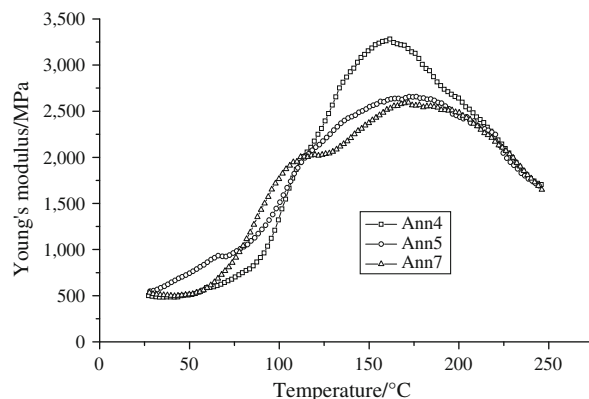
**Table 2** Maximum young's modulus values as a function of pH and the temperature

Copolymers	pH 4	pH 5	pH 7
Ann alone (auto condensation)	3660 (208 °C)		
Ann +8% paraformaldehyde		2800 (94 °C)	
Ann + 5 paraformaldehyde +5% urea	2300 (94 °C)		
Ann +5% paraformaldehyde +10% PMDI		2690 (101 °C)	
Ann +5 paraformaldehyde +20% PMDI	2300 (99 °C)	2300 (101 °C)	
Ann +5% paraformaldehyde +30% PMDI	3300 (99 °C)		

**Fig. 5** Young's modulus as a function of temperature at different pH for the tannins of Ann +5% paraformaldehyde +10% PMDI**Fig. 6** Young's modulus as a function of temperature and different pH values for the tannins of Ann +5% paraformaldehyde +20% PMDI

Furthermore, when the amount of PMDI was increased to 20 and 30%, the temperature of hardening was lowered at pH 4 and 7. At pH 4, the effect of autocondensation enhances the copolymerization and therefore leads to the early formation of the entanglement network. While at pH 7, copolymerization was the dominating reaction.

We observed that a mixture of tannin of Ann/paraformaldehyde/PMDI improves the quality of the glue and produced a tightened polymer network. The reason was due to the reaction between the methylol group produced from

**Fig. 7** Young's modulus as a function of temperature for Ann +5% paraformaldehyde +30% PMDI at different pH values

the reaction of the tannin with the paraformaldehyde which then reacts with isocyanate to form a urethane bridge [23, 37].

## Conclusions

From Table 2 which summarized the best results obtained by the reaction of Ann tannins with different co-reactants, we can conclude the following:

- Unlike other studied tannins [16, 23], Ann tannins were reactive at their initial acidic pH. Therefore, there is no need to modify the pH when used as tannin-based adhesives.
- From the achieved results of autocondensation and when compared with those achieved by other tannins (Pine, Pecan), it appeared that Ann tannins are very reactive and may produce exterior grade panels.
- The auto condensation of Ann showed that the tannin reactivity at high temperature is due to the reactivity of B-ring of catechol type which increases at higher temperature and contributes greatly to the formation of the network.
- The addition of 8% of paraformaldehyde in comparison with the systems 10% or 20% of PMDI was

economical. However, using a low percentage of paraformaldehyde with PMDI is beneficial as it reduced the formaldehyde emission.

- It should be noted that the urea gave the lowest strength than when formaldehyde is used alone, as it does not participate in cross-linking, and hence, urea cannot be used as a formaldehyde emission reducer, other co-reactants as hexamine and silica should be tried in a future study.
- The copolymerization of Ann with the PMDI begun at relatively high temperature (99101 °C) when compared with the other hardeners (paraformaldehyde and urea) and for the same pH, the increase of the quantity of PMDI was found to increase the system reactivity as indicated by the high values of Young's modulus and the lower values of *m*.
- It should be noted that the addition of 30% PMDI gave the best results at moderately low temperature. Furthermore, these results are similar to those obtained by tannin's autocondensation. Panels should be made from both to confirm the qualities.

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