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CURING PROCESS OF PHENOL-UREA-FORMALDEHYDE-TANNIN (PUFT) ADHESIVES
Kinetic studies by DSC and DMA

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Phenol-urea-formaldehyde-tannin (PUFT) adhesives have been prepared by copolymerization at room temperature of pine bark tannins with phenol-urea-formaldehyde (PUF) prepolymers prepared under varying operating conditions. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) have been used to analyse the curing of prepolymers and adhesives. DSC curves were obtained at three different heating rates and, by means of the Model Free Kinetics isoconversional method, chemical conversion *vs.* time at a given temperature was obtained. Mechanical conversion was calculated from DMA storage modulus data for those adhesives which gave the best results for plywood and MDF boards.

Keywords: *chemical cure, DMA, DSC, kinetics, mechanical cure, phenol-urea-formaldehyde-tannin adhesives*

Introduction

In the last years there has been a high growth of *Eucalyptus globulus* plantations in Galicia (NW of Spain) and new board facilities which use exclusively eucalyptus wood have been installed. Eucalyptus wood shows excellent mechanical properties, it is a hardwood with high strength and density. However, the utilization of commercial phenolic adhesives in the manufacture of exterior grade eucalyptus plywood requires a very rigorous drying process of the veneers to a 4–5% of humidity in order to avoid buffing in the hot press. This means a considerable energetic cost together with a reduction of the veneer quality.

Pinus pinaster is the tree species most often employed at industrial scale in Galicia. Its exploitation requires previous debarking, which makes this lignocellulosic material, mainly used as a fuel, the most abundant industrial waste in the timber industry of Galicia, with an output of approximately 100 000 t/year.

Thus, for a profitable exploitation of these Galician natural resources, it is very interesting, on one hand, to formulate wood adhesives that overcome the above mentioned drawbacks and, on the other, to search for alternative uses of pine bark based on its chemical composition. In an earlier stage, phenol-formaldehyde-tannin (PFT) adhesives were synthesized using tannin extracts from *Pinus pinaster* bark. The application of these adhesives to manufacture eucalyptus plywood showed promising results. These resins implied, with respect to conventional resole resins, not only a reduction of the consumption of petrochemical phenol, which was replaced with a renewable resource, but also the improvement of the application properties of the adhesive [1].

In a second stage, the formulation of phenol-urea-formaldehyde-tannin (PUFT) adhesives was studied. These PUFT adhesives were prepared by copolymerisation of *Pinus pinaster* bark tannins with phenol-urea-formaldehyde (PUF) prepolymers. A detailed analysis by ^{13}C-NMR spectroscopy together with an evaluation of the resin properties was performed in order to find out suitable preparation conditions of prepolymers prior to their copolymerisation with tannins [2]. PUFT adhesives were employed to prepare exterior grade medium density fiberboards (MDF) [3] and plywoods according to European standards.

The aim of this work is to study the curing process of the phenol-urea-formaldehyde-tannin adhesives using thermal analysis techniques: differential scanning calorimetry (DSC), which allows to determine the energy released during the curing process (the curing enthalpy, ΔH) and to evaluate the rate and extent of chemical conversion, and dynamic mechanical analysis (DMA), which accounts for the changes in the mechanical properties occurring during the conversion of the liquid resin into a crosslinked structure.

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Experimental

Preparation of PUF prepolymers and PUFT adhesives

PUF prepolymers were prepared in two stages considering the following variables: reaction time, reaction pH and the order of addition of reagents, as described in López-Suevos and Riedl [3] and Vázquez *et al.* [2]. The PUFT adhesives were prepared by copolymerization of 5–17% of tannins (35% aqueous solution) based on the mass of the liquid PUFT, with the PUF prepolymers at room temperature during 16–18 h. Table 1 describes the preparation conditions of prepolymers and adhesives.

The tannin extraction from pine bark was conducted under the following conditions, optimized in a previous work [4]: NaOH concentration 5% (based on oven dried bark), solid/liquid ratio 1:6 (mass/mass), temperature 90°C and time 30 min.

Differential scanning calorimetry (DSC) experiments

DSC measurements were carried out in a Mettler-Toledo DSC 821^e apparatus, equipped with a sample robot. A resin sample (10–20 mg) was sealed in a 120 μL medium-pressure stainless-steel crucible with a Viton O-ring that can withstand pressures up to 2 MPa. The temperature range scanned was from 25 to 250°C and three heating rates were used per adhesive: 2, 5 and 10°C min^{-1}. Temperature and enthalpy calibrations were conducted with indium.

The results were analysed using the STAR^e software supplied by Mettler-Toledo. The kinetics models used were the Borchardt and Daniels model (*n* order kinetics) and the Model Free Kinetics isoconversional method [5].

Dynamic mechanical analysis (DMA) experiments

DMA measurements were carried out in a 1-DMTA-V-3 equipment from Rheometrics Inc. Rectangular glass plates of 25.16·9.15·0.15 mm were employed as supports. A drop of adhesive was spread on each of five glass plates and then they were stacked. Another sample consisting of only glass plates was used as control. Both ends of the sample were clamped to a rigid frame with a torque of 15 cN.m, and the drive shaft was clamped to the centre of the sample. The choice of a dual cantilever deformation mode was based on the fact that it favours the strain of the less stiff material, in this case, the adhesive between the more rigid supports [6].

The dynamic time sweep tests were conducted in the following conditions: frequency = 1Hz, strain amplitude = 0.1%, and 140°C and 30 min or 120°C and 40 min. The DMA tests were carried out only on the PUFT adhesives which gave the plywood (PUFT(1.40)–17%) and medium density fiberboards (PUFT(1.40)–10%) with the highest mechanical properties.

Results and discussion

Figure 1 shows the DSC curves obtained at a heating rate of 10°C min^{-1} for the PUF(1,40) prepolymer and the PUFT(1,40)–17%, PUFT(1,40)–15%, PUFT-(1,40)–12% and PUFT(1,40)–10% adhesives.

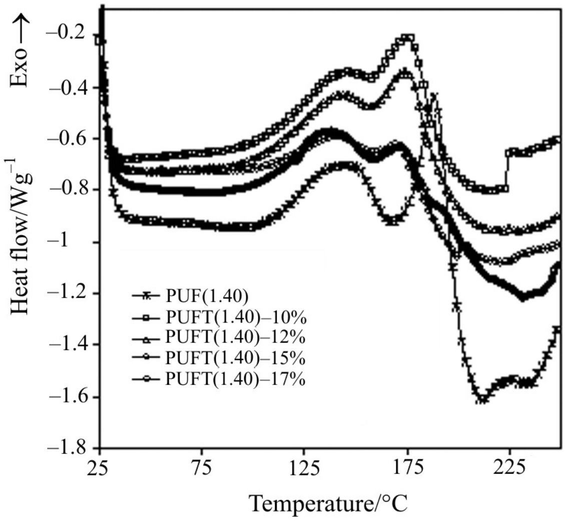

Fig. 1 Experimental DSC curves of PUF (1,40) prepolymer and PUFT(1,40)–17%, PUFT(1,40)–15%, PUFT(1,40)–12% and PUFT(1,40)–10% adhesives at a heating rate of 10°C min^{-1}

The PUF DSC curves present an exothermic peak with a maximum between 146 and 149°C. This peak was associated with the condensation of methylol groups with phenol to form methylene bridges and the condensation of two methylol groups to form dibenzyl ether bridges [7]. All of these prepolymers show a split peak with a second maximum at higher temperatures (186.1–195.6°C) attributed to reactions such as the condensation of the dibenzyl ether bridges to methylene bridges, eliminating formaldehyde, which demand higher temperatures as polymer mobility is reduced. Phillips *et al.* [8] found this split on phenolic resins with solid contents above 45% and the separation between the peaks was more evident the higher the solid content. Holopainen *et al.* [7] found the split when modifying the *F*/*P* ratio, the peaks being more separated the higher this ratio. The high concentration of methylol groups when the *F*/*P* ratio increases, favours the formation of methylene and methylene ether bridges. As a result, mobility is again reduced and the second peak is shifted to higher temperatures.

Table 1 Preparation conditions and properties of PUF prepolymers and PUFT adhesives

Prepolymer	Non-volatile solids/%	$\mu_{25°C}$/ mPa s	Reaction time		Reaction pH		Reactives		Adhesive	Non-volatile solids/ %	Tannins/% by mass of adhesive	Application
			1st stage/h	2nd stage/ min	1st stage	2nd stage	1st stage	2nd stage				
PUF (1,40)	41.1	13.5	1	40	3.0–3.5	9.5-10.0	CHOH Phenol	CHOH Urea	PUFT (1,40)–17%	38.9	17	Plywood
									PUFT (1,40)–15%	39.1	15	MDF
									PUFT (1,40)–12%	38.8	12	MDF
									PUFT (1,40)–10%	39.6	10	MDF
PUF (2,40)	39.9	14.8	2	40	3.0–3.5	9.5-10.0	CHOH Phenol	CHOH Urea	PUFT (2,40)–17%	39.5	17	Plywood
PUF (1,80)	42.5	133	1	80	3.0–3.5	9.5-10.0	CHOH Phenol	CHOH Urea	PUFT (1,80)–5%	40.2	5	Plywood
PUF (2,80)	42.3	42	2	80	3.0–3.5	9.5-10.0	CHOH Phenol	CHOH Urea	PUFT (2,80)–10%	39.9	10	Plywood
PUF_A (1,40)	40.3	11.3	1	40	9.5–10.0	9.5-10.0	CHOH Urea	CHOH Phenol	$PUFT_A$ (1,40)–17%	40.9	17	Plywood
PUF_B (1,40)	39.8	21.1	1	40	9.5–10.0	9.5-10.0	CHOH Phenol	CHOH Urea	$PUFT_B$ (1,40)–15%	39.3	15	Plywood

Table 2 Curing enthalpies and Borchardt and Daniels kinetic parameters for the PUF prepolymers at a heating rate of 10°C min^{-1}

Prepolymer	Peak 1					Peak 2					Total Enthalpy	
	T_{max}/°C	ΔH/J g^{-1}	E_a/kJ mol^{-1}	Ln k	n	T_{max}/°C	ΔH/J g^{-1}	E_a/kJ mol^{-1}	Ln k	n	ΔH_1/Jg^{-1}	ΔH_2/J g reactive $solids^{-1}$
PUF (1,40)	146.0	75.3	96.54	23.16	1.05	188.1	66.5	334.2	81.42	1.38	223.5	543.8
PUF (2,40)	148.9	18.8	115.8	29.34	1.16	186.1	73.7	300.9	75.09	1.52	220.5	521.3
PUF (1,80)	148.4	7.24	195.5	52.04	1.08	188.6	77.6	268	66.21	1.24	146.4	344.5
PUF (2,80)	148.6	7.59	181.8	48.0	0.95	188.3	73.5	286.7	71.37	1.40	167.4	419.5
PUF_A (1,40)	146.3	55.5	108.2	26.67	0.95	195.6	82.2	290.7	71.0	1.11	186.4	462.5
PUF_B (1,40)	148.3	27.7	86.41	20.24	0.75	192.3	54.2	301.5	74.34	1.34	146.0	366.8

T_{max}, peak temperature of the exotherm; ΔH – curing enthalpy; E_a, – activation energy; k – frequency factor; n – reaction order

Table 3 Curing enthalpies and Borchardt and Daniels kinetic parameters for the PUFT adhesives at a heating rate of 10°C min^{-1}

Adhesive	Peak 1					Peak 2					Total enthalpy	
	T_{max}/°C	ΔH/J g^{-1}	E_a/ kJ mol^{-1}	Ln k	n	T_{max}/°C	ΔH/J g^{-1}	E_a/ kJ mol^{-1}	Ln k	n	ΔH_1/J g^{-1}	ΔH_2/J g reactive solids^{-1}
PUFT (1,40)–17%	138.5	12.84	153.4	40.81	1.19	169.8	17.85	278.7	70.76	2.04	124.2	314.5
PUFT (1,40)–15%	139.2	25.89	152.2	40.78	1.43	171.9	19.71	335.3	86.91	1.46	145.6	372.5
PUFT (1,40)–12%	143.5	17.58	122.9	31.64	0.95	174.2	33.59	274.2	69.83	1.58	171.3	441.5
PUFT (1,40)–10%	144.4	13.31	137.5	35.99	1.04	175.0	36.77	235.6	59.22	1.23	198.5	501.2
PUFT (2,40)–17%	139.3	7.72	129.4	33.82	0.92	169.9	23.52	295.6	76.42	2.10	129.3	327.4
PUFT (1,80)–5%	–	–	–	–	–	177.2	137.6	80.8	16.84	0.69	130.9	325.6
PUFT (2,80)–10%	–	–	–	–	–	167.1	144.7	80.11	17.00	0.71	139.3	349.0
PUFT$_A$ (1,40)–17%	138.2	6.04	244.9	67.87	1.54	171.1	30.47	281.6	72.36	1.75	119.6	292.3
PUFT$_B$ (1,40)–15%	142.2	8.45	137.7	35.89	0.93	178.1	38.40	253.7	63.71	1.50	112.8	286.9

T_{max} – peak temperature of the exotherm; ΔH – curing enthalpy; E_a – activation energy; k – frequency factor; n – reaction order

Regarding the PUFT adhesives, the position of the maximum of both exothermic peaks is shifted towards lower temperatures (138–145 and 167–178°C).

Tables 2 and 3 present the values of the curing enthalpy of the PUF prepolymers and the PUFT adhesives obtained at a heating rate of 10°C min^{-1}. The ΔH_1 values are based on the mass of liquid resin while the ΔH_2 values are based on the resin solids. The ΔH_2 values were determined in order to evaluate the change in enthalpy due to the reactive solids.

As can be seen, the ΔH_2 increases with decreasing viscosity or degree of condensation for a given formulation and in similar preparation conditions. Considering proportionality between ΔH and the crosslinked created (number of links formed), the lower the heat released the lower the crosslinking [9] and, as a result, the lower the mechanical properties. This is the case of the PUF(1,40), PUF(2,40), PUF(2,80) and PUF(1,80) prepolymers, which only differ in the reaction times of both stages during their synthesis. PUF_A(1,40) and PUF_B(1,40) do not follow this trend, possibly because they were prepared entirely on a basic medium, which favoured a higher degree of crosslinking.

As discussed previously, the high temperature peak observed in the DSC thermograms was associated to the decomposition reaction of methylene ether bridges to methylene bridges eliminating formaldehyde [7]. This was supported with the observation that the curing enthalpy of the high temperature peak of the prepolymers (Table 2) and the ether groups content, which was evaluated by NMR in a previous work [2], followed the same trend.

In the case of the PUFT adhesives, the lower values of enthalpy of curing can be explained by two different reasons. First, these adhesives have undergone a previous copolymerisation of a PUF prepolymer with the tannins, i.e. they are highly condensed polymers, which implies fewer linking opportunities. Second, the tannins are oligomers that do not require excessive crosslinking to polymerise.

Regarding the PUFT(1,40) adhesives, the lower the tannin content the higher the total enthalpy of curing. Moreover, there is also a significant increase in the curing enthalpy corresponding to the second peak of the PUFT(1,40) adhesives (Table 3). As discussed before, this second peak is associated with the presence of methylene ether groups in the resins, resulting from the reaction of methylol groups. Therefore, if the methylol groups decrease because they react with the tannins, then fewer ether groups will be formed and, consequently, the area of the second peak will decrease.

Curing kinetics

Tables 2 and 3 show the kinetics parameters of the Borchardt and Daniels model for the PUF prepolymers and the PUFT adhesives: reaction order, *n*, frequency factor, *k*, and activation energy, E_a.

The reaction orders corresponding to the first peak of the curing reaction are close to the unity in most of the resins, which is in agreement with those obtained for the condensation stage of other PF resins and of the *o*-hydroxymethyl-phenol [10, 11]. The activation energies corresponding to the first peak of the PUF prepolymers ranges from 86.4 to 195 kJ mol^{-1}. Sebenik *et al.* [10] reported a value of 94.2 kJ mol^{-1} for the condensation of *o*-hydroxymethyl-phenol using DSC at a heating rate of 4°C min^{-1}. This suggests that the condensation reaction of PUF(1,40) and PUF_B(1,40) (96.5 and 86.4 kJ mol^{-1}, respectively) is mostly dominated by the *o*-hydroxymethyl-phenol. The significant variability in the values of reaction order and activation energy for the curing reaction of phenolic adhesives reported in the literature [12–15]: *n*, between 1.3 and 2.0, and E_a, between 121 and 215.9 kJ mol^{-1} must be emphasized. Finally, both exothermic peaks of the PUFT(1,80) and PUFT(2,80) adhesives overlapped so that an individual analysis was not possible.

Although the results obtained using the Borchardt and Daniels model are acceptable to establish comparisons between resins, the chemical conversion predictions by this model should be used with caution because it could lead to unreliable results. Therefore, an isoconversional method has been used because it allows the evaluation of the activation energy as a function of the conversion without defining a kinetics model [5]. Figure 2 presents the experimental DSC curves for the PUFT(1,40)–17% adhesive at heating rates of 2, 5 and 10°C min^{-1}, and the corresponding simulated ones using the Model Free Kinetics.

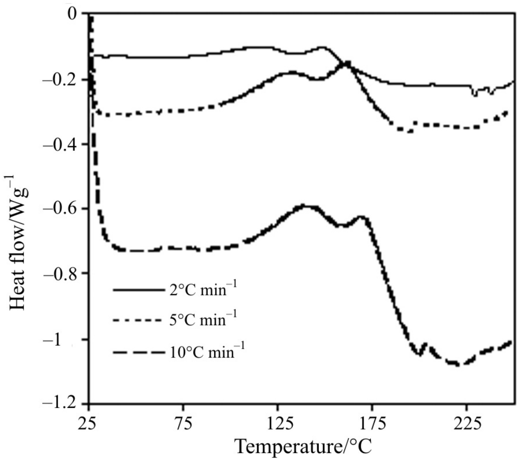

Fig. 2 Experimental and simulated DSC curves of the PUFT(1,40)–17% adhesive at heating rates of 2, 5 and 10°C min^{-1}

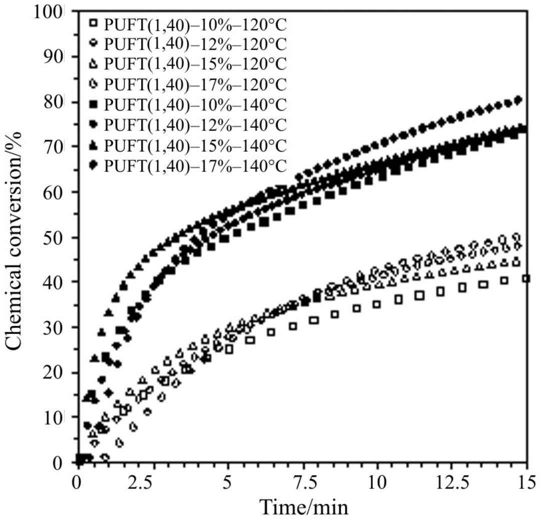

Fig. 3 Conversion *vs.* time for PUFT(1,40)–17%, PUFT(1,40)–15%, PUFT(1,40)–12% and PUFT(1,40)–10% adhesives at 120 and 140°C

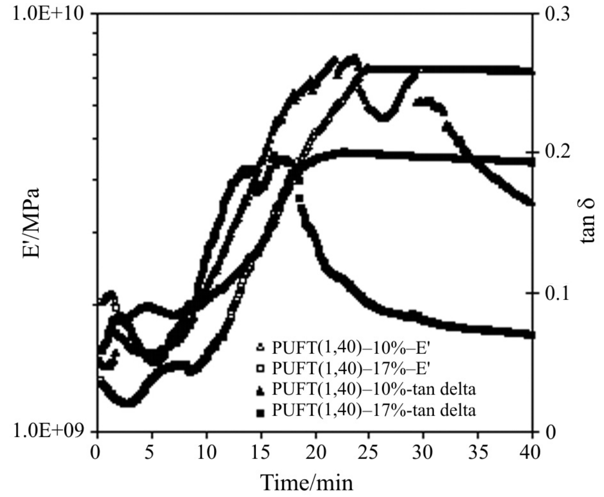

Fig. 4 Storage modulus (E') and tan δ *vs.* time for PUFT(1,40)–17% and PUFT(1,40)–10% adhesives at 120°C

The excellent concordance observed in all cases guarantees the results obtained for the degree of chemical conversion in function of time at the chosen temperature. Figure 3 shows the chemical conversion predictions for all the PUFT(1,40) adhesives (with different tannin contents) at 120 and 140°C. The higher chemical conversion degrees at both temperatures for the PUFT(1,40)–15%, PUFT(1,40)–12% and PUFT(1,40)–10% adhesives within the first minutes are gradually counteracted by those of the PUFT(1,40)–17% at longer times. This behaviour in the initial minutes could be explained due to the higher mobility of the small polymer segments in the lower molecular mass PUFT(1,40) adhesives, i.e. those with lower tannin contents. This is because the higher the mobility of the polymer segments the higher the reactivity and, consequently, the faster the reaction rate. On the other hand, the differences in the chemical conversion degrees at higher times could be explained qualitatively with the curves presented in Fig. 1. The curing reaction of the PUFT(1,40)–15%, PUFT(1,40)–12% and PUFT(1,40)–10% adhesives takes place in a larger temperature range than that of the PUFT(1,40)–17%, which explains the necessity for longer times for complete curing.

In order to complete the curing kinetics study of the PUFT adhesives, the DMA technique was used to conduct a new set of experiments to evaluate the mechanical curing rate at different temperatures. Figure 4 shows the variation of the storage modulus (E') and tan δ *vs.* time at 120°C for those adhesives with the best performance in the manufacture of plywoods (PUFT-(1,40)–17%) and MDF boards (PUFT(1,40)–10%).

Among the different criteria for determining the gel point [16, 17], the maximum of the tan δ curve, based on the point where there is the greatest difference between the elastic and viscous behaviour of the adhesive, was selected. As shown in Fig. 4, the gel time decreased significantly when the adhesive tannin content was increased from 10 to 17%. However, the maximum rigidity ($E'_{\max}$), corresponding to the finishing point of the resin curing reaction, decreased.

Several procedures have been proposed to calculate the degree of mechanical cure of thermoset resins from DMA measurements, based on the changes of the storage modulus [16, 17] or on the area of the tan δ curve [18, 19]. In this work, the degree of mechanical cure was calculated according to the former criterium, by using the following equation:

$$\text{Mechanical conversion (\%)} = \left(\frac{E'(t) - E'_{\max}}{E'_{\max} - E'_{\min}} \right) 100 \quad (1)$$

where $E'(t)$ is the value of the storage modulus at a given time t, $E'_{\min}$ the value of the storage modulus when it started to increase sharply (0% of mechanical conversion) and $E'_{\max}$ the maximum of the E' curve (100% of mechanical conversion).

Figure 5 compares the mechanical and chemical conversions *vs.* time for the PUFT(1,40)–10% and PUFT(1,40)–17% adhesives at 140°C. As it can be seen for both adhesives, the chemical conversion rates are higher within the first minutes but afterwards the mechanical conversion increases faster and it reaches the complete curing when the chemical conversion degrees are below 70%.

On the other hand, the mechanical curing rate is significantly higher for the adhesive with a higher degree of condensation (PUFT(1,40)–17%). In fact, the PUFT(1,40)–17% adhesive would require 7 min at 140°C to reach the complete mechanical curing as oppose to the 11 min for the PUFT(1,40)–10%. Consid-

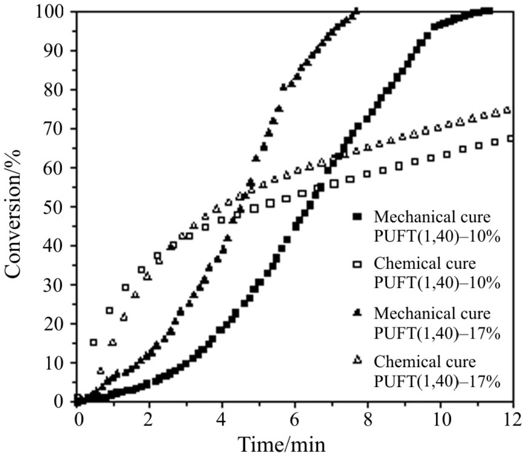

Fig. 5 Chemical *vs*. mechanical cure for PUFT(1,40)–17% and PUFT(1,40)–10% adhesives at 140°C

ering that the temperature in different locations of the board depends mainly on the hot press time together with the temperature of the plates and the thermal properties of the mat or wood, in most of the cases the hot press time is insufficient to reach a complete mechanical curing everywhere in the board. Therefore, only the resin located closer to the board's surface will thoroughly cure. However, it must be pointed out that during the posterior hot-stacking, the boards remain at high temperature for a long time, which is generally enough to complete the mechanical curing.

Conclusions

The DSC curves of the PUF prepolymers show an exothermic peak between 146 and 149°C and a second peak at higher temperatures (186–196°C). Both peaks shift to lower temperatures in the PUFT adhesives.

The curing enthalpy (based on reactive solids) of the PUF prepolymers increases the lower the degree of condensation. In the PUFT adhesives, the enthalpy of curing decreases respectely to the PUF prepolymers they were obtained from. This enthalpy of curing also decreases when increasing the tannin content in the PUFT(1,40) adhesives.

The isoconversional method 'Model Free Kinetics' has been successfully used to model and simulate the curing process of the PUFT adhesives, and to predict the degree of chemical conversion at a given temperature as a function of time. The degree of mechanical cure obtained by DMA was compared with the chemical cure obtained by DSC. The chemical conversion rate is higher within the initial minutes but then the mechanical cure rate increases faster and is completed before.

Among all the PUFT(1,40) adhesives, the PUFT(1,40)–17%, with the largest tannin content, showed the highest chemical conversion rate at 120 and 140°C. Moreover, this adhesive also reached the mechanical cure in the shortest time at both temperatures. This is a great advantage from the industrial point of view as it allows for shorter hot-press times for a given temperature, and therefore increases productivity.

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