Eucalyptus Tar Pitch Substitution of Phenol in the Preparation of Novolak-Type Resins Cured with Hexamethylenetetramine

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Wood tar pitch, sometimes referred to as biopitch, is the residue from the distillation of tar recovered during charcoal making processes. The biopitch from *Eucalyptus* tar, which has guaiacyl and syringyl units in its molecular structure, exhibits novolak behavior and this phenolic oligomer can be cured with hexamethylenetetramine (HMTA). In this work, mixtures of commercial phenolic resins and *Eucalyptus* tar pitch were cured and characterized by infrared spectroscopy, elemental and thermogravimetric analyses. Their acetone-insoluble contents were determined and their electrical properties were investigated. The effects of pitch and HMTA contents on phenolic resin properties were modelled using statistical techniques. The regions of optimum formulations were indicated. The results showed that pitch decreases the thermal stability and the acetone-insoluble content of the phenolic blends, whereas HMTA addition had an opposite effect. The statistical model applied indicated that, in terms of acetone-insoluble content, phenolic resin can be substituted for pitch up to a composition of 50 wt %. Electrical studies showed that pitch–phenolic blends have insulating properties.

Siderurgical activities based on charcoal have been carried out for over two centuries. In southeastern Brazil these are concentrated in the state of Minas Gerais, which accounts for nearly 88% of all the activities involving charcoal in the country. The iron-making industry based on charcoal stands out. A total wood consumption of more than 40 million ton/year is converted into 6.5 million ton/year of charcoal which is used to produce pig iron and ferro-alloys.[1] It can be regarded as a clean iron making approach using renewable charcoal instead of coke (coal tar residue).

Most importantly, Brazilian siderurgical industries help to maintain homogeneous forests of *Eucalyptus* by applying recent technologies of planting, cultivation, and soil handling. *Eucalyptus* application on a large scale is possible because of favorable climate conditions in Brazil, where a tree takes only seven years to fully mature as opposed to twenty years in milder climates. The utilization of homogeneous *Eucalyptus* plantations avoids the use of native forests and therefore helps to maintain the country's forest biodiversity.

During carbonization, apart from charcoal, which corresponds to 33% by weight of wood, non-condensable gases (23%) and pyroligneous liquor (44%) are also generated. Upon decantation, the latter produces pyroligneous acid and tar. The tar is further fractionated into an aqueous fraction, an oily fraction and pitch. The aqueous fraction contains organic acids such as acetic acid and other organic products (methanol, ketones, etc.), whereas the oily fraction is a source of phenolic compounds that can be converted into phenolic materials and applied as varnishes and adhesives. Maltol, cyclotene, and syringol are just a few specialty chemicals that can also be obtained from the oily fraction.[2]

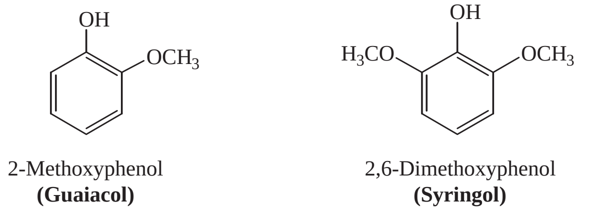

Figure 1. Guaiacol and syringol units present in wood tar pitch.

Wood tar pitch is sometimes referred to as biopitch and consists of a complex mixture of macromolecular aromatic compounds. Biopitch from *Eucalyptus* corresponds to 35–60% by weight of wood tar. It contains heavy fragments with guaiacyl–syringyl units in their structures (Figure 1) which show considerable chemical reactivity. It is a thermoplastic material with $T_g = 30$–$35\,^\circ$C and a high oxygen content (about 23–26%) arising from methoxyl, carbonyl, hydroxy, and carboxylic groups.[3] In addition, the pitch exhibits a polyol behavior and as a consequence has been studied as a precursor for polyurethane foams,[4] polyurethane elastomers,[5,6] coatings,[7] and eco-composites.[8] These studies have also revealed a wide range of potential applications in carbon-based materials.[9–11]

Our previous structural studies revealed that pitch contains a large number of phenolic nuclei thereby resembling phenolic resins of the novolak type.[3] As such, when subjected to thermal treatment in the presence of a curing agent, it undergoes a polymerization reaction, extending the crosslinking of its chains and yielding a hard material, i.e. like a novolak, to eventually become a thermosetting resin.

In this study, we have prepared blends of wood tar pitch and traditional phenolic resins and investigated their curing behav-

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Table 1. Composition of the Modified Phenolic Resins

	A				B				C				D			
Samples	A1	A2	A3	A4	B1	B2	B3	B4	C1	C2	C3	C4	D1	D2	D3	D4
Resin/%	100	100	100	100	90	90	90	90	60	60	60	60	20	20	20	20
Pitch/%	0	0	0	0	10	10	10	10	40	40	40	40	80	80	80	80
HMTA/%[a)]	0	5	10	20	0	5	10	20	0	5	10	20	0	5	10	20

a) Refers to the mixture pitch + commercial resin − additional HMTA.

ior with hexamethylenetetramine (HMTA) (1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane). The thermal stabilities and electrical properties of the crosslinked materials were determined and the effect of varying the proportions of pitch, phenolic resin, and curing agent on such properties as acetone-insoluble content and infrared absorption were evaluated using a statistical approach.

We believe that this study is of relevance to the development of green materials and thereby to the control of climate problems. The biopitch used in this work comes from a renewable source which is also an industrial residue (condensed smoke emanated from *Eucalyptus* carbonization masonry ovens). Furthermore, the application of statistical methods to the formulations provides a quantitative evaluation of the new materials.

Experimental

Materials. Wood tar pitch was kindly donated by the Aços Especiais Itabira (ACESITA) Company. Phenolic resin (novolak), HMTA, and acetone were commercial products and were used as received. The phenolic resin already contained 9% wt of HMTA.

Curing of the Resins. The wood tar pitch and the novolak were ground and mixed in different proportions to make a series of 10.0 g of samples to which HMTA in amounts ranging from 0–20 wt % was added (Table 1). Thus, representing the percentages by weight of HMTA, phenolic resin, and wood tar pitch by x_H, x_R, and x_P respectively, such that $x_H + x_P + x_R = 100$, three-component mixtures, with x_H varying from 0.02 to 0.25, x_R from 0.15 to 0.90, and x_P varying from 0 to 0.8 were prepared.

Each sample was subjected to a thermal treatment during 13 h in a oven (FANEM-ORION 515), with the temperature varying according to the following program: 60 °C for 2 h, 90 °C for 2 h, 105 °C for 1 h, 150 °C for 1 h, 180 °C for 1 h, and 200 °C for 1 h. This program was chosen for correspondence with industrial processes.

Statistical Modelling. The effects of changing the ingredient proportions of a mixture on their physicochemical properties can be conveniently modelled using multivariate statistical techniques.[12,13] Calculations employ the simple conventional multiple linear regression method applied to a set of physicochemical property values as the regressand and mixture ingredient proportions as the regressors. However, since the percentages by weight of the mixture ingredients must always add up to one hundred, models incorporating this information must be used instead of those that are normally employed, in which experimental parameters can be adjusted independently of one another by the investigators. For this reason, the model equations for the mixtures have slightly different mathematical forms than the more common regression equations.

The models are presented in linear, quadratic, and cubic forms. The linear model is simply a linear combination of the percentages by weight of the components of the mixtures. For our three-component system, we have:

$$y = b_H x_H + b_P x_P + b_R x_R + e \tag{1}$$

where the y variable represents the physicochemical property being investigated, b_H, b_P, and b_R are regression coefficients for the HMTA, pitch, and resin, respectively, and "e" is the experimental error.

The quadratic model contains the terms of the linear model but includes cross-product terms:

$$\begin{aligned} y = {} & b_H x_H + b_P x_P + b_R x_R + b_{HP} x_H x_P \\ & + b_{HR} x_H x_R + b_{PR} x_P x_R + e \end{aligned} \tag{2}$$

The b_{HP}, b_{HR}, and b_{PR} coefficients represent interactions between the different ingredient. Significant positive values for these coefficients indicate a synergetic interaction between the two mixture components for the physicochemical property under scrutiny. A significant negative value implies that the two ingredients involved have an antagonistic interaction and that their simultaneous presence results in a lower y value. More sophisticated models containing higher order terms that involve non-linear interactions between components can also be applied. Analysis of variance (ANOVA) is used for choosing the most adequate statistical model. The applied criteria minimize the error between experimental data and model predictions while allowing a sufficient number of degrees of freedom for describing experimental error.

Successful statistical experiments require adequate experimental planning involving the selection of appropriate ingredient proportions that allow a precise description of the physicochemical property. These can be determined once the relevant ranges of the experimental investigation have been specified.

The regression analyses were carried out on a microcomputer using software developed in our laboratory.[12]

Determination of Acetone-Insoluble Content (AI). After curing, the resins were ground and extracted with acetone using a Soxhlet extractor, following DIN-53700. The insoluble content corresponds to the thermoset portion of the resin, with a high cross-linked structure. The higher the AI content, the more cured the resin. The extraction process was monitored by the refractive index of the acetone.

Infrared Spectroscopic Analysis. Infrared spectra of the blends and cured materials were carried out in KBr pellets (1% wt). Spectra were analysed by the Baseline Method,[14] a semi-quantitative approach which allows the evaluation of the varying intensity of the bands taking the absorption at 1600 cm^{-1} as reference.

Elemental Analysis. Carbon, hydrogen, nitrogen, and oxygen (by difference) content of cured blends were determined on a Perkin-Elmer 2400 Elemental Analyzer. The hydrogen to carbon (H/C) ratio was calculated in order to assess the aromaticity of the products; the lower the H/C ratio, the higher the resin aromaticity.

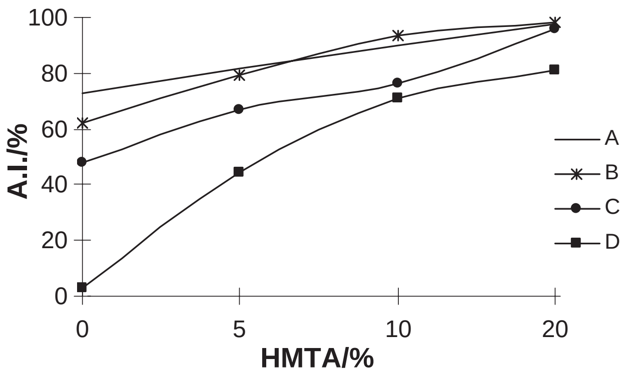

Figure 2. Curing curves (acetone-insoluble content versus % HMTA). A, B, C, and D correspond to the formulations shown in Table 1.

Thermogravimetric Analysis (TGA). Cured samples were analysed by TGA, in platinum crucibles, under the following conditions: dry N_2 atmosphere ($50\,mL\,min^{-1}$), temperature from 25–750 °C and heating rate of $10\,°C\,min^{-1}$. TGA curves were obtained from a Shimadzu TGA-50 thermobalance.

Electrical Properties. Samples D1 to D4, C2 and bio-pitch had their electrical resistance and dielectric constants determined with an Eco Chemie PGSTAT Auto Lab potentiostat.

Results and Discussion

Acetone-Insoluble Content (AI). Pitch is more soluble than the resin and, as the pitch content in the mixture increases, the level of acetone-insoluble materials decreases (Figure 2). Although pitch shows considerable reactivity, this poor behavior in the curing reaction might be attributable to a possible high syringol content, since this molecule has methoxyl groups in both ortho-positions. As for the curing agent, the higher the HMTA content of the blends, the more effective the cure and an increasing acetone-insoluble content is observed as the HMTA content increases.

The effect of high pitch content and low levels of HMTA on the curing efficiency is clearly shown by sample D1 (Figure 2), which presented a negligible acetone-insoluble content. For this reason, a higher HMTA content would be necessary for effective curing of this material.

Acetone-Insoluble Content (AI) Modelling. Multiple linear regressions were applied to the data in Table 1 in order to rationalize the insolubility values of the materials under investigation. Linear, quadratic, and special cubic mixture model equations were determined. However, the quadratic model was clearly superior to the other models so only the regression results for this model are detailed here.

Using all the data from Table 1, the AI parameter is best represented by the equation:

$$\begin{aligned} \mathrm{AI} = &-940.6x_\mathrm{H} - 11.6x_\mathrm{P} + 7.4x_\mathrm{R} + 1770.9x_\mathrm{H}x_\mathrm{P} \\ &(\pm 361.3) \quad (\pm 8.2) \quad (\pm 16.7) \quad (\pm 436.4) \\ &+ 1735.9x_\mathrm{H}x_\mathrm{R} + 10.4x_\mathrm{P}x_\mathrm{R} \\ &(\pm 535.7) \qquad (\pm 28.3) \end{aligned} \tag{3}$$

Values in parentheses are 99% confidence interval errors for the corresponding model coefficients. The most prominent features of this equation are the two large cross terms involving HMTA and the pitch and resin proportions. Since the coefficients of these terms are positive and very similar in magnitude, synergetic effects on the AI property of the same size are indicated for the HMTA–pitch and HMTA–resin interactions. The linear term containing the HMTA proportion is significantly different from the linear terms for the pitch and resin proportions. Its negative value indicates this model is not valid for large HMTA proportions, which are not of practical interest and were not tested in our experimental design. The linear terms for pitch and resin are very small.

Table 2. Regression Analysis (ANOVA) of AI Obtained from eq 4

Source	Sum square	Degrees of freedom	Square average	F test
Regression	7749.75	5	1549.95	—
Residual	368.55	24	15.3562	100.93
Lack-of-fit	256.81	9	28.53	—
Pure error	111.74	15	7.45	3.83
Total	8118.3	29	—	—

It is tempting to conclude from these results that resin can be replaced by pitch with no prejudicial effect on the AI values. However eq 3 must be interpreted with some caution, since the quadratic mixture model exhibited statistical lack of fit relative to the experimental points when submitted to ANOVA. Analysis of the residuals—the differences between AI values predicted by eq 3 and the corresponding experimental values—revealed the major source of this discrepancy. AI values of 3.8 and 2.8, observed for the samples labelled D, are much smaller than those for the other mixtures studied, which ranged from 41.4 to 98.6. These samples did not result in curing and, therefore, their results should not be used in the modelling since they belong to a different model than the other data points.

Because of their markedly low AI values, a second regression was performed excluding the two D-labelled results. The modified regression equation with its corresponding 99% confidence interval errors is:

$$\begin{aligned} \mathrm{AI} = &-620.4x_\mathrm{H} + 8.3x_\mathrm{P} + 17.9x_\mathrm{R} + 1268.3x_\mathrm{H}x_\mathrm{P} \\ &(\pm 431.4) \quad (\pm 13.9) \quad (\pm 20.7) \quad (\pm 529.6) \\ &+ 1280.7x_\mathrm{H}x_\mathrm{R} - 0.9x_\mathrm{P}x_\mathrm{R} \\ &(\pm 640.9) \qquad (\pm 35.9) \end{aligned} \tag{4}$$

This new equation resembles that one obtained with the complete experimental data set. Although the individual coefficients show large changes, the HMTA–pitch and HMTA–resin synergic terms are still large, positive and approximately equal, as well as being significant at the 99% confidence level. Note that the negative linear term in the HMTA proportion is much less important than in eq 3. Furthermore the ANOVA for the regression results for eq 4 (Table 2), does not provide evidence for lack of fit at the 99% confidence level, since the calculated F value of 3.83 is smaller than 3.89, the tabulated 99% confidence F value with 9 and 15 degrees of freedom. Also, the mean square regression/mean square residual ratio of 100.9 is much larger than its associated F value of 3.90 at the 99% confidence level with 5 and 24 degrees of freedom.

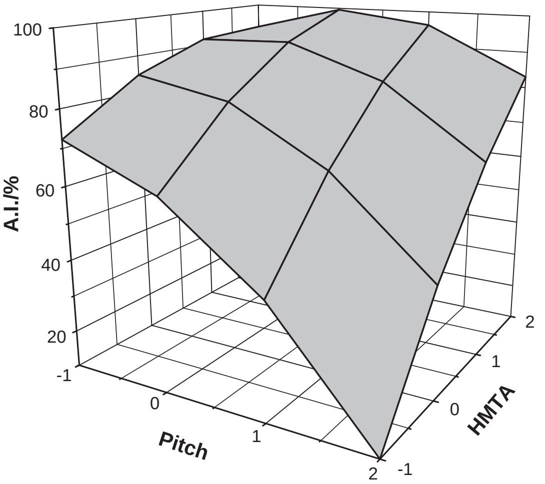

Figure 3. Response surface curve obtained from eq 4 for AI content. Pitch parameters: -1 (0%), 0 (10%), 1 (40%), and 2 (80%). HMTA parameters: -1 (0%), 0 (5%), 1 (10%), and 2 (20%).

Confirmation of the good statistical fit for this model also comes from an examination of the residual values. A plot of these values against predicted AI values obtained from eq 4 displays a completely random distribution, as expected for regression models with good fits to the experimental values. This was not the case for the residuals of eq 3 owing to the two results with very low AI values.

The maximum level of acetone insoluble content is achieved when the pitch concentration is low and HMTA content is high. From eq 4 a response surface curve (Figure 3) and a contour curve (Figure 4) can be drawn in order to locate a probable optimum region. It is possible to infer from these graphs that high levels of AI content can be achieved by adding more HMTA to blends with pitch. However, HMTA addition will raise the cost of the material, an economic factor which must be taken into account.

A working equation for the effects of HMTA, pitch and resin proportions on the AI values can be expressed as follows:

$$\mathrm{AI} = -620x_\mathrm{H} + 1268x_\mathrm{H}x_\mathrm{P} + 1281x_\mathrm{H}x_\mathrm{R} \quad (5)$$

Keeping HMTA values constant, the change in AI values, $\Delta\mathrm{AI}$, for the substitution of resin by pitch is given by $\Delta\mathrm{AI} = -13x_\mathrm{H}\Delta x_\mathrm{P}$ where Δx_P is the increase in the weight percent of pitch. For the highest HMTA value used in our experiments the expression becomes $\Delta\mathrm{AI} = (-13)(0.24)\Delta x_\mathrm{P}$. For a pitch proportion increase corresponding to 50% of the three-component mixture, the AI value decreases by only 1.5 which is well within the experimental error for the experiments performed here, $(7.45)^{1/2} = 2.7$. It should be noted that these results are only valid for the HMTA, pitch and resin ranges employed in our investigation. These ranges delimit the shaded region shown in Figure 4. The different degrees of shading in this figure represent contour regions indicating intervals showing how the AI values change for variations in all three-mixture ingredient proportions.

Infrared Absorption Spectroscopy. Figure 2 shows that the acetone-insoluble content increases with increasing amounts of HMTA. This trend can also be visualized in the response surface curve obtained from eq 4 for AI content (Figure 3). In order to verify how the amount of HMTA affects the infrared absorptions of the products, the series of resins prepared with 10% pitch (group B in Table 1) was analysed by infrared spectroscopy. The relative absorptivities are presented in Figure 5.

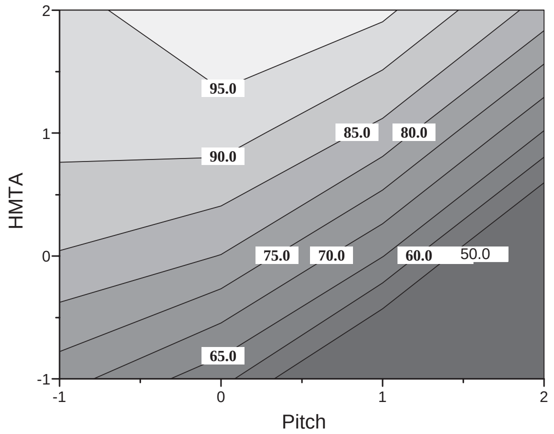

Figure 4. Contour curve for AI content obtained from eq 4. Pitch parameters: -1 (0%), 0 (10%), 1 (40%), and 2 (80%). HMTA parameters: 1 (0%), 0 (5%), 1 (10%), and 2 (20%).

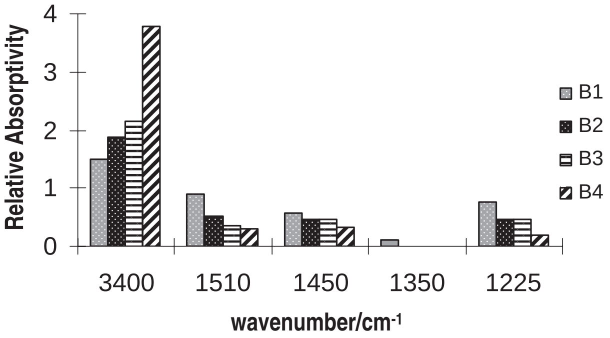

Figure 5. Effect of HMTA addition to the IR absorptions of the blends (For sample identification, refer to Table 1).

Addition of HMTA results in decreasing aromaticity of the mixtures, as indicated by the set of absorptions around $1510\,\mathrm{cm}^{-1}$. The curing agent is a source of methylene bridges and the insertion of these groups between the phenolic nuclei increases the aliphatic content of the resin molecular skeleton. Furthermore, the intensity of the bands at $3400\,\mathrm{cm}^{-1}$ shows an increasing trend arising from the incorporation of N–H groups from HMTA within the cured blends.

These resins are represented in Figure 4 by the points B1 (0,-1), B2 (0,0), B3 (0,1), and B4 (0,2). In this figure, the lighter the shade, the lower the values for the IR absorption at $1500\,\mathrm{cm}^{-1}$, related to aromaticity, and the higher the values for the absorption at $3400\,\mathrm{cm}^{-1}$, assigned to the N–H stretching.

The reduction in absorption intensities for the bands around $1510\,\mathrm{cm}^{-1}$ is even more dramatic when pitch addition is considered (Figure 6). This indicates that pitch is less aromatic than phenolic resins alone. However, no obvious trend is observed for the remaining bands, so all that can be inferred is

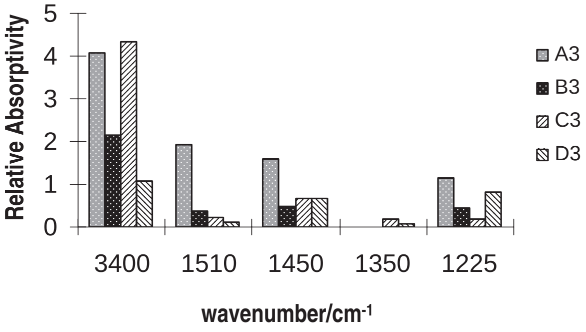

Figure 6. Effect of Pitch addition to the IR absorptions of the blends (For sample identification, refer to Table 1).

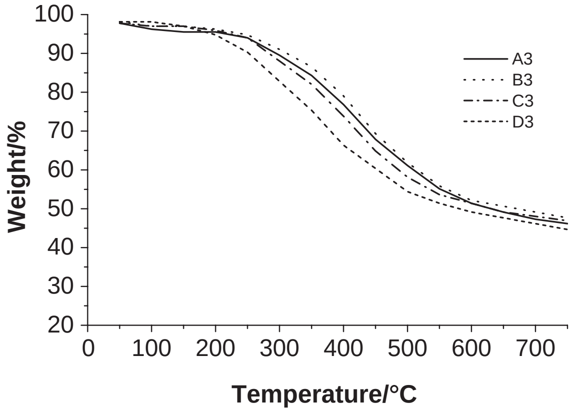

Figure 7. TG curves (N_2 atm.) for blends with 10% HMTA and different levels of pitch (For sample identification, refer to Table 1).

that a more complex structure is achieved when pitch is added to the blend.

The series of resins analysed by IR (Figure 6) can be located in Figure 4 by the points A3(−1,1), B3(0,1), C3(1,1), and D3(2,1), with the right hand side of the graph corresponding to less aromatic resins. Thus, for any given amount of HMTA, the aromaticity of the resin decreases with increasing amount of pitch, in accordance with the results obtained from the infrared analysis.

Thermogravimetric Analysis. Phenolic resins, in general, have good thermal stability. Thermogravimetric analyses of the samples studied indicate that addition of pitch decreases the thermal stability of the resins (Figure 7), sample D3 being less stable by about 50 °C than sample A3. This can be explained by the high oxygen content in the pitch structure and by the presence within the structure of molecules of lower molecular weight. The lower content of carbon residues observed for series D samples can also be explained in terms of the lower aromaticity of pitch when compared with phenolic resins.

The series of resins represented in Figure 7 can also be located in Figure 4 by the points A3(−1,1), B3(0,1), C3(1,1), and D3(2,1). In this case, the left hand side of the graph corresponds to resins with higher thermal stability.

It is possible to obtain blends in which the reduction in thermal stability by adding pitch is compensated by the addition of HMTA. This is illustrated in Figure 8, where a blend containing 40% pitch and 10% HMTA (C3) shows the same thermal stability as a commercial phenolic resin (A1). Resins A1 and C3 are represented by the points (−1,−1) and (1,1) respectively in Figure 4, so there is no simple relation between AI content and thermal stability. However, the samples containing high levels of HMTA and low levels of pitch have higher percentages of carbon residue at the end of the thermal process.

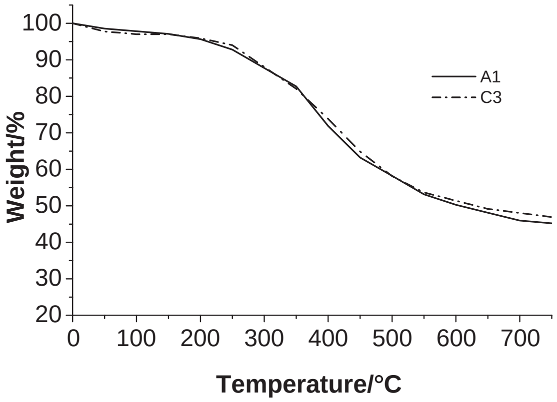

Figure 8. TG curves (N_2 atm.) for phenolic blend C3 and commercial resin A1 (For sample identification, refer to Table 1).

Table 3. Sampling Composition Determined from Elemental Analysis

Sample	C/%	H/%	N/%	O/%[a]
Pitch	67.51	7.1	0.52	24.87
Phenolic resin	75.21	6.77	0	18.02
A4	74.81	6.12	2.35	16.72
B4	75.68	6.22	2.39	15.71
C3	74.19	6.47	1.99	17.35
C4	73.57	6.16	2.7	17.57
D4	70.37	6.7	2.87	20.06

a) Estimated by difference.

Elemental Analysis. The curing reaction promotes the incorporation of N–H groups within the originally nitrogen-free resin. Accordingly, there is a progressive increase in the nitrogen content as HMTA is added to the mixture (Table 3).

Since biopitch has considerable oxygen content, it increases the proportion of oxygen in the blends while only having a slight effect on the H/C ratio. Nevertheless, the lower the H/C ratio, the higher the material aromaticity (Figure 9), thus, these results support our previous discussion on the acetone-insoluble content. In fact, pitch addition causes a reduction of the blend aromaticity; hence the curing reactions are less efficient, leading to lower acetone-insoluble content.

Electrical Properties. Phenolic resins are well known for their insulating properties. The dielectric behavior of the blends was investigated and average resistivities of $10^2\,\Omega\,\mathrm{m}$ were obtained, confirming their insulating characteristics. Dielectric constants (***k***) were measured for a series of the blends (Figure 10). The values obtained were relatively small when compared with those of typical dielectrical materials.

A comparison of the dielectric constants for pitch and the C2 sample indicates that the presence of phenolic resin decreases the ***k*** values of the blends. A possible explanation

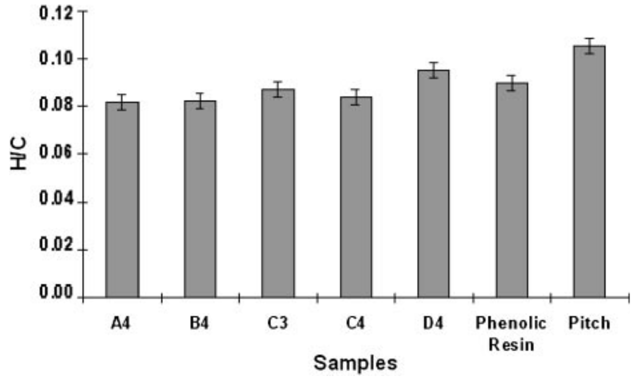

Figure 9. H/C ratio for the blends, phenolic resin and pitch (For sample identification, refer to Table 1).

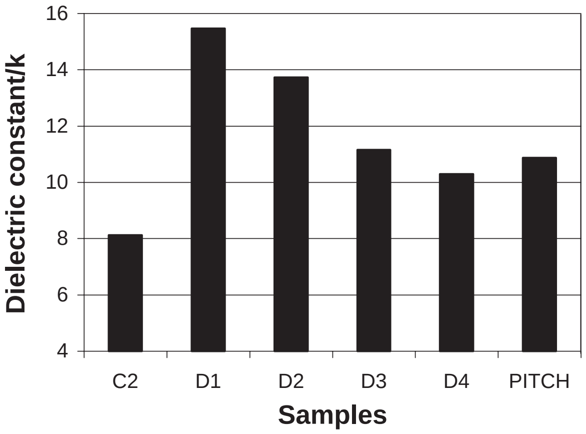

Figure 10. Dielectric constants (***k***) of the blends and pitch (For sample identification, refer to Table 1).

for this observation is that phenolic resin structure is more organized than pitch structure, allowing for some electrical charge dislocation. When the material is cured, the crosslinking in its structure is greatly extended, thereafter preventing the electrical charge to flow easily in the tridimensional structure. Indeed, HMTA addition decreases the ***k*** values of blends, as can clearly be seen for the series D1 > D2 > D3 > D4 in Figure 10.

Conclusion

Blending with pitch decreases the thermal stability (N_2 atmosphere) and the acetone-insoluble content of phenolic blends, whilst the inclusion of HMTA has the opposite effect. Thus, in order to use pitch as a component in the preparation of phenolic blends for commercial applications, it is necessary to increase the amount of HMTA, in order to compensate for the losses caused by the addition of pitch. The best formulation is one that permits higher contents of pitch, without compromising the properties of the material and its economic feasibility.

The model applied herein indicates that, in terms of AI content, phenolic resin can be substituted for pitch over a considerable compositional range ($\leq 50\%$). A narrower range is to be subjected to more detailed investigation in order to find the optimum composition. Economic constraints are likely to curb the extent of HMTA addition, an important factor in any potential technological application. Electrical studies showed that blending phenolics with pitch has little effect on the insulating properties of the resultant thermosets. However, their possible application as dielectric materials also needs a more complete investigation.

Phenolic resins are commodity products while biopitch, comprising almost 50% of wood tar, is a natural product. It is important to point out that most of the volatiles evolved during *Eucalyptus* carbonization are lost to the atmosphere or are recycled to masonry ovens in order to be burnt and thereby improve the energetic efficiency of the carbonization process.

If the possible reduction in price of phenolic resins is considered, favoring market sectors that use large volumes of resins, such as moulding powders, insulating materials and automotive industries, the prospect of developing resins based on wood tar pitch is very encouraging. The production of polymeric materials of industrial relevance using wood tar pitch as a raw material will also boost the application of by-products from charcoal-making activities while reducing the environmental impact of such activities.

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