

Evaluation of Alfa Grass Soda Lignin as a Filler for Novolak Molding Powder

Samir Hattali,¹ Ahmed Benaboura,¹ Stéphane Dumarçay,² Philippe Gérardin²

¹Faculté de Chimie, Université de Bab Ez Zouar, Alger, Algérie

²LERMAB, UMR INRA ENGREF UHP 1093, Université Henri Poincaré Nancy-1, Faculté des Sciences et Techniques, 54506 Vandoeuvre les Nancy Cédex, France

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ABSTRACT: Behavior of Alpha grass soda lignin was investigated for the preparation of novolak molding powders. Thermal analysis of the different investigated formulations indicated that molding powders prepared from Alpha grass soda lignin were more resistant to thermal degradation compared to a standard formulation prepared from wood flour. Limiting oxygen index determined for the different composites confirmed the higher thermal stability of Alpha grass soda lignin composites. Mechanical properties tested either from Shore hardness tests or from impact strength measure-

ments revealed a slight decrease of mechanical properties for composites prepared from Alpha grass soda lignin. All these results showed the possibility to replace imported wood flours by locally available Alpha grass soda lignin to obtain phenolic composites with quite similar properties. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1065–1068, 2005

Key words: Alpha grass soda lignin; black liquor; composite; novolak resin; molding powder

INTRODUCTION

Alpha grass (*Stipa tenacissima* L.), also called Esparto grass, is one of the main sources of cellulosic fibers for the paper industry in Algeria.¹ Three mills (Celpap Company) produce bleached pulp using Alfa Grass as raw material. The process uses soda cooking followed by hypochlorite bleaching, producing large amounts of so-called black liquors. Several methods of valorization have been reported in the literature for the residual lignin dissolved in black liquors of different lignocellulosic materials. The main applications are the preparation of wood adhesives,^{2,3} phenolic resins,^{4–9} and the processing of leather.¹⁰ The aim of this article is to study the behavior of Alpha grass soda lignin, obtained after acidification of the black liquors, in the preparation of molding powders instead of conventional wood flours. Indeed, the replacement of wood flours by locally available industrial by-products like Alpha grass soda lignin could be an important economic interest for Algeria, where wood resources are limited.

EXPERIMENTAL

Alpha grass lignin—Isolation

Lignin was isolated from black liquor of Alpha grass (*Stipa tenacissima* L.).¹ The black liquor was acidified

with concentrated sulfuric acid to pH 4.5 and the solution centrifuged (20 min, 5000 rpm). The precipitate was separated, treated with distilled water, and the resulting solution again centrifuged (20 min, 5000 rpm). The recovered solid material was dried at 70°C for 24 h and stored over P₂O₅ under vacuum.

Molding powders

Molding powders were prepared from an industrial formulation by replacing wood and olive cores conventional loads by Alpha grass soda lignin. Wood flour consists of a mixture of spruce (*Picea abies*) and pine (*Pinus sylvestris*), 90/10, with a maximum moisture content of 16%. Novolak resin was obtained as commercial grade from the Algerian National Petrochemical Company ENIP, ARZEW CP.1Z. The reference molding powder was prepared by mixing this resin (46.8%) with wood flour (22%), olive cores (13%), asbestos (10%), hexamethylene tetramine (6%), naphthalene (0.3%), lime (0.3%), and black indoline (1.4%) as coloring matter.

Modified molding powders were prepared in a similar manner by replacing the wood flour and olive cores by either Alpha grass lignin or wood flour in the proportions described in Table I.

Cure reaction

All these formulations were molded using a WABASH 50,152 TRM apparatus, Wabash Metal Products Company Inc., Hydraulics Division, Wabash, Indiana,

Correspondence to: P. Gérardin (philippe.gerardin@lermab.uhp-nancy.fr).

TABLE I
Resin and Filler Composition of the Different Molding Powders

Sample designation ^a	Novolak resin (%)	Wood flour (%)	Olive cores (%)	Alpha grass soda lignin (%)
REF	46.8	22	13	0
NR	81.8	0	0	0
AG-5	76.8	0	0	5
AG-15	66.8	0	0	15
AG-25	56.8	0	0	25
AG-35	46.8	0	0	35
AG-45	36.8	0	0	45
WF-5	76.8	5	0	0
WF-15	66.8	15	0	0
WF-25	56.8	25	0	0
WF-35	46.8	35	0	0
WF-45	36.8	45	0	0

^a AG-X/WF-X, sample containing X% of Alpha grass/wood flour.

USA. The cure reaction was carried out in a mold of $200 \times 100 \times 5$ mm under pressure (204 kgf/cm^2) during 17 min at a temperature of 170°C .

Mechanical properties

Shore hardness test

The Shore hardness test was carried out at room temperature according to NFT 51–09 standard on a Shore MGF CO durometer. Five measurements were carried out for each sample.

Impact strength

Samples (5 replicates) were cut from each plate and shaped according to ASTM D256 standard ($63.5 \times 12.7 \times 4.0$ mm) notched in the middle. Impact tests were carried out at $23 \pm 2^\circ\text{C}$. An average value was calculated from each composite.

Thermogravimetric analysis

Thermogravimetric analyses at a heating rate of $10^\circ\text{C}/\text{min}$, under an air atmosphere and a temperature range of 50 to 700°C , were performed on a METTLER TA 3000 apparatus, METTLER TOLEDO, Viroflay, Cedex, France. Experiments were also performed at 170°C during 20 min to evaluate the thermal stability of the different molding powder formulations during curing.

Flammability

Flammability of the molded materials was evaluated according to ASTM 2853–70 standard, by using a STANTON REDCROFT FTA flammability unit,

STANTON REDCROFT, London, England. Results are expressed in terms of the limiting oxygen index in the surrounding atmosphere (LOI) necessary to support flaming combustion of the polymer during 3 min.

RESULTS AND DISCUSSION

The thermal stability of the different formulations was evaluated using two methods. The first one involves the measurement of the limiting oxygen index (LOI),¹¹ which corresponds to the minimum percentage of oxygen in the surrounding atmosphere necessary to support the flame combustion during 3 min. The second is based on the analysis of thermogravimetric curves¹² of the different molding powder formulations, from which it is possible to determine $T_{1/2}$, which corresponds to the temperature at which half of the material is decomposed (Table II).

In parallel to this temperature, it is also possible to observe different exothermic peaks corresponding to the degradation temperatures of the main components of the mixture (Fig. 1). Experiments performed at 170°C allowed the evaluation of molding powder thermal stability during curing.

The thermal stability of the different molding powder formulations increases with the quantity of novolak resin. Weight losses measured after 20 min at 170°C are more important in the case of formulations involving wood flour compared to those involving Alpha grass soda lignin (compare AG-5 to WF-5 or AG-25 to WF-25). The higher stability of the Alpha grass soda lignin formulation could be easily explained in terms of the chemical composition, which is relatively near that of phenolic resin.

Thermogravimetric analyses performed in the temperature range of 50 to 700°C indicate the same tendencies. Degradation of formulations containing no-

TABLE II
Thermal Properties of the Different Formulations and Molded Materials

Sample designation	Weight loss (%) ^a	$T_{1/2}$ ($^\circ\text{C}$) ^b	Main exothermic peaks ($^\circ\text{C}$)	LOI (%)
REF	6.02	558	525/575	29.9
NR	3.87	612	600	36.1
AG-5	4.07	585	565	31.8
AG-25	4.85	570	538	30.1
AG-35	—	—	—	29.6
AG-45	—	515	505	29.2
WF-5	5.79	—	—	30.5
WF-25	5.85	538	530/600	29.3
WF-35	—	—	—	27.8
WF-45	—	474	440	27.5

^a After 20 min at 170°C .

^b Temperature at which half of the material is decomposed.

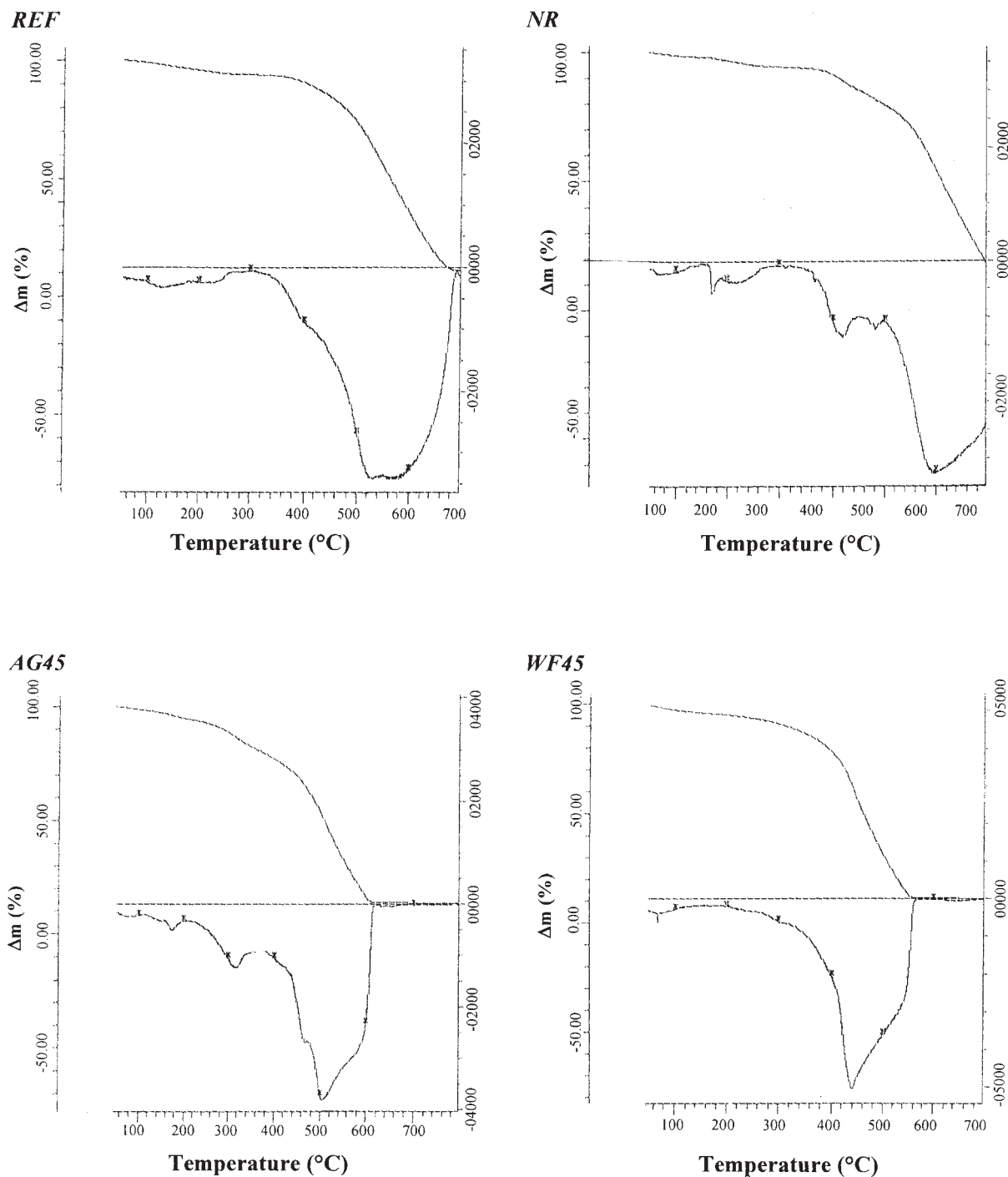


Figure 1 TG and DTG curves of the formulations.

volak resin starts at higher temperatures comparatively to formulations containing wood flour or Alpha grass soda lignin fillers. The thermogravimetric curve of a reference sample indicates two peaks at 525 and 575 °C, corresponding, respectively, to wood and novolak resin degradations. Degradation of phenolic resin alone appears at a higher temperature (600 °C), while the behavior of Alpha grass soda lignin is intermediate with that of the two other components. For

the same filler concentration, the use of Alpha grass soda lignin instead of wood flour leads to formulations with improved thermal stability (compare AG-25 and AG-45 to WF-25 and WF-45). These results are in good agreement with results previously reported in the literature¹³ concerning the fire resistance of phenolic resins directly related to their structure. The thermal degradation of these polymers involving crosslinking of phenolic units resulting in low flame

TABLE III
Mechanical Properties of the Composites

Composite designation	Hardness (Shore D scale)	Impact strength (kJ/cm ²)
REF	83	26.88
NR	88	42
AG-5	85	32.19
AG-15	85	28.42
AG-25	81	25.73
AG-35	78	22.98
AG-45	76	21.23
WF-5	87	33.13
WF-15	85	28.56
WF-25	83	27.41
WF-35	81	25.6
WF-45	78	22.85

spread rates could also explain the higher stability of formulations prepared from Alpha grass soda lignin compared to those prepared from wood flour. Flammability estimated in terms of oxygen quantity indicates the same tendencies. Thermal stability is more important for composites obtained from formulations containing a high percentage of novolak resin, and Alpha grass soda lignin gives better results than wood flour. For the same concentration of novolak resin (46.8% in REF, AG-35, and WF-35), the Alpha grass soda lignin reference formulations lead to materials with similar LOI, while wood flour formulations afford material with a higher flammability (compare REF AG-35 and WF-35).

Mechanical properties are reported in Table III. The Shore hardness tests applied to the different molded composites indicate that the mechanical resistance to penetration decreases as a function of the quantity of novolak resin. Results obtained with Alpha grass soda lignin or wood flour for similar phenolic resin concentrations are very close, indicating that surface hardness of the composite is not influenced by the nature of the filler. Impact strength measurements indicate that composites obtained from wood flour formulations present higher impact strength resistance compared to composites containing Alpha grass soda lignin. The cellulosic fibers contained in wood flour are probably at the origin of this better behavior com-

pared to lignin, which has no reinforcing action.¹⁴ The decrease in tensile strength and impact properties corroborates results recently reported by Kharade and Kale on the effect of lignin on novolak resins.¹⁴ However, filler composition has only a limited effect on the mechanical properties and allows the use of one or the other of these components. Impact strength resistances are very close for a similar phenolic resin concentration (46.8% in REF, AG-35, and WF-35), indicating again that the filler has only a limited effect on the performance of the composite.

CONCLUSION

All these results demonstrate the possibility of substituting wood flours by Alpha grass soda lignin, a locally available by-product of the paper industry in Algeria, for the preparation of phenolic composites. Properties of composites thus obtained are quite similar to those of composites prepared from traditional formulations involving wood flours. The thermal stability of composites prepared from Alpha grass soda lignin are slightly increased compared to the same composites prepared from wood, while mechanical properties are generally slightly decreased.

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