Journal of Thermal Analysis, Vol. 49 (1997) 477-481

STUDY OF PHENOLIC RESIN/EVA BLENDS BY THERMAL ANALYSIS

C. G. Mothé[1] *and M. I. B. Tavares*[2]

[1]Escola de Química da Universidade Federal do Rio de Janeiro, Centro de Technologia,
Cidade Universitária, Ilha do Fundao, CP 68522, Cep 21949–900
[2]Instituto de Macromoléculas Professora Eloisa Mano da Universidade Federal do Rio de
Janeiro, Centro de Technologia, Cidade Universitária, Ilha do Fundao, CP 68525,
Cep 21945–970, RJ, Brazil

Abstract

The properties of polymeric blends originate from the synergistic association of their components. In this investigation, phenolic resins obtained by the reaction of cashew-nut shell liquid (CNSL) and aldehyde are used in several applications. Mixtures of CNSL with industrial reject ethylene-co-vinyl acetate (EVA reject) were prepared with an EVA reject content up to 70%. The thermal compatibility and stability were evaluated by means of thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC). For blends containing a high percentage of EVA reject, the TG curves clearly show two decomposition stages, one at 350°C and the other at 450°C (onset 467°C). The DTG curves of the blend containing 70% CNSL exhibit decomposition at 240°C. The DSC curves show that the samples containing a high percentage of EVA reject are incompatible, with T_g values around –30°C.

Keywords: DSC, EVA blends, phenolic resin, TG-DTG

Introduction

Phenolic resins include a wide variety of products resulting from the reactions of phenes with aldehydes. This process can be carried out by heating the reactants until chemical condensation occurs. Cashew-nut shell liquid (CNSL) is as a natural source of unsaturated phenolic monomers. The cashew-nut tree (Anacardiun occidentale Linn N. Ö. Anacardiaceae) is native to Brazil. CNSL-based products include laminates, mouldings and friction materials, plasticizers, paints, varnishes, antioxidants and adhesives. The fundamental aspects of the blends, such as the structure-property correlations and compatibility, need extensive investigation.

Thermogravimetry is a method that reveals the continuous change in sample mass as a function of temperature and/or time. It provides information on thermal stability, the composition of the initial sample; the intermediate compounds formed and any type of residue [1].

Differential scanning calorimetry measures thermal flux heats and temperatures where transitions take place. It can be used as a rapid technique for quality assurance in many processes. The thermal history changes such morphological features

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

of the material as crystallinity, miscibility, tensile strength and glass transition [2] and affects the subsequent processing or product performance.

Experimental

Sample preparation

Mixtures of CNSL and industrial reject ethylene-co-vinyl acetate (EVA reject), containing 17% of vinyl acetate (VA), were prepared in a roll (Brestoff) at 80°C in 10 min at 20 rpm. The EVA content ranged up to 70%. The mixtures were cured at 130°C in a Carver press.

TG/DTG measurements

The experiments were carried out on a Perkin-Elmer TGA-7 instrument, with dynamic scanning from 50 to 700°C in nitrogen, at a rate of 20°C min^{-1}. The mass of the analysed samples was 3–5 mg.

DSC measurements

The thermal behaviour was observed by DSC on a Perkin-Elmer DSC-7 and on a Mettler TA 4000 system. Samples containing 5 to 10 mg of material were heated at a rate of 20°C min^{-1} from –100 to 100°C in nitrogen atmosphere.

Results and discussion

Figure 1 depicts the thermogravimetric curves (TG) of different compositions of CNSL/EVA reject. It can be seen that there are tow decomposition stages for EVA reject itself and mixtures with high EVA reject content (70, 65, and 60). The first stage occurred at around 350°C with a slight mass loss. The major decomposition occurred at 450°C (onset 467°C). The 350°C mass loss was due to the splitting-off of VA side-groups from the polymer backbone; the 450°C mass loss involved the breakdown of the backbone. Both EVA reject and CNSL resin gave a 14% residue. As the quantity of CNSL in the mixture increased, a slight decrease in thermal stability was observed. A slight increase in the residue, up to 20%, was found for the 50/50 w/w composition.

Derivative thermogravimetric (DTG) curves (Fig. 2) for different compositions of CNSL/EVA reject showed that the major decomposition took place at around 450°C. The blend containing 70% of CNSL resin decomposed at 240°C.

Table 1 lists thermal properties measured by DSC, such as T_g and T_m. The glass transition temperatures of all samples were below zero. The blend compositions presented only one T_g, which can be attributed to sample homogeneity. The melting temperatures varied very little, although for the 30/70 blend the peak of fusion increased to 84.4 °C.

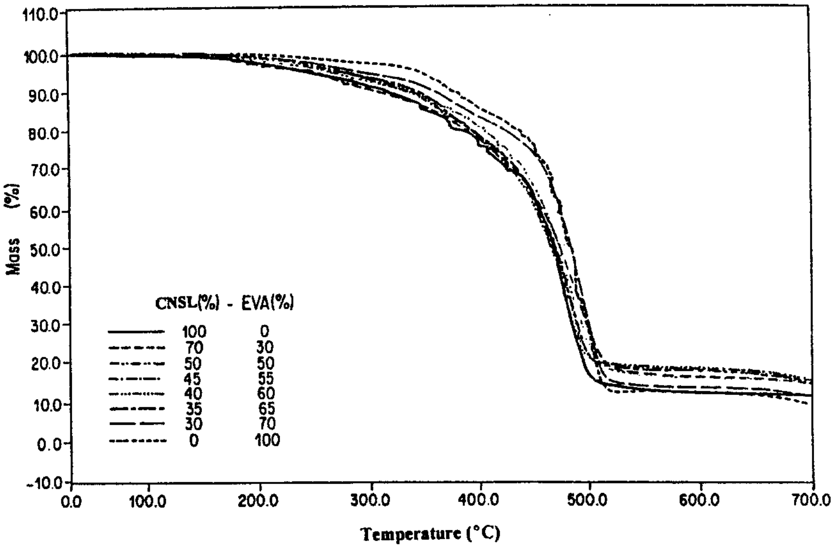

Fig. 1 Thermogravimetric curves for CNSL/EVA reject blends

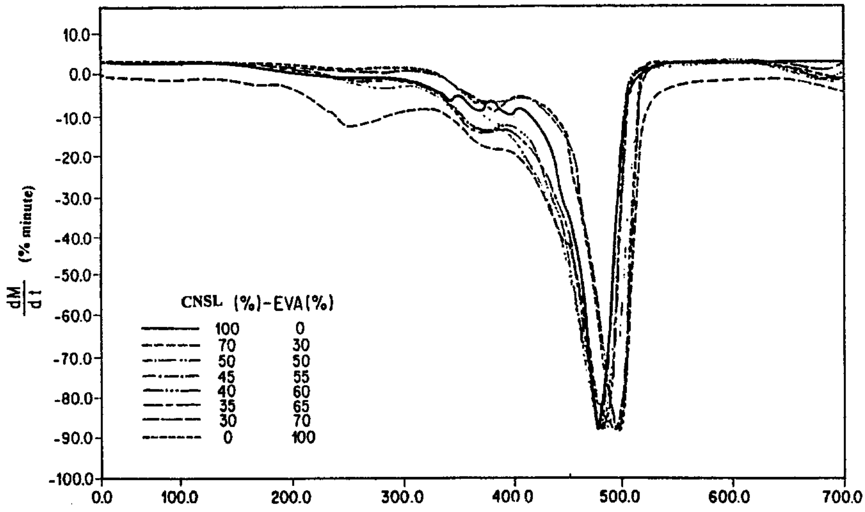

Fig. 2 Derivative thermogravimetric curves for CNSL/EVA reject blends

The principal transition temperature *vs.* composition data are shown in Table 1. Figure 3 illustrates a phase diagram. This diagram reveals three morphological states. Between the two lines are rubbery (liquid amorphous) and crystalline phases. Above the crystalline fusion, the samples are in the liquid amorphous phase.

Table 1 Values of glass transition temperature (T_g) and melting temperature(T_m) for samples with different ratios of CNSL and EVA reject

% of CNSL	T_g/°C	T_m/°C
0	–39.5	83.6
30	–27.3	84.4
45	–29.8	81.2
50	–29.8	83.2
70	–	81.2
100	–10.0	–

Table 2 Proton spin-lattice relaxation time in the rotating frame ($T_1^H\rho$) for distinct compositions of CNSL/EVA reject blends

CNSL/EVA reject ratio	$T_1^H\rho$/ms
0/100	1.6/2.2
30/70	1.7/2.1
35/65	1.3/2.2
40/60	2.0
45/55	1.5
50/50	3.3
70/30	3.6

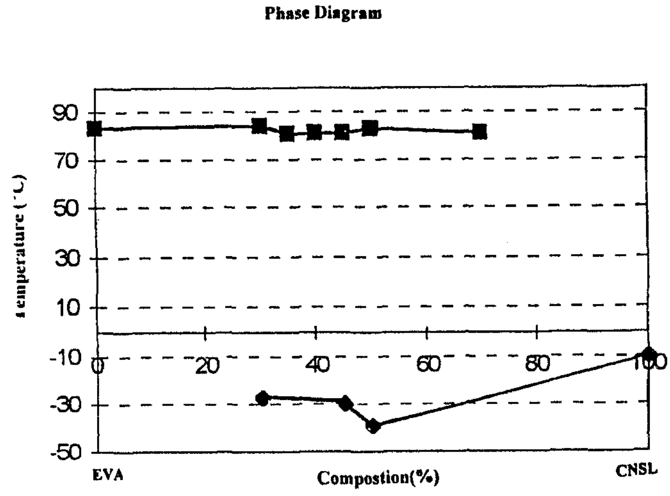

Fig. 3 Phase diagram of CNSL/EVA reject blends

The proton spin-lattice relaxation in the rotating frame, measured by carbon-13 cross-polymerization (CP/MAS), yields relaxation data from each resolved carbon type in the molecule in the solid state (Table 2). These data confirm the results afforded by thermal measurements [2, 3].

The interpretation of proton $T_1\rho$ listed in Table 2 is based on the chemical environment and the strength of the interaction between the two polymers in the blend. The initial polymers present a bicomponent proton $T_1\rho$, due to the presence of domains with distinct mobilities. As the content of CNSL (40–70) in the mixture increases, there is a tendency to obtain one value of this parameter, as a consequence of sample homogeneity, or compatibility, due to the fact that the long-range communication between the protons is effective. Focusing on the composition CNSL/EVA reject=45/55, a slight decrease in proton $T_1\rho$ may be an indication of a strong dipolar interaction between the two polymers, where the spin-diffusion is effective. For the blends with 50 and 70% of CNSL, the values of proton $T_1\rho$ are higher than for the 45/65 composition, which may suggest a plasticization effect of CNSL, as the chains seem to be separated; this does not mean incompatibility, but only more mobility.

Conclusion

From the thermal analysis data and the NMR response, the blends formed by CNSL/EVA reject display homogeneity up to the 50/50 composition. The overall results clearly demonstrate that a phase separation occurs when the quantity of EVA reject in the blend is above 50%. In our opinion, NMR and thermal analyses (TG and DSC) are complementary techniques.

* * *

The authors would like to thank PETROBRAS/CENPES/DIQUIM for the NMR facilities and thermal measurements.

References

1 M. A. Martins, C. G. Mothé and M. I. B. Tavares, Polymer Testing, 15 (1996) 91.
2 C. G. Mothé, S. M. Castro and M. I. B. Tavares, Polymer Testing, 15 (1996) 473.
3 C. G. Mothé and M. I. B. Tavares, Actas del Simposió Argentino de Polímeros, Vol. 1, Cordoba, Argentina, 1995, p. 267.