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Thermal characterization of mica–epoxy composite used as insulation material for high voltage machines

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Abstract The study of mica–epoxy-based composite has a great role in high voltage machines industry. Beside electric properties, this composite should present compatible mechanical and chemical, in this case thermal characteristics to insulate properly the conductor strand, avoiding short-circuits, and leading electrical current with minimal losses. Improvement of the quality is possible through the knowledge of raw materials and system. This study aims to list a complete thermal characterization of mica composite, its components, epoxy resin, anhydride methylhexahydrophtalic, mica tape and zinc naphthenate, and thermoanalytical interactions between them. These data shows intrinsic properties of the system, which is so relevant to its great electrical and thermal performance. Thermal analysis allows the detailed study of curing process and thermal decomposition, predicting and suggesting mechanisms, beside future and possible optimization to the system. Composite system glass transition (T_g) was obtained through an important and very respected methodology, presenting the value of $T_g = 138 \pm 2$ °C, finally characterizing the material.

Keywords Electric insulation · Mica composite · Thermal analysis · Cure characterization · Chemical interactions

Introduction

In early years, thermosetting resins and especially epoxy resins had acquired a wide and very respectable role in applications as a cover for surfaces and electronic components, power moldings, and as a matrix resins for advanced composites. The versatility in formulation also makes epoxy resins applicable industrially for electrical devices insulating materials [1, 2]. High voltage electric machines need a main insulation in their conductor strands, to minimize short-circuits and to conduct electric current properly. This insulation is the main factor to a high efficiency in the energy production and machine durability. The composite has in its composition a mineral which avoid the electric charge propagation and a resin to support it. A common characteristic shared by all variation of this insulation system is the use of a mica tape (supported mica in glass fabric) as a base material and synthetic resins of thermal curing as support material. The insulation system is based on VPI technique (vacuum/pressure/impregnation) in a controlled temperature, vacuum, and pressure cycle. Conductors are wrapped with a dry mica tape that contains an accelerator, zinc naphthenate (N-Zn), which is responsible for two components for the reaction between the impregnation mixture, a resin, diglycidyl ether of bisphenol-A (DGEBA) and the hardener, methylhexahydrophthalic anhydride (MHHPA). The main insulation tape consists in a glass fabric support, a thin mica tape, made of muscovite non-calcined, a reinforced material—that also bonds the glass support to the tape—and the accelerator. This tape is wrapped continuously for all winding length [3]. This composite is used as a matrix in high performance, and feature high specific strength and stiffness and good thermal stability. At elevated temperatures and at high levels of compressive stress at ambient temperature,

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the molecular structure of the matrix is fundamental to provide its mechanical properties, which in turn contribute to the performance of the composite [4]. The epoxy-based system studied in this study is an anhydride as a hardener, with a metallic salt as an accelerator. Anhydride allows the formation of a very high crosslinked chain density in the final polymer, raising mechanical and electrical properties.

Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) are specially useful to observe and define the chemical interactions of each substance and mixtures, and their comparisons when they are part of a composite. Through a particular mass loss, it is possible to set a degradation pattern of one pure substance and from the whole composite as well. Characteristic events related to decomposition or polymerization can be observed carrying TG curves of mixtures with the standard composition and taking off one of the compounds present in composite.

Differential Scanning Calorimetry (DSC) has been used extensively to monitor and characterize the epoxy thermosetting systems cured by carboxylic acid anhydrides, considering that the reaction occurs by consecutive step addition esterification involving these organic functions intermediates and significant addition etherification as a side reaction [5, 6]. Two intrinsic phenomena are very important in curing process, gelation and vitrification. The first one is related to gel point and is essential to determine the processing flow, once the system viscosity grows up to infinite and decrease the curing reaction rates. However, this phenomenon does not prejudice the cure process unlike vitrification. This transition of a viscous liquid or elastic gel to a glass may be an obstacle to the curing, even though being reversible, due to its diffusion control instead of chemical control [7]. Glass transition temperature (T_g) is also a characteristic of each material, specially thermoset polymers. By definition, it is the temperature which defines when the polymer chains or network start their movements and it is the transition of a rigid and glass structure to a flexible and rubbery structure. Some standards are used to measure this so-relevant property and in this study the standard ASTM (American Society for Testing and Materials) D3418-08 was used [8].

Conjugation with both techniques (DSC and TG) helps to understand some events involving mass loss and energy variation simultaneously. In addition, kinetics studies and lifetime predictions can be extrapolated to real operation temperatures. This study aims to list a complete thermal characterization of mica composite, its components (resin, hardener, accelerator, and mica tape) and thermoanalytical interactions between them. The properties of the system, which is so relevant to its great electrical and thermal performance are very important to know how optimize and increase its efficiency.

Methods and materials

The epoxy resin, DGEBA, was acquired from Huntsman, having commercial name HY 790, was used as received. This resin is liquid at room temperature; it is bifunctional and presents an epoxy equivalent weight of 167–171 g eq^{-1}.

The hardener, MHHPA, was acquired from Huntsman, having commercial name HY1102, was used as received. This material is a clear liquid at room temperature; it has an acid number more than 660 mg KOH g^{-1} and a maximum acid value of 1%.

The mica tape that is impregnated through the VPI (vacuum, pressure, and impregnation) process, described later, contains fine mica paper with basic weight per area unit, zinc naphthenate accelerator, epoxy-based binder on a 23 g m^{-2} density fiberglass fabric support material. Pure accelerator was also used as received from supplier (Borchers) having commercial name Solingen Zinc in mineral oil.

The test objects were prepared by the impregnation of 16 mica tape layers, in the manufacturing plant, just like as the regular production. This process starts with the drying step in the VPI tank under vacuum for at least 10 h. Then the impregnation mixture (resin and hardener) is transferred from the storage tank to the impregnation vessel, and the pressure phase begins under nitrogen for a specified period of time.

The DSC curves were obtained using NETZSCH DSC 200 F3 equipment previously calibrated; the scan was made in temperature range from 30 to 280 °C. The experiments were carried out using about 15 mg sample mass in aluminum pans, under a 50 mL min^{-1} nitrogen dynamic atmosphere, in a heating rate (β) of 10 °C min^{-1}. Only in the ASTM measurement, β is recommended to be 20 °C min^{-1}.

TG curves were obtained using NETZSCH Thermo Microbalance TG 209 F3 equipment previously calibrated; the scan was made in temperature range from 30 to 600 °C. The experiments were carried out using 30 mg (composite) and 10 mg (pure component) sample in Al_2O_3 crucibles, under a 10 mL min^{-1} N_2 dynamic atmosphere, with a β of 10 °C min^{-1}.

Results and discussion

An exploratory study was done using TG to the characterization of each component present in the composite. This procedure has been chosen to provide information about thermal characteristics of each raw material. The Fig. 1 illustrates TG and DTG curves of each composite component obtained under N_2 dynamic atmosphere. A comparison with available data about their properties in

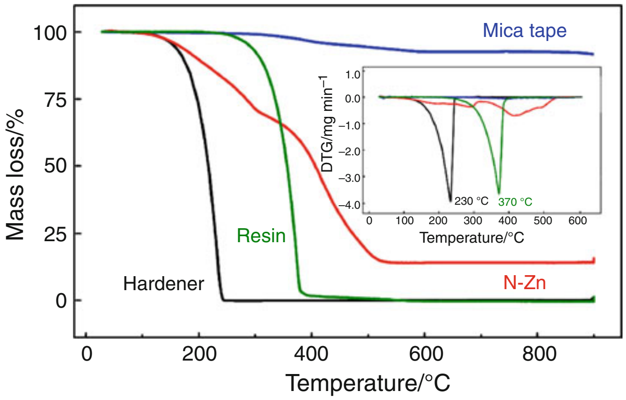


Fig. 1 TG/DTG curves of components obtained under N_2 atmosphere (10 °C min^{-1}), Pt pan, and β of 10 °C min^{-1}

Table 1 Degradation temperature data for pure components [9]

Component	Degradation temperature/°C	
	Experimental	Literature
Resin	322	>300 [9]
Hardener	207	203
Mica tape	348	–
N-Zn	251	250

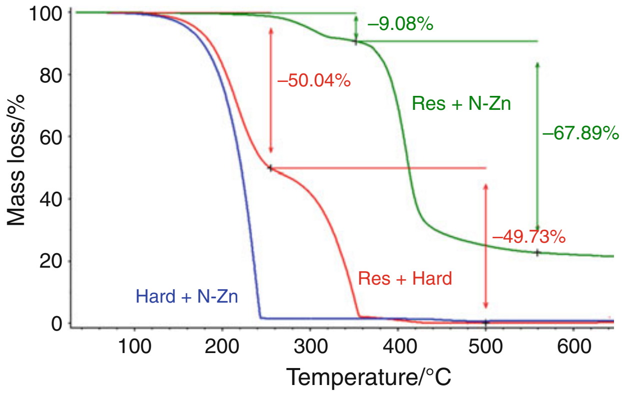


Fig. 2 TG curves of mixtures: resin/hardener, hardener/N-Zn, and resin/N-Zn under N_2 atmosphere (10 mL min^{-1}), Al_2O_3 pan, and β of 10 °C min^{-1}

literature was done. Chemical interaction between the components is important to understand the system and the synthesized polymer and to suggest mechanisms to the cure. Curing process of epoxy–anhydride system is more complex than other epoxy-based systems due to the lower reactivity of anhydride. First, it is interesting to study how each component can affect the thermal behavior of the others. The experimental values and corresponding data from literature are presented in Table 1.

Hardener and N-Zn decomposition temperatures were provided by each supplier material safety data sheet. In Fig. 2, it is possible to observe TG curves of mixtures Resin/Hardener, Hardener/N-Zn, and Resin/N-Zn. Comparing to TG/DTG curves of each component (Fig. 1), the mixture Hardener/N-Zn do not present any visible interference of accelerator in heating process, relating to mass loss, it loses mass in almost the same temperature of pure hardener. Resin/Hardener (1:1) mixture presents the same degradation pattern of both pure components, showing two events at onset 200 °C from hardener and 320 °C, approximately from resin, highlighting the non-interaction that have between them, in this temperature without any sort of additive, as one of the components evaporates before the temperature necessary for both to react with no initiator. Finally, it can be observed that in the mixture of Resin/N-Zn (1:0.03), there is a first (8.7%) mass loss related to resin degradation and at approximately 360 °C, there is a great mass loss due to a thermal decomposition of a resultant polymer. This polymerization occurred between 180 and 280 °C, as it can be observed in Resin/N-Zn mixture DSC curve (Fig. 3) represented by two exothermic events (T_{peak} = 210 and 260 °C) in a temperature range which TG curve did not present mass variation. In addition, in Fig. 3 in the pure components DSC curves (resin and N-Zn) were not observed in any exothermic event until 300 °C. This fact confirms that accelerator can open the epoxy rings of DGEBA, starting a polymerization, with little amount of N-Zn. In Resin/N-Zn mixture DSC curve, it can be observed at the end of polymerization the partial resin evaporation evidenced by an endothermic event (T_{peak} = 344 °C).

Chemical interactions of the tape with both components of impregnation mixture, resin and hardener, were prepared with a tape without N-Zn aiming the definition of the interaction only with mica, glass oven, and epoxy binder. Figure 4 presents TG and DTG of the resin and hardener with and without the tape.

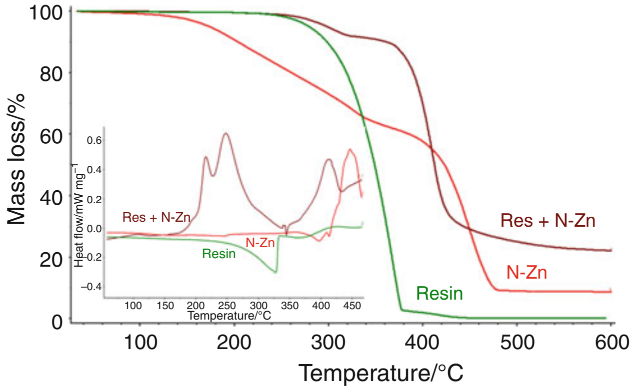
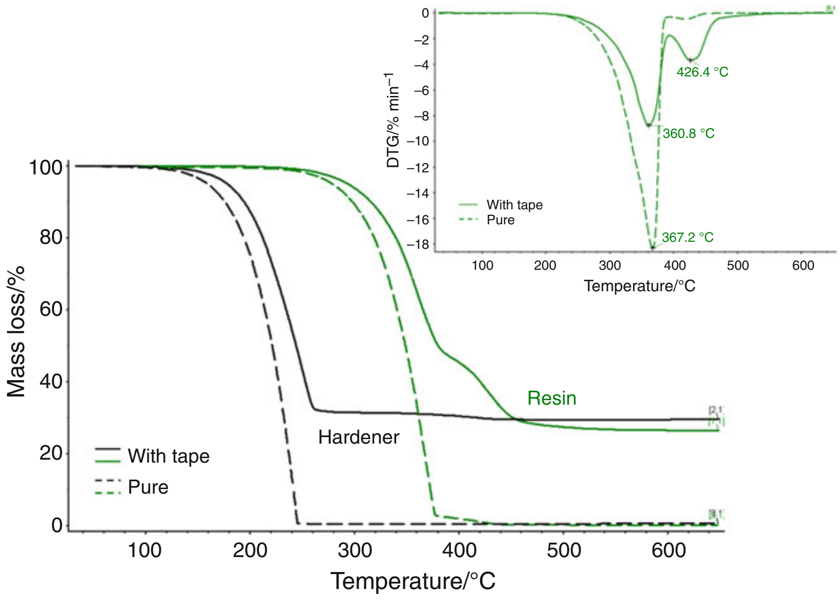


Fig. 3 TG curves of resin, N-Zn and resin/N-Zn under N_2 atmosphere (10 mL min^{-1}), Al_2O_3 pan, and β of 10 °C min^{-1} and DSC curves under N_2 atmosphere (50 mL min^{-1}), Al pan, and β of 10 °C min^{-1}

Fig. 4 TG/DTG curves of resin and hardener with and without mica tape under N_2 atmosphere (10 mL min^{-1}), Al_2O_3 pan, and β of 10 °C min^{-1}

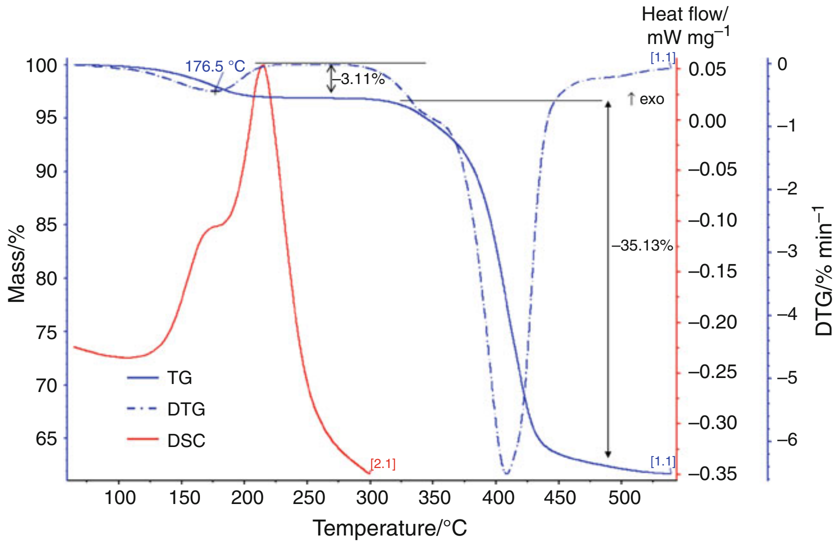


As it can be observed in the curve (Fig. 2), hardener, again, shows no interaction with the tape, presenting the same shape and profile pure or with the tape. With the physical obstacle to evaporate and decompose, the substance with the tape presents a little shift of degradation temperature. On the other hand, the interaction shown by resin with tape is an exothermic event at 426 °C, as it can be evidenced in DTG. It means that between these two components, the epoxy rings can open, the molecules are allowed to react and the product of this polymerization has a decomposition event at this higher temperature.

Complementing these data, the whole composite was studied. The samples were prepared not only just like in the manufacturing plant, as in fact, with the production bars. Body proofs were inserted in the impregnation tank and it was impregnated in the nominal conditions, respecting regular impregnation time and temperature, with all the variation that production products are submitted to. After that, body proofs were cut and prepared and thermoanalytical curves were obtained.

DSC and TG curves were obtained curing the material in dynamic process. Analyzing DSC curve, it is possible to observe the cure peak divided in two overlapped events. Epoxy–anhydride polymerization is a polycondensation and presents a mass change in curing process. Consequently, this first exothermic event is not a curing event, but evaporation [9b]. Complementing the calorimetric curve with a thermogravimetric curve, it is clear that the first mass loss event occurred in approximately 160 °C and this mass loss (about 3% mass) cannot be observed as an endothermic

Fig. 5 TG/DTG curves of uncured insulating composite under N_2 atmosphere (10 mL min^{-1}), Al_2O_3 pan and β of 10 °C min^{-1} and DSC curve under N_2 atmosphere (50 mL min^{-1}), Al pan and β of 10 °C min^{-1}



event due to the magnitude curing exothermicity that contains both events, overlapped and probably annulled.

The second weigh loss in the TG curve with onset at 323 °C is related to the composite degradation, which has mass loss of approximately 35%, corresponding to mica paper and fiberglass fabric, as inorganic materials. The curing event in the DSC curve (Fig. 5) presents two exothermic overlapped events. Both peaks are related to the complex curing of the system. Simulating ideal conditions, it was mixed with some resin and hardener, without the tape, with different amounts of accelerator.

The results are on going. The mixtures with higher concentration of zinc naphthenate presented lower cure temperatures than mixtures with less amount of accelerator, requiring more temperature to start the curing process. Two different events are observed with different concentrations of N-Zn, with a variable intensity. Preliminary experiments in laboratory under ideal conditions mixing resin, hardener, and accelerator in different concentrations presents the event at lower temperature to be more preeminent when it has more accelerator and the second one becomes dominant when the mixture has lower content of N-Zn.

Glass transition temperature of composite was made according to ASTM D3418-08 and composite presented a value of 138 ± 2 °C. The heat associated value with this transition is 0.07 J g^{-1} K^{-1}.

Conclusions

All thermal characterization was done with pure components and degradation temperatures were concordant to those related in literature. Chemical interactions were obtained through TG curves and among the pure components, the resin presented interactions (polymerization) with accelerator and mica tape. Decomposition temperature was defined in the first mass loss, at 138 °C, probably due to hardener evaporation and composite degradation temperature was defined at 323 °C. Glass transition temperature of composite was made according to ASTM D3418-08 and composite presented a value of 138 ± 2 °C.

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