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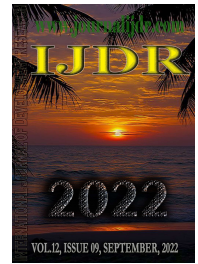
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RESEARCH ARTICLE

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PROPERTIES OF POLYESTER VARNISH COMPOSITES WITH ORGANOPHILIC CLAY

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ABSTRACT

In this work, a polyester-based electrical insulator varnish modified with soy oil was used to obtain composites by the incorporation of organophilic vermiculite (VMT-org). The dispersion of the VMT-org in the polymeric matrix was performed using an ultrasonic processor. Composites were produced with inorganic particle contents of 1, 3 and 5% (by weight of resin). TGA results showed no significant change in the thermal degradation temperatures. However, the incorporation reduced the maximum rate of degradation. The DSC results showed that the incorporation of VMT-org had two different states, caused by curing the varnish, resulting in two T_g values. The SEM observation showed good dispersion of inorganic particles. XRD analysis suggested that molecules of varnish were intercalated in the lamellae of VMT-org for the 1 and 5% composites, while the lamellae were exfoliated in the 3% composite.

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INTRODUCTION

The use of polymers, including recycled ones, continues to grow in Brazil and the rest of the world, prompting increasing research focused on improving the properties of these materials, particularly thermal and mechanical ones, since although they present several advantageous properties, polymers are very susceptible to degradation triggered by temperature, humidity and mechanical stress, among other factors (Siqueira *et al.*, 2021). One of the topics that has been extensively studied in recent years is the effectiveness of composite systems based on polymer matrices and different types of fillers. Since there is growing global concern among consumers, companies and governments with sustainable goals, mineral fillers have been increasingly studied as natural products to obtain composites. This is especially the case of mining wastes (Almeida *et al.*, 2021). The literature contains many studies focused on the use of minerals, such as muscovite, bentonite and vermiculite. The results of these studies reinforce the strong influence of the filler on the improvement of mechanical and thermal properties of polymers, including barrier properties and hydrophobicity of composites (Gerardo *et al.*, 2020; Pereira *et al.*, 2020; Souza *et al.*, 2022; Libano *et al.*, 2019; Reis *et al.*, 2019). In particular, vermiculite has an expandable lamellar structure, can be easily organophilized, thus facilitating its interaction with polymers, and also has adsorbent properties that make it a potential choice for use to remove of various substances, such as drugs, from water bodies (Rosa *et al.*, 2022).

Libano *et al.* (2019), for example, organophilized vermiculite by chemical treatment with sodium chloride and alkyldimethylbenzylammonium chloride, and obtained composites at concentrations of 2, 5 and 8% with high density polyethylene (HDPE). The composites showed a progressive increase in density and hardness and reduction in melt flow index (MFI) values with increasing mineral concentration. These results were attributed to restriction of the material's flow due to the action of vermiculite as a reinforcing filler in the HDPE matrix. In another study, Reis *et al.* (2017) organophilized vermiculite using stearyl dimethyl ammonium chloride to treat the mineral. The organophilic clay was used to obtain bionanocomposites with poly (3-hydroxybutyrate-co-3-hydroxyvalerate) - PHBV and was compared with the performance of the same composite obtained using natural vermiculite. XRD and SEM results showed the formation of nanocomposites with a more uniform structure and greater exfoliation of vermiculite in the system with the organophilized mineral than with the untreated mineral. In this context, this work investigated the influence of the use of organophilic vermiculite in the polymer matrix of an electroinsulating varnish modified with soy oil.

EXPERIMENTAL PROCEDURES

Materials: The varnish (ISO 9222) used is made from polyester resin modified with soybean oil, and was provided by the company Isolasil S/A (São Paulo, Brazil). The organophilization of vermiculite was

carried out in the laboratories of Rio de Janeiro State University (UERJ).

Production of composites: Composites were produced with mass percentages of 1, 3 and 5% of VMT-org, by mixing and dispersing VMT-org in an electro-insulating varnish based on polyester resin modified with soybean oil. The dispersion of VMT-org in the varnish was carried out using a Hielscher UP100H/100W sonicator for two hours. (Kim *et al.*, 2012) (Figure 1). The composite samples were named according to the VTM-org content. Thus, the following nomenclature was used: composite 1%, composite 3% and composite 5%.

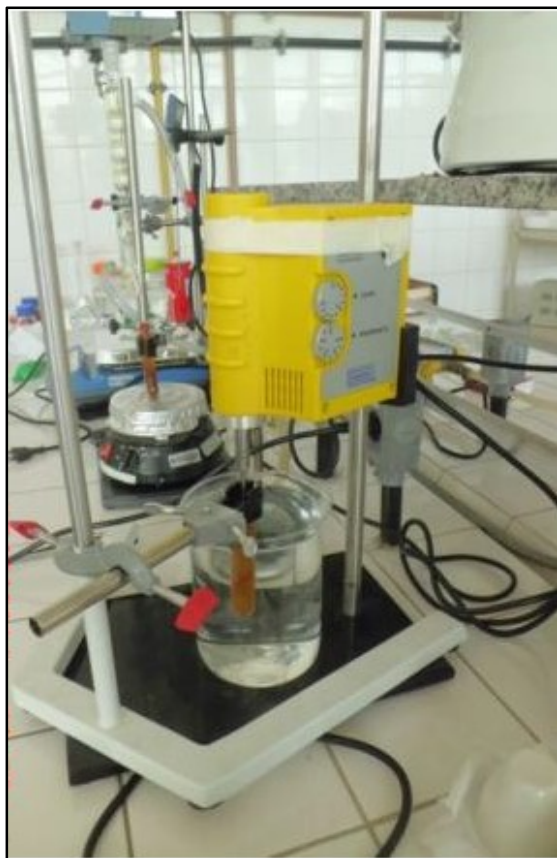


Figure 1. Sonication process used for the diffusion of VMT-org in the varnish

Characterization: For characterization, the specimens for the different tests (thermogravimetric analysis, differential scanning calorimetry, scanning electron microscopy and X-ray diffraction) were produced using square molds (30 x 30mm) (Figure 2). The specimens were cured in an oven at temperature ranging from 140 to 150 °C for a period of 4 to 5 hours. Subsequently, all specimens underwent two-hour post-curing.



Figure 2. Specimens for the different tests

Thermogravimetric analysis (TG): Thermogravimetry was performed in a TA Instruments model Q600 SDT analyzer with a heating rate of 10 °C/min under nitrogen atmosphere.

Differential scanning calorimetry (DSC): The DSC analysis was performed with a Netzsch model DSC 200 F3 instrument. The samples were first heated to a temperature above the T_g, held at that temperature for 10 min, and then cooled to 50 °C below the T_g. Afterwards, the samples were heated to the limit temperature of 200 °C also at a heating rate of 10°C/min under nitrogen atmosphere.

Scanning electron microscopy (SEM): The dispersion of VMT-org particles in the polymeric matrix of the varnish was evaluated through SEM with a Jeol model JSM 1610LV microscope. The surface of the samples was coated with a thin gold film and the electron beam acceleration voltage used was 20 kV.

X-ray diffraction (XRD): These analyses were carried out with a Rigaku Ultima IV X-ray diffractometer, using copper K α radiation ($\lambda = 1,4\text{\AA}$), voltage of 40 kV, current of 20 mA, and 2 θ sweep between 2 to 90°.

RESULTS AND DISCUSSION

After performing the TGA of the varnish and composites produced, we carried out a comparative analysis between their thermal stabilities. The thermogravimetric curves of Figures 3 and 4 show a comparative overlap between the different TG and DTG curves.

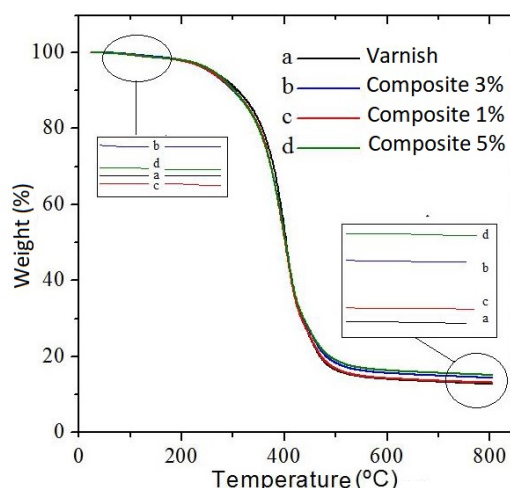


Figure 3. Comparative overlay of TG graphs of materials

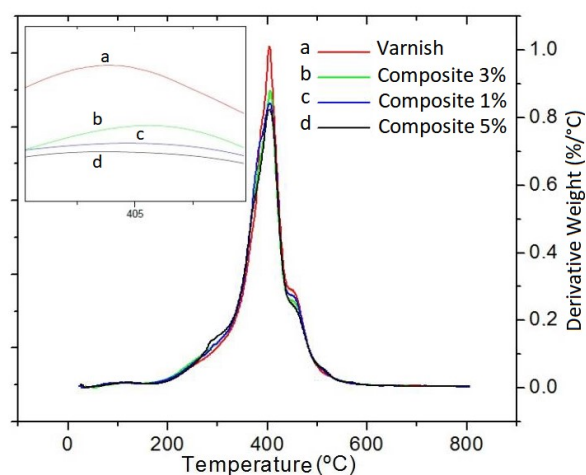


Figure 4. Comparative overlay of materials DTG graphics

Through these curves, it is possible to observe that at temperatures up to 180°C, limit of the working range of the ISO 9222 electro-insulating varnish, the 3% composite has higher thermal stability than the other materials. This composite lost 1.56% of its mass at 180 °C, while the varnish, the composite 1% and the composite 5% lost 1.68%, 1.77% and 1.67% of their initial masses, respectively, demonstrating that all materials underwent thermal degradation within the working range established by the manufacturer. It is also interesting that the addition of 1% and 5% by mass of VMT-org in the varnish did not promote significant thermal improvements to the composite produced. The 3% composite had the best performance, as indicated by the expansion of the peaks of the DTG curves (Figure 7), where peak degradation rate of this composite occurred at higher temperatures than the other materials. The arrows drawn in the enlargement of the peaks of the DTG graphs highlight that the peaks of the thermal degradation rates occurred at higher temperatures in the sequence: varnish; 5% composite; 1% composite and 3% composite, confirming that the 3% composite had greater thermal stability than the other materials studied. The high thermal stability of polymers in the presence of clay nanoparticles may have been due to the barrier effect caused by the exfoliated clay layers, creating a tortuous path, making it difficult for volatile products to diffuse through the polymeric material (Bunekar *et al.*, 2018; Zhu *et al.*, 2019; Gou *et al.*, 2020; Baniasad *et al.*, 2021; Khan *et al.*, 2022).

The results of the DSC analysis are shown in Figures 5 to 7.

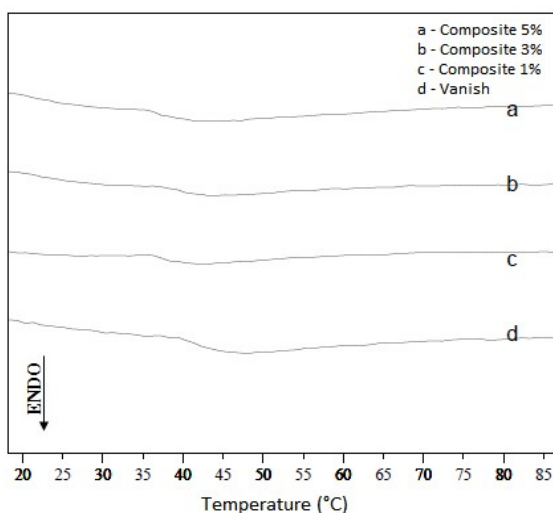


Figure 5. DSC curves of varnish and composites

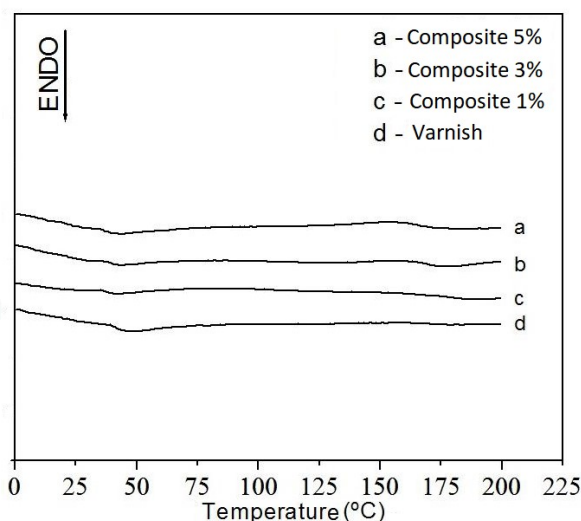


Figure 6. Enlargement of the first TG region

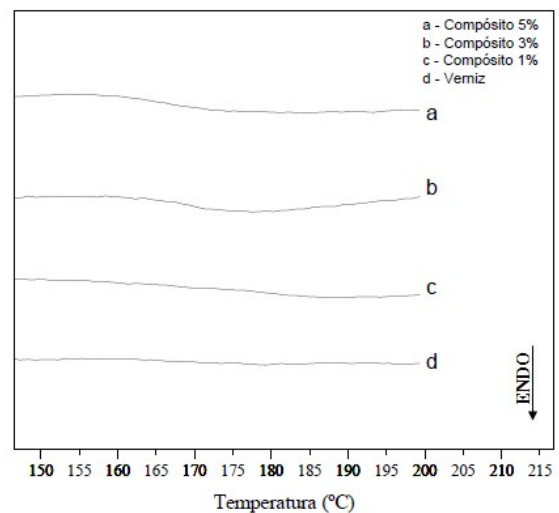


Figure 7. Enlargement of the second TG region

Two T_g values (T_{g1} and T_{g2}) were observed for the composites and only one T_g for the varnish (Table 1).

Table 1. Variation of glass transition temperatures with VMT-org contents

VMT-org content (%m)	T_{g1} (°C)	T_{g2} (°C)
0	42,28	-
1	37,10	175,8
3	40,00	167,6
5	38,60	165,9

Kim *et al* (2012) obtained composites having increasing T_g with rising content of silica nanoparticles, attributing this fact to the strong interaction between these nanoparticles and the polymer matrix of the varnish. Unlike the results obtained in the present study, where the T_g values decreased with the increase in VMT-org, Yan *et al* (2013) found a decrease in T_g with increasing percentage by mass of carbon nanotubes in polycarbonate composites. The authors attributed the result to increased polymer mobility in polycarbonate composites with carbon nanotubes. This increase in mobility could also be explained by the presence of soybean oil, acting as a plasticizer in the varnish under study for T_{g1} (Paiva *et al.*, 2006; Darros, 2013). Santos (2011) observed a small decrease in the crystallization temperature of nanocomposites by the use of flow aids because they were completely adsorbed on the surface of the nanoparticle used. The big difference between the T_g values obtained in the present study between the electroinsulating varnish ISO 9222 and the one used by Kim *et al* (2012), both with a polyester resin as base, is probably caused by the addition of soybean oil in the composition of the former. This oil works as a plasticizer, causing the T_g to decrease proportionally with the percentage added to the varnish (Torres *et al.*, 1998; Darros, 2013). Another interesting observation is that two glass transition temperatures were observed for the materials under study. This situation can probably be explained by the existence of different curing conditions of these materials or due to the addition of mineral filler. Both situations can generate a second region of low crystalline order, with stronger interactions than the first, requiring higher temperatures for the chains to acquire mobility. SEM analysis was used to evaluate the microscopic morphology of the VMT-org and 3% composite particles (Figures 8a and 8b, respectively).

The photomicrograph presented indicates that the VMT-org contains lamellar crystals. Minerals composed of very thin sheets or layers (lamellae) are apparently easier to disaggregate, facilitating the dispersion and and disaggregation of lamellar crystals in the polymer matrix (Sirelli, 2008; Libano *et al.*, 2019). The X-ray diffractograms of VMT-org, varnish and composites are shown in Figure 9. In the diffractograms of the composites with 1% and 5% by mass of VMT-org, it is possible to observe characteristic peaks of VMT-org at $2\theta =$

4° and 5.95°, and also the band between the 2θ regions of approximately 10° to 30°, characteristic of ISO 9222 varnish. The characteristic peaks of the VMT-org are closer to each other, and in comparison with the VMT-org, the first peak shifted to the right in the diffractogram (from 3.25° to 4°), and the second peak shifted to the left (from 6.45° to 5.95°), indicating there was a small increase in the interplanar distance, which can probably be explained by the small intercalation of the varnish polymer matrix between the clay layers (Cherifi *et al.*, 2018; Khelifa, 2019). Regarding the interplanar distances referring to the two characteristic peaks of the VMT-org, the first decreased from the original value of 27.1 Å to 22.0 Å, while the second increased from 13.6 Å to 14.84 Å.

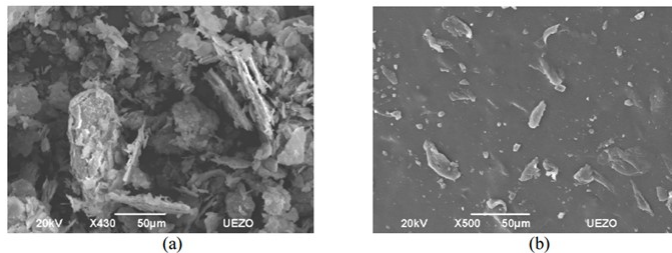


Figure 8. Micrographs obtained by SEM of VMT-org particles (a) and 3% composite (b)

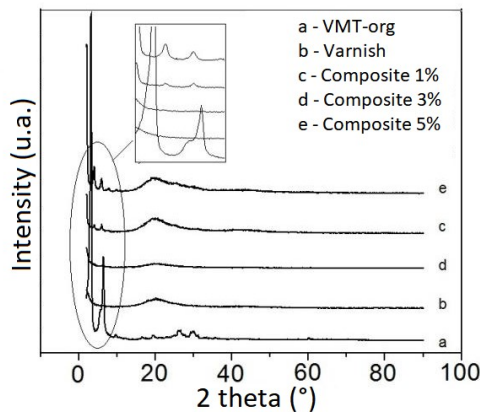


Figure 9. X-ray diffractograms of VMT-org, varnish and composites

In the diffractogram of the composite with 3% (d) mass of VMT-org, the characteristic peaks of VMT-org practically disappeared, suggesting the formation of a composite with exfoliated clay (Al-Shamrani, 2017; Chen *et al.*, 2017; Adak *et al.*, 2018). The band between the 2θ regions of approximately 10° to 30°, characteristic of ISO 9222 varnish, was maintained.

CONCLUSION

In this work, composites were prepared by incorporating different percentages of VMT-org in the polymer matrix of the ISO 9222 electro-insulating varnish. The TG results revealed that the composite with 3% by mass of VMT-org had better thermal stability. The DSC results showed that the incorporation of VMT-org caused two different curing states in the varnish, resulting in two T_g values. SEM analysis revealed good dispersion of inorganic particles. XRD analysis suggested there was intercalation of the varnish molecules in the lamellae of the VMT-org for the 1 and 5% composites, and exfoliation of the lamellae for the 3% composite.

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