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Article

Thermal behavior and Fire resistant properties of Vinyl Ester Resins Modified with Dimethyl Methylphosphonate and Diatomite

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Abstract. The thermal behavior and flame-retardant performance of vinyl ester resins (VER) modified with dimethyl methylphosphonate (DMMP) and diatomite (DE) were investigated. Differential Scanning Calorimetry (DSC) was performed using a NETZSCH DSC 300 Caliris Select instrument (Germany). Measurements were conducted in Concavus aluminum crucibles under a nitrogen atmosphere with a constant flow rate of 40 mL/min. VER was modified using three types of fillers: DE alone, a physical mixture of DMMP and DE, and DMMP immobilized on DE. These modifications resulted in distinct values for glass transition temperature, glass transition range, and heat capacity change (ΔCp). These parameters provide insight into the chain mobility and flame-retardant properties of the materials. The narrow transition range and lowest ΔCp observed for the immobilized DMMP sample indicate the increase in thermal stability of the material compared to the other samples, which corresponds with the LOI and flammability tests. This includes increased decomposition temperature and enhanced char formation, offering improved protection under real fire conditions. These results demonstrate the effectiveness of modifying VER with immobilized DMMP as a strategy for producing flame-retardant materials and may provide guidance for the development of new fire-safe composites.
Keywords: VER, DMMP, diatomite, glass transition temperature, heat capacity change, immobilized

1. Introduction

Vinyl ester resin (VER) is one of the well-known thermosetting polymers. It is based on an epoxy resin that has reacted with a saturated carboxylic acid, such as acrylic or methacrylic acid. These resins consist of oligomers derived from diglycidyl ether of bisphenol A (DGEBA), while styrene is typically used as a reactive diluent and crosslinking agent [1], [2], [3].

The resulting resin contains vinyl groups that participate in polymerization. Vinyl ester resin is therefore considered a hybrid of epoxy and polyester chemistry.

VER combine desirable mechanical and chemical characteristics, exhibiting high mechanical strength, chemical resistance, thermal stability, and good processability. Owing to these properties, vinyl ester resins are widely used in the production of fiberglass-reinforced products, construction materials, aerospace components, and wind energy structures.

However, despite their versatile properties, vinyl ester resins possess high flammability and therefore do not meet the requirements for fire-resistant materials. One of the approaches to solving this problem is the incorporation of fillers and functional additives [4], [5], [6], [7].

Phosphorus-containing compounds are traditionally considered effective flame retardants due to their relatively high fire-protection performance [8]. However, for vinyl ester resins in particular, there are still very few flame retardants that simultaneously enhance fire resistance without compromising the intrinsic properties of the matrix. For example, many flame retardants significantly reduce the onset temperature of mass loss and lead to deterioration of mechanical properties [9], [10], [11].

One of the additives capable of imparting flame-retardant properties to the matrix is dimethyl methylphosphonate (DMMP). Its flame-retardant mechanism is based on flame inhibition through the interaction of generated radicals with H· and OH· radicals, thereby suppressing flame propagation [12]. However, DMMP cannot be directly incorporated due to its volatility and migration within polymer matrices [13], [14], which results in a short-lived effect.

This issue can be addressed by retaining DMMP within the pores of a carrier material that also exhibits flame-retardant properties. The introduction of porous carriers has a long history, as it helps to retain volatile flame retardants and prolong their effect. For example, Cheng [15] used the incorporation of DMMP in the pores of the copper oxide to apply tis composite to modify the flexible polyurethane foam. This resulted in an excellent flame retardant.

Scientists from the University of Science and Technology of China have found a way to ensure the long-term fire-retardant properties of DMMP by immobilizing DMMP in the micro- and nanoporous channels of diatomite (DE) and then introducing it into vinyl ester resin (VER) [16].

Diatomite is a sedimentary material consisting mainly of silicon oxide. Due to the fact that diatomite is formed from the remains of algae, it has a good porous structure (pore sizes 5-500 nm), which makes it a good carrier of flame-retardant molecules [17]. Diatomite-based composites demonstrate fire-resistant properties and help suppress smoke formation and heat release [18].

These two flame retardants must be used together in an integrated manner, as each has its own disadvantages when used separately. When added, diatomite can increase the viscosity of vinyl ester resin.

The morphological properties of polymers are typically evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). From curing kinetics and thermal transitions, it is possible to determine the glass transition temperature, polymer chain mobility, structural homogeneity, interfacial constraints, and even the formation of char-forming centers [19].

In this study, the results of differential scanning calorimetry analysis of vinyl ester resin-based composites containing DMMP and diatomite (DE@DMMP) are presented. The analysis and determination of parameters such as the onset, maximum, and endset glass transition temperatures, the change in heat capacity (ΔCp), and the glass transition range provide insight not only into the plasticity and chain mobility of the material but also into the flame-retardant performance of the composite.

2. Methods

Vinyl ester resin-based composite samples containing DMMP and diatomite (DE@DMMP) were prepared by colleagues at the University of Science and Technology of China (Hefei, China) as part of a project funded under the program-targeted grant of the Science Committee of the Ministry of Science and Higher Education (Grant No. BR28712729) [16].

Four vinyl ester resin samples were tested, and their characteristics are presented in the following Table 1.

Table 1 – Content of samples [16]

Substrates (g)	**Samples**			
	Pure VER	VER 3	VER 2	VER 1
Resin	100	75	75	75
Diatomite (DE)	/	/	12.5	25
DE@DMMP	/	25	/	/
DMMP	/	/	12.5	/
Promoter	1.5	1.125	1.125	1.125
Catalyst	1.5	1.125	1.125	1.125

The composite containing DE@DMMP was prepared by first vacuum-immobilizing DMMP within the pores of DE (producing DE@DMMP), after which the resulting filler was incorporated into vinyl ester resin (VER) with stirring until a homogeneous dispersion was achieved. The mixture was degassed under vacuum, then a curing accelerator and initiator (each at 1.5 wt.% relative to the resin) were added, poured into molds, and cured at room temperature until the composite was fully formed.

VER 3 is the sample prepared using the technology of DMMP immobilization within diatomite pores, whereas VER 2 was obtained by physically mixing DMMP and diatomite, and VER 1 contains only diatomite added to the resin.

Successful adsorption of DMMP on the surface of diatomite (DE) was confirmed by comparative FTIR analysis, reported in our previous study [16]. The VER 1 system showed absorption bands at 1090–1030 cm^{-1} (Si–O–Si valence vibrations) and 800 cm^{-1} corresponding to the SiO_2 structure.

In the VER 2 system with physically mixed diatomite and DMMP, the FTIR spectrum is a linear superposition of the spectra of the individual components, showing both the diatomite bands at 1090–1030 cm^{-1}, and the P=O valence vibrations at 1250–1230 cm^{-1}, P–O–C vibrations at 1040–1020 cm^{-1}, and $–CH_3$ valence vibration bands at 2960–2840 cm^{-1}, characteristic of DMMP. This indicates that the components practically do not interact.

The FTIR spectrum of VER 3 with immobilized DMMP shows a noticeably different character. The positions of some peaks remain unchanged, but the intensities of the bands corresponding to P=O, P–O–C, and $–CH_3$ vibrations have decreased, indicating the localization of DMMP in the diatomite pores.

SEM analysis was also performed, confirming that the regular pores of the diatomite in the VER 3 sample are filled with DMMP.

The thermal properties of the samples were studied using differential scanning calorimetry (DSC) on a NETZSCH DSC 300 Caliris Select instrument (Germany). Measurements were carried out in Concavus aluminum crucibles under a nitrogen atmosphere with a constant flow rate of 40 mL/min. Sample masses ranged from 10.28 to 10.55 mg. To eliminate the thermal and mechanical history of the material, samples underwent a double scanning cycle over a temperature range of 0 °C to 180 °C at a heating and cooling rate of 10 K/min.

The measurement protocol included a first heating to 180 °C with an isothermal hold of 10 minutes, followed by cooling to 0 °C with a 10-minute isothermal period, and a second heating to 180 °C. This data was not taken into account in the analysis. All thermal effects, including the glass transition temperature, were determined exclusively based on the results of the second heating cycle. The data obtained was processed using NETZSCH Thermal Analysis Proteus 9.1.1 software.

3. Results and Discussion

The results of the analysis of the thermal properties of VER modified by DMMP and DE using differential scanning calorimetry are shown in the following Figure 1.

The absence of a distinct exothermic peak indicates a gradual curing process, reflecting high structural homogeneity.

As can be seen from the figure, the maximum of glass transition temperature T_g(Max) of the pure VER is the highest. VER 1, the sample with added diatomite, shows a slight decrease in the exothermic transition temperature. Next is VER 3 (DE@DMMP), the sample prepared by immobilizing DMMP on diatomite. The lowest glass transition temperature (Max) is observed for the composite prepared by physically mixing DMMP and DE with VER.

The following table presents the onset, maximum, and endset glass transition temperatures, as well as the changes in heat capacity (ΔCp) for the samples, determined by processing the DSC signals using NETZSCH Thermal Analysis Proteus 9.1.1 software (Table 2).

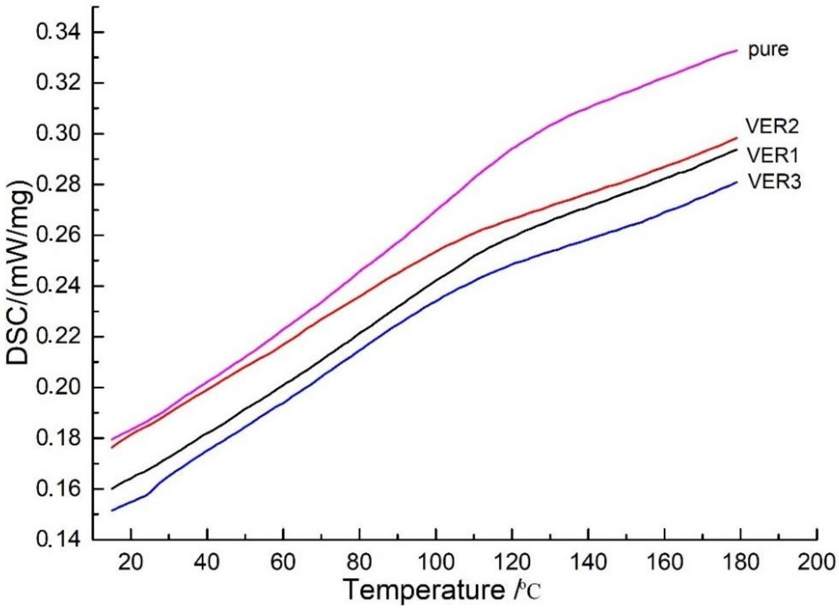

Figure 1 – DSC analysis result: VER 1 – VER with Diatomite; VER 2 – VER with physically mixed DMMP and Diatomite; VER 3 – VER with DMMP immobilized on diatomite

Table 2 – Parameters of DSC analysis

	Onset ^{0}C	Max^{0}C	Endset ^{0}C	ΔC_pJ/g*K
Pure VER	66.6	109.0	126.0	0.135
VER 1	51.8	92.1	112.7	0.132
VER 2	57.6	65.0	72.1	0.031
VER 3	76.2	78.3	80.3	0.016

Pure VER, VER 1, VER 2, and VER 3 exhibited a single transition, with the exothermic temperature ranges of 66.6–126 °C, 51.8–112.7 °C, 57.6–72.1 °C, and 76.2–80.3 °C, respectively. It is evident that the pure VER and the VER with diatomite display a wider glass transition range compared to VER 2 and VER 3, that indicates an increase in the structural homogeneity of the polymer matrix of latter samples. The composite obtained by immobilizing DMMP on diatomite (VER 3) showed the narrowest glass transition range (5.1 °C).

A decrease in glass transition temperature corresponds to an increase in polymer chain mobility, with DMMP playing a key role in this effect. This contributes to a limited increase in the mobility of polymer chains.

Among all samples, VER 3 exhibited a higher T_g (Onset), confirming the effective fixation of DMMP within the diatomite.

VER with diatomite, compared to VER 2 and VER 3, demonstrates a higher T_g (Max), indicating that diatomite alone does not affect chain mobility and does not act as a plasticizer. Comparing samples with physically mixed DE and DMMP (VER 2) and immobilized DE@DMMP (VER 3), the immobilized system minimizes the plasticizing effect.

The change in heat capacity decreases in the series Pure VER-VER 1-VER 2-VER 2. The lowest ΔCp value 0,016 J/g*K observed for the system with immobilized DMMP indicates a decrease in the proportion of mobile polymer segments involved in the glass transition process. This behavior indicates the formation of a more limited interphase region and increased restrictions on the mobility of interphase chains. Such structural restrictions can increase the energy required for the rearrangement of polymer chains and their thermal destruction. At the same time, a decrease in the number of mobile segments reflects a higher degree of structural organization of the composite.

All modified samples showed a decrease in heat capacity compared to pure VER, with the system with immobilized DMMP showing the smallest change. These structural features may contribute to the increased thermal stability of the material, but the DSC data themselves mainly reflect changes in chain mobility and interphase interactions.

We previously tested the fire-resistant properties of VER-based composites using limiting oxygen index (LOI) measurements and UL-94 vertical burning tests [16].

Pure VER has an LOI of 21% and is not self-extinguishing, indicating high flammability. VER 1 with diatomite showed the same results as the pure sample. In experiments with VER 3, there was noticeable progress in LOI 25%, and in the UL-94 test, it achieved class V-2, showing improved self-extinguishing ability.

VER 3 with immobilized DMMP showed an LOI value of 26%, and in the UL-94 test, it achieved a V-0 rating.

The results of differential scanning calorimetry analyses, LOI registration, and UL-94 flammability tests confirm the increased fire resistance of the VER sample with DMMP immobilized on diatomite compared to VER with diatomite and VER with physically mixed DMMP and diatomite.

4. Conclusions

In this study, samples based on vinyl ester resin with the addition of DMMP and diatomite were subjected to thermal property analysis using differential scanning calorimetry. Four samples were tested: pure vinyl ester resin, VER 1 – 75% VER and 25% DE, VER 2 – physical mix of 75% VER, 12.5% DMMP, and 12.5% DE, VER 3 – 75% VER and 25% DMMP immobilized on DE. The DSC curves show no clear exothermic peak, indicating a smooth curing process. However, the NETZSCH Thermal Analysis Proteus 9.1.1 program identified parameters such as onset, max T_g, endset, and ΔC_p. According to the analysis of these data, the glass transition temperature of the pure sample is higher than the others, and VER 3 has a higher T_g compared to VER 2. In other words, although DMMP is a plasticizer, its immobilization on diatomite minimizes this effect. All modified samples showed a decrease in heat capacity compared to pure VER, with the system with immobilized DMMP showing the smallest change. The narrowing of the glass transition range observed for VER 2 and VER 3 indicates an increase in the structural homogeneity of the polymer matrix. These structural features may contribute to an increase in the thermal stability of the material, which is consistent with the results of TGA and flammability tests. The results of this work can be used to develop new fire-resistant composites with predetermined properties.

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Use of Artificial Intelligence (AI): AI used only for improve the English of the paper

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