

## THERMALLY CLEAVABLE HYBRID MATERIALS<sup>♦</sup>

Constantin Gaina, Oana Ursache, Viorica Gaina\*

„Petru Poni” Institute of Macromolecular Chemistry,  
Aleea Gr. Ghica Voda 41 A, Iasi, RO-700487, Romania

\*Corresponding author: [vgaina@icmpp.ro](mailto:vgaina@icmpp.ro)

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**Abstract:** Thermally cleavable hybrid materials were prepared by the Diels-Alder cycloaddition reaction of poly(vinyl furfural) to *N*-phenylmaleimido-*N'*-(triethoxysilylpropyl)urea followed by the sol-gel condensation reaction of triethoxysilyl groups with water and acetic acid. Thermal and dynamic mechanical analysis, dielectric and FTIR spectroscopy were used to characterize the structure and properties of the composites. The size of the inorganic silica particles in the hybrid material varied dependent on the silica content. The DSC study of the prepared materials revealed that the cleavage process of the formed cycloadducts takes place at temperatures varying between 143-165°C and is an endothermic process.

**Keywords:** *acetalization of polyvinyl alcohol, Diels-Alder cycloaddition, hybrid materials, maleimide, sol-gel condensation*

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## INTRODUCTION

Polymer-inorganic nanocomposite materials are promising systems for many applications due to their extraordinary properties arising from the synergism between the properties of these two different building blocks [1-2]. Some studies have revealed that introducing inorganic component derived from Si-containing precursor into an organic polymer can form a homogeneous nanocomposite membrane with enhanced physicochemical stability and separation performance [3-10]. The final bulk properties of the hybrid organic-inorganic composites synthesized by sol-gel method depend on the homogeneity of the sol-gel mixture. PVA/silica system has attracted recent attention due to the good chemical stability, film-forming ability and high hydrophilicity and pervaporation properties [11-12] and hydrogel behavior. Different routes have been proposed to prepare PVA/silica nanocomposites *in situ* by sol-gel method, starting from PVA solutions, tetraalkoxysilane and trialkoxysilane [11-13]. The PVA-silica hybrids have been prepared by sol-gel method, starting from tetraethylorthosilicate, tetramethylorthosilicate or trialkoxysilane and PVA and were characterized for potential applications in drug delivery, or selective membrane for immobilization of carriers for biocatalyst. PVA must be cross-linked in order to be useful for a wide variety of applications [14].

In this work we described the synthesis and characterization of new hybrid PVA materials with thermally cleavable groups obtained from poly(vinyl furfural) and new maleimide monomers containing triethoxysilane groups able to react by the sol-gel process.

## EXPERIMENTAL

### Measurements

The FTIR spectra were recorded on a Bruker Vertex 70 Instruments equipped with a Golden Gate single reflection ATR accessory, spectrum range 600-4000  $\text{cm}^{-1}$ . The  $^1\text{H}$ -NMR spectra were recorded on a Bruker NMR spectrometer, Avance DRX 400 MHz, using  $\text{CDCl}_3$  as solvent and tetramethylsilane as an internal standard. Differential scanning calorimetry (DSC) measurements were done using a Du Pont Instruments 912 DSC with a heating rate of  $10^\circ\text{C}/\text{min}$ , in nitrogen. Thermogravimetric analysis (TGA) was carried out in air with a F. Paulik Derivatograph at a heating rate of  $10^\circ\text{C}/\text{min}$ . Dynamic mechanical experiments were made using a Diamond Perkin Elmer instrument that applies a sinusoidal stress to the sample and measure the resulting strain. The force amplitude used was well within the linear viscoelastic range for all investigated samples. The thermo-mechanical properties were evaluated, starting from room temperature up to beyond the temperature corresponding to glass transition, at a heating rate of  $4^\circ\text{C}/\text{min}$  and a frequency of 1 Hz, under nitrogen atmosphere. The size of films was of  $10 \times 10 \times 0.5$  mm for the tension attachment. Dynamic contact angles (advancing and receding contact angle) were performed by the Wilhelmy plate technique, using a Sigma 700 precision tensiometer produced by KSV Instruments. The sample plate dimensions were  $50 \times 8$  mm and rate of immersion-emersion was 5

mm/min in water. Immersion depth was 5 mm in standard conditions. All measurements were obtained as the average of 3 measurements. The dielectric measurements were carried out using a Concept 40 Dielectric Spectrometer (Novocontrol GmbH Germany). The samples were prepared in the form of films with thickness of about 0.04 - 0.07 mm. They were sandwiched between two silver electrodes of 20 mm diameter and placed inside temperature controlled sample cells. The complex permittivity:  $\epsilon^*(f) = \epsilon'(f) + i\epsilon''(f)$  has been determined in the frequency ( $f$ ) range from 1 to  $10^6$  Hz and at temperature range from 0 to 250°C. The AC voltage applied to the capacitor was equal to 1 V. Temperature was controlled using a nitrogen gas cryostat and the temperature stability of the sample was better than 0.1°C.

## Reagents and Materials

Poly(vinyl alcohol) (**PVA**) white crystalline form (Lobafein Chemie AG,  $M_w = 65000 - 78000$  Da, containing 2% of acetate groups), 2-furaldehyde 98% (Aldrich), (3-aminopropyl) triethoxysilane (Aldrich), tetraethoxysilane 98% (**TEOS**) (Aldrich), *N,N'*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *p*-toluenesulfonic acid (***p*-TSA**) were used as received. 4-Maleimidophenyl isocyanate (**MPI**) was prepared according to a method presented in the literature [15].

*N*-[4-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)phenyl]-*N'*-propyl-3-triethoxysilane (**1**) was prepared by the addition reaction of (3-aminopropyl) triethoxysilane to **MPI** in methylene chloride. To a solution of **MPI** (2.14 g, 10 mmol) in 50 mL of methylene chloride cooled at 0-5°C in an ice bath, (3-aminopropyl) triethoxysilane (2.33 g, 10 mmol) was added gradually. After stirring for 2 h at 0-5°C and 2 h at room temperature, the solvent was evaporated by reduced pressure and the product was dried under vacuum at 50°C for 6 h. The product was obtained in 93% yield, mp = 145-150°C decomp.

Elemental analysis calculated for  $C_{21}H_{31}N_3O_6Si$ : C, 56.10; H, 6.95; N, 9.35; Si, 6.25 %. Found: C, 56.45; H, 7.07; N, 9.27; Si, %. FTIR (KBr),  $cm^{-1}$ : 3393, 3293, 3103, 2974, 2930, 2883, 1718, 1660, 1606, 1550, 1517, 1401, 1318, 1244, 1158, 1108, 1078, 957, 827, 786 and 690.  $^1H$ -NMR ( $CDCl_3$ ),  $\delta$  (ppm): 7.35 (d, 2H,  $J = 8.8$  Hz, aromatic protons), 7.33 (s, 1H, Ph-NH-CO-), 7.17 (d, 2H,  $J = 8.8$  Hz, aromatic protons), 5.52 (s, 1H, NH-CH<sub>2</sub>-), 3.82 (q, 6H, -CH<sub>2</sub>-O-), 3.22 (dd, 2H, CH<sub>2</sub>-NH), 2.12 (t, 9H, -CH<sub>3</sub>), 1.63 (m, 2H, -CH<sub>2</sub>-), 0.65 (q, 2H, -CH<sub>2</sub>-Si).

Poly(vinyl furfural) (**PVF**) was prepared by acetalization of **PVA** in DMSO as solvent, in the presence of ***p*-TSA** according to a method described in the literature [16,17]. The degree of acetalization was determined by  $^1H$ -NMR spectrum using eqn. (1) [18].

$$(FA) = \frac{2}{\frac{A_{CH_2}}{A_{H_5}} - 2} \quad (1)$$

where: (FA) is the mol of vinyl acetate,  $A_{CH_2}$  represents the total peak area of methylene chloride protons and  $A_{H_5}$  represents peak area of H<sub>5</sub> protons of furan ring which appears at 7.6 ppm. A typical procedure is presented below. **PVA** (11 g, 0.25 mol, based on -CH<sub>2</sub>-CH-OH as unit) was dissolved in DMSO (200 mL) in a round bottom flask. Then,

*p*-TSA (2 g, 1% w/v of the reaction medium) and 2-furaldehyde (10 mL, 0.12 mol) was added. The reaction mixture was heated and stirred at 60°C for 24 hours, then cooled at room temperature and poured in water. The solid was filtered, then washed well with water and finally dried in a vacuum oven at 60-65°C for 24 hours, yield 82%.

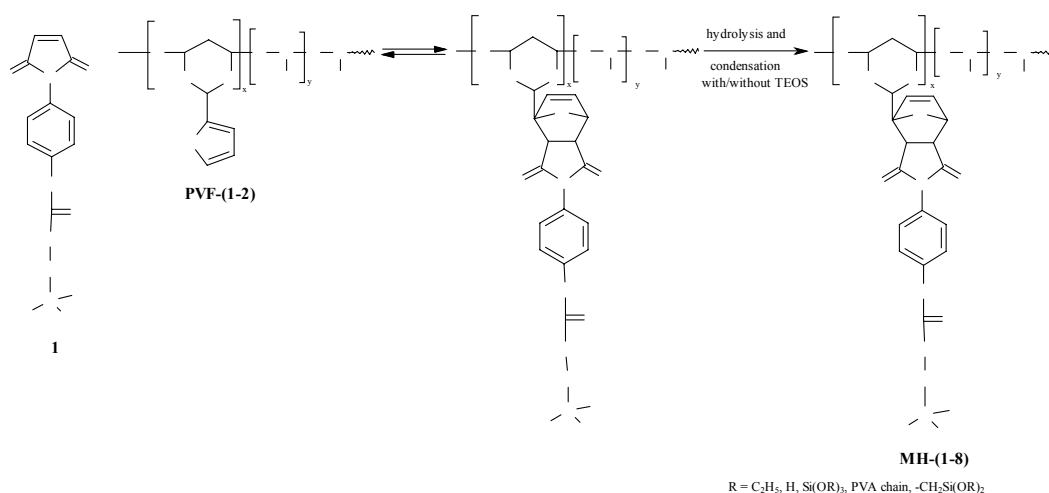
**Preparation of hybrid material films MH-(1-8)** To a solution of **PVF-1** (1 g) dissolved in 3.5 mL of DMF at room temperature, monomer **1** (0.9 g) was added and stirred at 80°C for 8 h. Then, a known amount of **TEOS**, water (1.5 mL) and concentrated acetic acid as catalyst were added. The solution was stirred at 60°C over night and the resulting homogenous solution was cast onto a glass plate and dried at 80°C for 12 h. The mass ratio of **1** to **PVF** was varied at 0.72, 0.9, 2.0 and 2.48 and **TEOS** to **PVF**-cycloadduct based on maleimide **1** ranged between 1.32 and 2.42 (Table 1).

**Table 1.** Composition of hybrid materials

Sample	PVF	$m_{PVF}$ [g]	$m_I$ [g]	$m_{TEOS}$ [g]	SiO <sub>x</sub> [%]
MH-1	2	1.25	0.9	-	7.5
MH-2	2	0.5	1	-	11.5
MH-3	2	1	2.48	-	12.5
MH-4	2	1.25	0.9	2.8	28.5
MH-5	2	1	2.48	4.6	30.4
MH-6	1	1	0.9	-	8.4
MH-7	1	1	0.9	2.8	30
MH-8	1	1	0.9	4.6	34

## RESULTS AND DISCUSSION

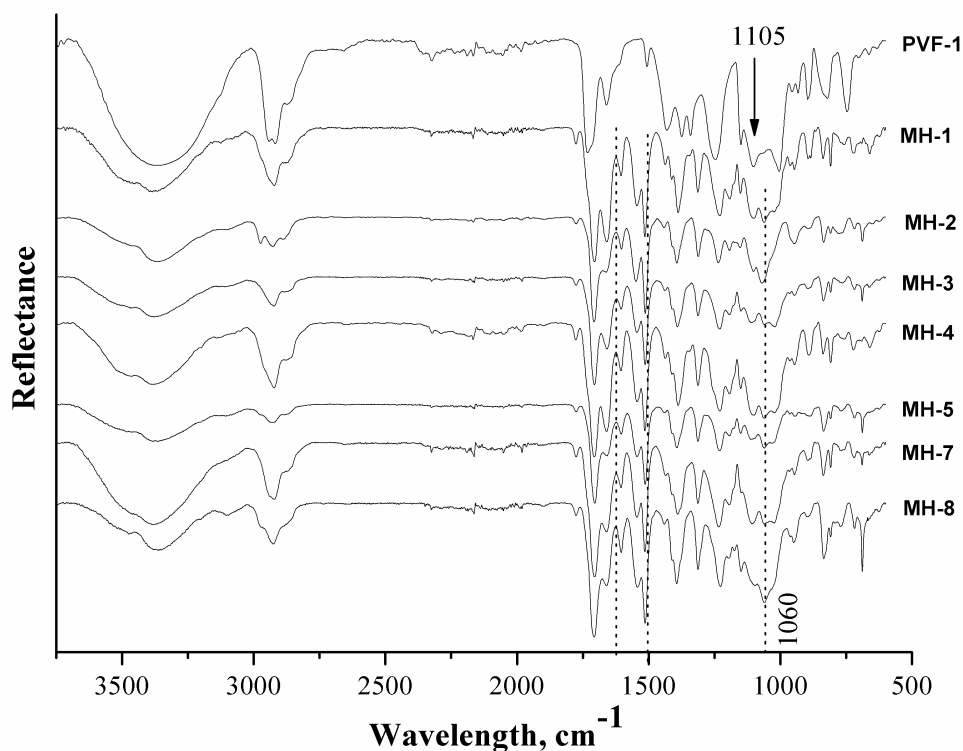
The incorporation of silicone groups into a **PVA** matrix was performed by Diels-Alder reaction of monomer **1** to **PVF** followed by the sol-gel condensation of triethoxysilyl groups with water and acetic acid (Figure 1).



**Figure 1.** Reaction scheme for the preparation of hybrid material films

The condensation reaction of triethoxysilyl or tetraethoxysilyl groups' reaction may arise with the same or different groups or the OH remained unacetalized with furfural. The incorporation of silicone groups into **PVF-(1-2)** was confirmed by ATR-FTIR studies. Figure 2 shows the spectra of **PVF** and their hybrid films with **TEOS**.

A characteristic strong and broad band appeared at around  $3400\text{ cm}^{-1}$  in the spectra of **PVF-(1-2)** corresponding to stretching vibrations of the hydroxyl groups. The intensity of this peak decreased with increasing the  $\text{SiO}_2$  content. This is attributed to reaction of OH groups from **PVF** with  $\text{Si(OH)}_x$  groups. Also, the ATR-FTIR spectra of **MH-(1-8)** present new bands around  $1600\text{--}1500\text{ cm}^{-1}$  assigned to CO-NH ( $1550\text{ cm}^{-1}$ ) and aromatic ring ( $1510\text{ cm}^{-1}$ ). The intensity of  $>\text{CH-OH}$  bands from **PVF-1** at  $1105\text{ cm}^{-1}$  decreased with increasing mass ratio of **TEOS** from membrane compositions. Also, new bands appeared at  $1060\text{ cm}^{-1}$  attributed to CO and Si-O groups, suggesting formation of Si-O-C bonds in the resulting membrane [19].



**Figure 2.** The ATR-FTIR spectrum of **PVF** and their hybrid films with **TEOS**

Thermal behavior of hybrid materials **MH-(1-8)** was evaluated by DSC, TGA, DMA measurements and dielectric spectroscopy. The DSC curves of **PVF-(1-2)** and **MH-(1-8)** are presented in Figure 3 and the data in Table 2.

The glass transition temperature of **PVF-(1-2)** was clearly observed around  $74^\circ\text{C}$ . With addition of monomer **1** and **TEOS** the  $T_g$  of **PVF-(1-2)** disappears and a new endothermic peak appears which is specific for the retro Diels-Alder reaction around  $143\text{--}165^\circ\text{C}$  [19]. Also, DSC scans of hybrid materials exhibited an exothermal peak ranged between  $216$  and  $246^\circ\text{C}$  due to the thermal polymerization reaction of maleimide groups resulted from retro Diels-Alder and dehydration reactions of **PVF** chains.

The dielectric loss permittivity ( $\epsilon''$ ) versus temperature curves of **PVF** and **MH** films showed two transitions, the first one in the range of 60-109°C attributed to  $\alpha$  transition and the second one in the range of 147-189°C corresponding to the retrodienic process (Table 2).

**Table 2.** Thermal behaviour of hybrid materials films **MH-(1-8)**

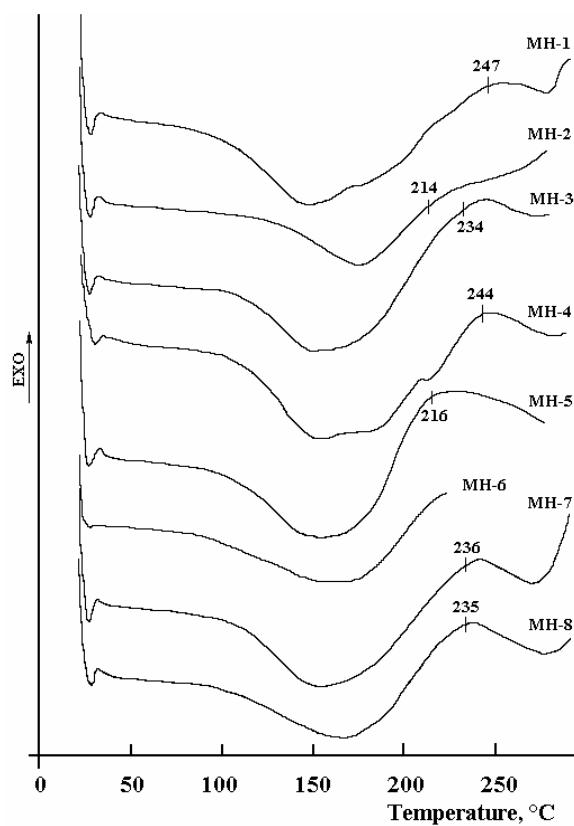
Sample	DSC		Dielectric relaxation		DMA	
	$T_g^a$	$T_{endo}^b$	$\epsilon_1''^c$	$\epsilon_2''^c$	$\tan \delta_1$	$\tan \delta_2$
<b>PVF-1</b>	74	264*	60	147	86.9	-
<b>PVF-2</b>	74	264*	109	168	104	182
<b>MH-1</b>	-	143	109	173	-	-
<b>MH-2</b>	-	175	-	-	-	-
<b>MH-3</b>	-	160	-	-	-	-
<b>MH-4</b>	-	154	103	189	-	-
<b>MH-5</b>	-	157	105	188	130	214
<b>MH-6</b>	-	165	98	168	124	202
<b>MH-7</b>	-	160	103	175	-	-
<b>MH-8</b>	-	165	106	178	132	197

<sup>a</sup> Vitrification temperature by DSC

<sup>b</sup> Temperature of the endothermic peak attributed to the retro-Diels-Alder reactions

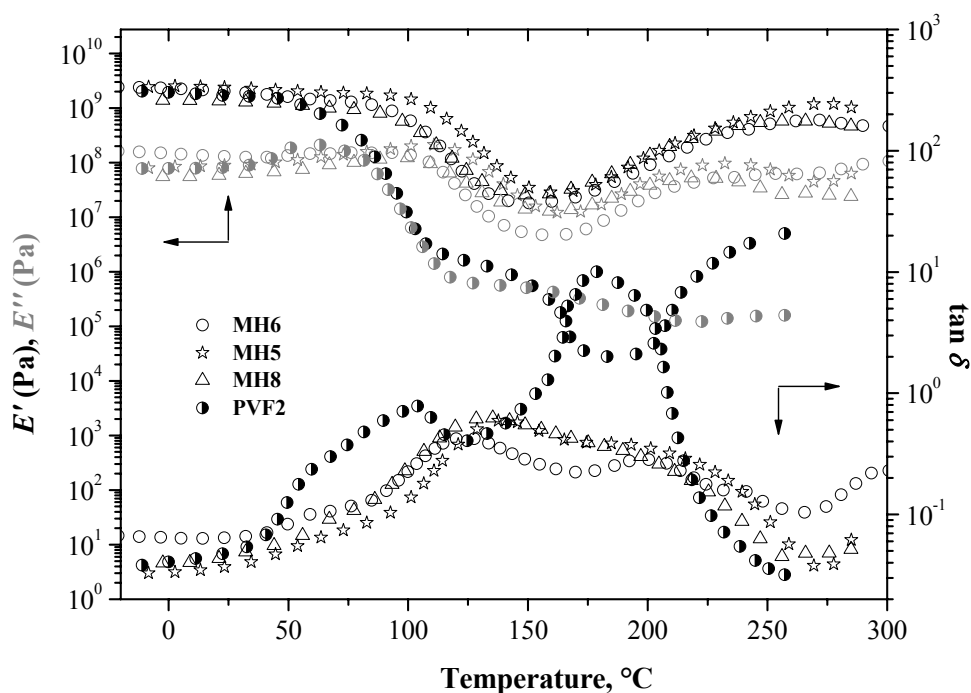
<sup>c</sup> Maximum of  $\epsilon''$  by dielectric measurements

\* Endothermic peak temperature attributed to the melting process



**Figure 3.** DSC curves of **MH-(1-8)**

The storage modulus ( $E'$ ), the loss modulus ( $E''$ ) and the loss factor ( $\tan \delta$ ) are plotted as a function of temperature (Figure 4) and the data of  $\tan \delta$  are presented in Table 2. The drops in  $E'$  curves, the peak of  $E''$  and  $\tan \delta$  plots report on physical transitions in materials. The **PVF-2** and **MH-(5, 6, 8)** presented higher storage modulus values, from 1000 MPa for **PVF-2** to 1350 MPa for **MH-8**. The value of  $E'$  at 20°C increases from 1800 MPa for **PVF-2** to 2427 MPa for **MH-5** and decreases to 1355 MPa for **MH-8**. The modulus of **PVF-2** rapidly decreases with increasing temperature; the two-stage decrease was observed around the glass transition temperature of **PVF-2** and at the high temperature above 145°C. The storage modulus decreases slowly with increasing the silica content, then increases at higher temperature values. In general,  $\alpha$ -relaxation process is indicated by the low temperature peak in the  $\tan \delta$  plots and represents the glass transition. This peak shifts to high temperature and its intensity decreases slightly with increasing the monomer **1** and **TEOS** content in materials.



**Figure 4.** Storage modulus (black line), loss modulus (grey line) and dissipation factor  $\tan \delta$  profiles of **PVF-2** and **MH-(5,6,8)**

The TGA measurements were carried to understand the thermal stability of the **PVF/silica** hybrid materials. The TGA data were presented in Table 3.



**Table 3.** Thermal stability of hybrid materials of polyvinyl alcohol

Sample	IDT <sup>a</sup> [°C]	Decomposition temperature range, °C (weight losses, %)			Y <sub>c</sub> <sup>b</sup> [%]
		stage I	stage II	stage III	
PVF-1	210	210-380 (44)	380-490 (29.8)	490-700 (18.4)	5
PVF-2	235	235-350 (43.6)	350-455 (20)	455-700 (29)	9
MH-1	250	250-375 (26)	375-550 (23)	550-700 (21)	20
MH-2	255	255-380 (25)	380-560 (23)	560-700 (18)	24
MH-3	258	258-380 (24)	380-550 (22)	550-700 (18)	34
MH-4	260	260-390 (26)	390-550 (19)	550-700 (21)	32
MH-5	265	265-385 (24)	385-560 (23)	560-700 (17)	36
MH-6	253	253-385 (24)	385-560 (23)	560-700 (21)	32
MH-7	268	268-380 (18)	380-555 (21)	555-700 (21)	40
MH-8	278	278-385 (16)	385-560 (25)	560-700 (17.2)	42.8

<sup>a</sup> Initial decomposition temperature;<sup>b</sup> Char yield at 700°C

Generally, all the hybrid materials **MH-(1-8)** and **PVF-(1-2)** undergo three distinct weight loss stages. The first decomposition stage varied in the range of 210-390°C and the corresponding weight loss ranging between 16-44 % decreases with increasing the inorganic content (Table 1) and is attributed to the elimination of water molecules from **PVF** chains [20] and acetic acid from acetate groups. In the second decomposition stage varying between 350 and 560°C, break down of the polymer backbone takes place. Specifically, it can be assigned to the degradation of nonconjugated polyene [21]. The main decomposition of this process takes place around 430°C. The third stage of weight loss is determined by scission and cyclization reactions [22]. Temperature and the weight loss corresponding to this stage varied in the range of 455-700°C and 17-29%, respectively. The initial decomposition temperature (*IDT*) of **MH-(1-8)** ranged between 250 and 278°C and increases with increasing the inorganic content. Also, the char yield at 700°C (*Y<sub>c</sub>*) increases with increasing the inorganic content from 20% to 42.8%.

## CONCLUSIONS

Novel hybrid materials films based on poly(vinyl furfural) were prepared by cycloaddition-condensation reactions with *N*-[4-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)phenyl]-*N'*-propyl-3-triethoxysilane and **TEOS**. The obtained films show improved the thermal properties compared with those of **PVA** and **PVF** and the retrodiene process occurs simultaneously with the glass transition.

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