Effect of microcrystalline Cellulose on dielectric properties of latex hybrid composites

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Abstract

Dielectric measurements were performed on EVA/VeoVa matrix and its hybrid composites reinforced with microcrystalline cellulose (MCC) and multiwalled carbon nanotubes (MWCNT) in the relative weight fraction 9:1. In this dielectric study, the following hybrid composites weight fractions were undertaken : 0.5%, 1%, 2% and 4%. Dielectric spectra were carried out in the frequency range from 10^{-1} Hz to 10 MHz and the temperature range from -35°C to 140°C. The dielectric analysis at low temperatures of these hybrid composites revealed the effect of MCC on the secondary relaxations namely β_{wet1}, β_{wet2} and β_{cell} relaxations. Their appearance was mainly originated from the influence of adsorbed water on the local structure and dynamics of cellulose molecules. As at normal environment condition, adsorbed water in cellulose is mostly bound water, this latter could be further categorized as tightly-bound water and loosely-bound water. These latter gave rise to the β_{wet2} and β_{wet1} relaxations, respectively. The former relaxation appearing at higher MCC weight fraction could be explained by a higher MCC hydrophilic character. The dielectric analysis at high temperatures of these hybrid composites has shown the presence of the interfacial polarization effect (MWS), α and α' relaxations. Analyzing α and α' relaxations according to Vogel-Fulcher-Tammann law and Havriliak-Negami model allowed probing the reinforcement/matrix interactions in accordance to weight fraction of the hybrid composites.

Studied materials

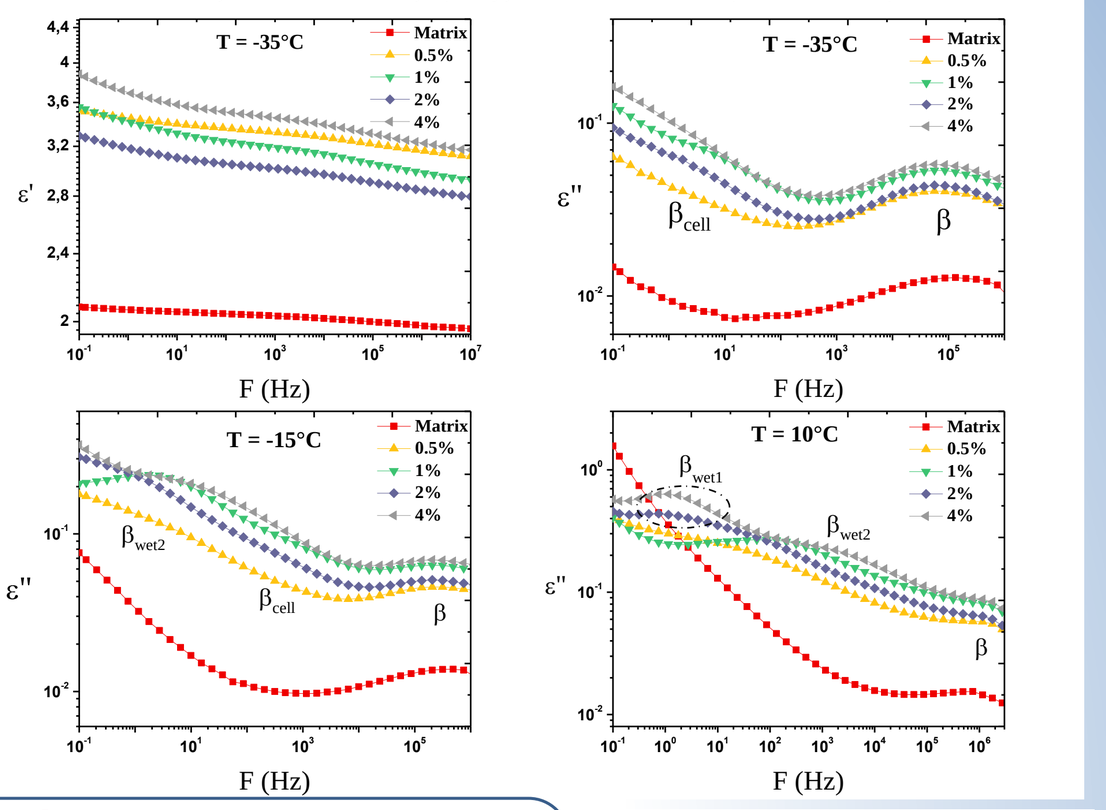
The vinyl resin emulsion (W301), supplied by the Moroccan Association of Polymers (MAP, Morocco), contained 12% of Ethylene, 70% of Vinyl acetate and 18% of Vinyl ester of Versatic Acid. The latex contains 51.7 wt% of the resin with a viscosity of 7600 mPa.s. The composites (VR/MCC/MWCNT) were prepared using the vinyl resin as a matrix reinforced with 0.5, 1, 2 and 4 wt% of microcrystalline Cellulose and multiwalled Carbon nanotubes in the relative volume fraction ratio of 9:1.

Results and discussion

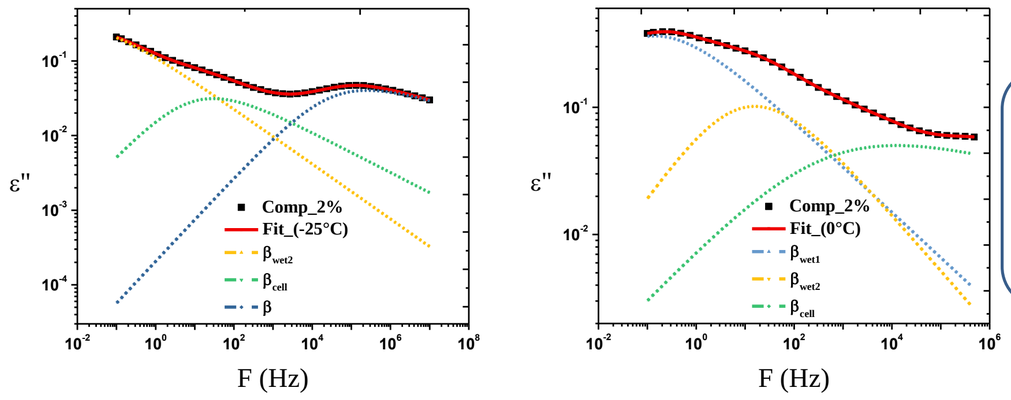
1. Low temperature analysis

The variation of ε′ and ε″ curves with frequency for the EVA/VeoVa terpolymer and its hybrid composites evidenced the presence of different relaxation phenomena. The dielectric analysis at low temperatures of these composites revealed the effect of MCC on the secondary relaxations. The dielectric permittivity spectrum reveals an enhancement in comparison with the matrix for T below glass transition temperature T_g. This increase is originating from adsorbed water in MCC according to its weight fraction in hybrid composite materials and from dynamics of MCC molecules. As results, the loss factor curves, ε″, have shown the presence of two dielectric relaxations β_{wet2}, β_{cell} . These are attributed to tightly-bound water and to local cooperative molecular motions of the MCC main chain, respectively. Additional dielectric relaxation is observed for higher weight fraction i. e. 2% and 4%. This latter is associated with β_{wet1}, which originates from loosely-bound water. This latter starts to appear outside of the first hydration layer in MCC.

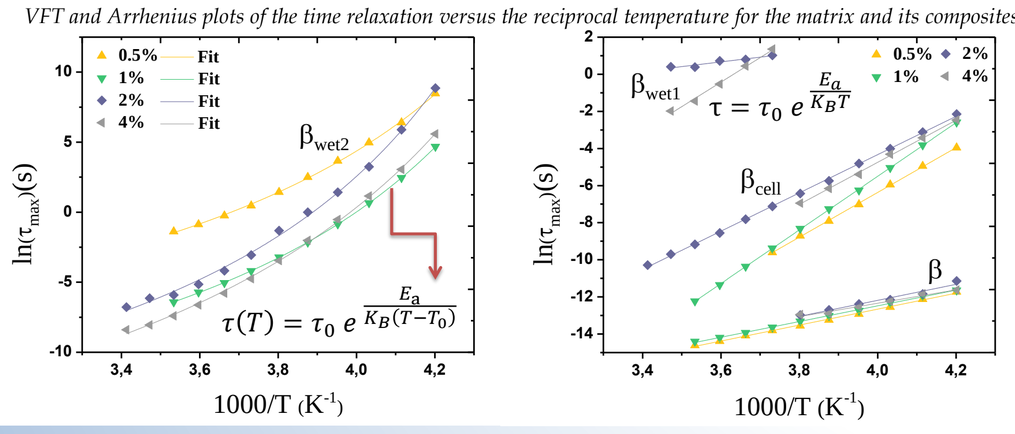
The variation of ε′ and ε″ curves with frequency for the matrix and its composites at low temperatures



Fitting procedure at -25°C and 0°C with the deconvolution of the loss factor



VFT and Arrhenius plots of the time relaxation versus the reciprocal temperature for the matrix and its composites

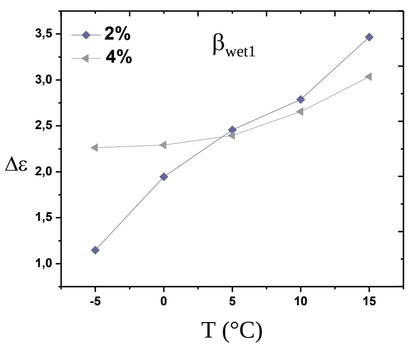


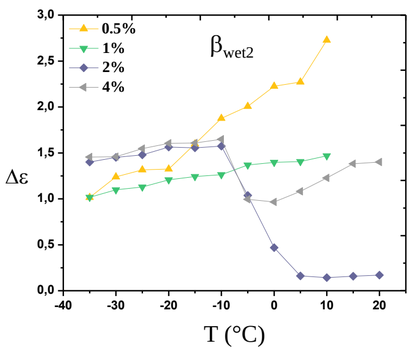
Havriliak-Negami (H-N) analysis:

In order to study the molecular dynamic of the EVA/VeoVa matrix and its composites, we proposed to analyze the nature of the dielectric relaxations using H-N equation:

$$\varepsilon^*(\omega) = -i\left(\frac{\sigma_0}{\varepsilon_0\omega}\right)^S + \sum_{i=1}^{n}\left(\varepsilon_\infty + \frac{\Delta\varepsilon_i}{[1+(i\omega\tau_{HN_i})^{\alpha_{HN_i}}]^{\beta_{HN_i}}}\right)$$

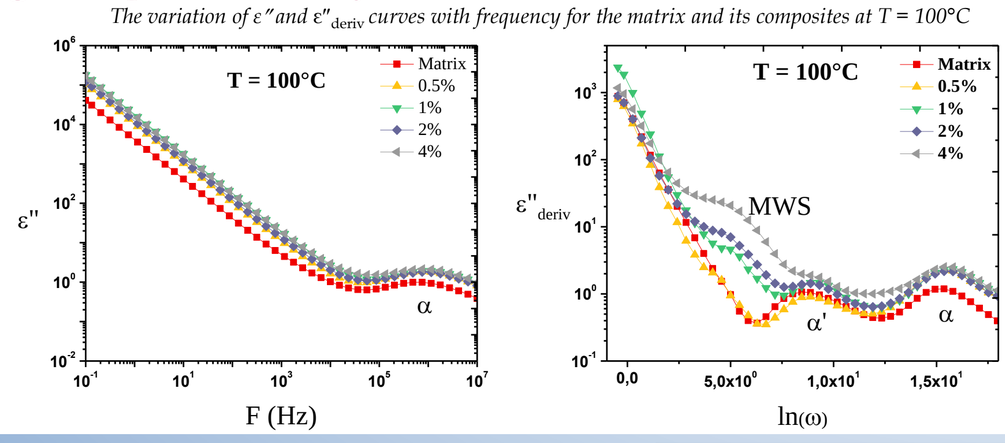
		Comp_0.5 %	Comp_1 %	Comp_2 %	Comp_4 %
β_{cell}	τ (s)	1.900 e-24	3.341 e-28	1.593 e-20	1.686 e-22
	E_a (eV)	1.0394	1.2444	0.8887	0.9778
β_{wet2}	τ (s)	5.104 e-06	2.356 e-08	7.821 e-09	3.749 e-10
	E_a (eV)	0.0866	0.0868	0.0956	0.1180
β_{wet1}	τ (s)	-	-	2.048 e-04	1.451 e-21
	E_a (eV)	-	-	0.2193	1.1384
β	τ (s)	1.086 e-13	1.669 e-13	1.628 e-13	2.340 e-12
	E_a (eV)	0.3703	0.3649	0.3718	0.3111



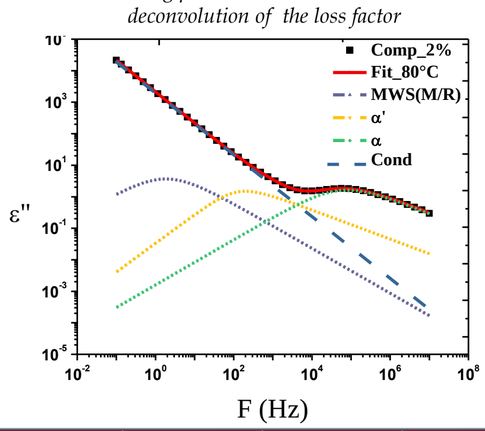


2. High temperature analysis

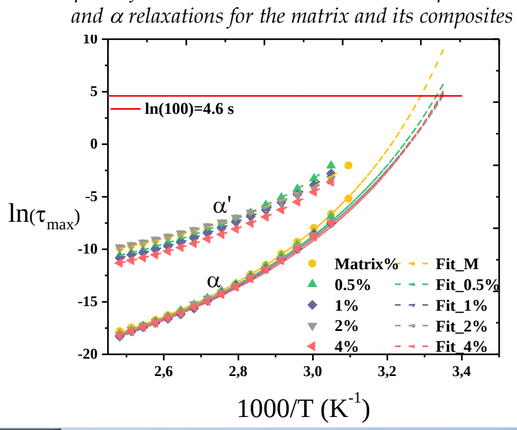
The variation of ε″and ε″deriv curves with frequency for the matrix and its composites at T = 100°C



Fitting procedure at 80°C with the deconvolution of the loss factor



VFT plots of the time relaxation versus the reciprocal T of α′ and α relaxations for the matrix and its composites



Three dielectric relaxations were detected at high T. The high frequency α process is attributed to local segmental dynamics, which generally requires local correlated movement of a few terpolymer's backbone bonds. The low frequency α′ relaxation which moves at higher T than the α mode and corresponds to the mobility of more repeating units in each chain. Apparently, a new relaxation phenomenon seemed to occur in the composite materials when presenting the curves of the derivative loss factor ε''_{deriv}. In fact, the lately noticed relaxation, which was masked by the conduction process, showed a set of peaks from 55°C to 130°C and at low frequencies and was attributed to the interfacial polarization effect, MWS, owing to the accumulation of charges at the reinforcements/matrix interfaces.

		Matrix	Comp_0.5 %	Comp_1 %	Comp_2 %	Comp_4 %
α′	τ (s)	9.720 e-08	1.755 e-08	9.913 e-09	6.358 e-08	9.384 e-09
	E_a (eV)	0.0775	0.0868	0.0949	0.0894	0.0889
	T_0	259.271	264.143	257.492	249.659	258.716
α	τ (s)	3.993 e-13	1.494 e-13	8.265 e-14	1.137 e-13	2.647 e-13
	E_a (eV)	0.133	0.150	0.160	0.158	0.139
	T_0	257.431	251.009	246.417	246.278	252.765
	D	5.994	6.924	7.517	7.433	6.396
	m	114.427	101.211	94.488	95.376	108.234
	T_g (DSC)	28.780	26.729	26.046	25.959	27.653
	T_g (BDS)	30.984	27.159	25.876	25.594	26.165

- The activation energy of α relaxation varies with the incorporation of MCC/MWCNT into the VR proving the existence of an interaction: reinforcements/matrix.
- The comparison of the dielectric fragility, m, evidenced its decrease for all composites in comparison with the matrix. This variation has shown a repulsive interaction between the matrix and the reinforcements.
- the T_g of each composite diminishes in comparison with the matrix and the relaxation time of its α relaxation becomes shorter. Besides, the Vogel-Fulcher temperature, T_0, decreased after the addition of the reinforcements in the matrix. In fact, the macromolecules mobility of the terpolymer is facilitated due to repulsive interactions between the matrix and the fibers.