J Mater Sci (2010) 45:4141–4150
DOI 10.1007/s10853-010-4503-7

Silicone-modified cellulose. Crosslinking of cellulose acetate with poly[dimethyl(methyl-H)siloxane] by Pt-catalyzed dehydrogenative coupling

George Stiubianu · Carmen Racles ·
Maria Cazacu · Bogdan C. Simionescu

Received: 22 October 2009 / Accepted: 7 April 2010 / Published online: 23 April 2010

Abstract Cellulose acetate was reacted in different ratios with poly[dimethyl(methyl-H)siloxane] containing 25 mol% Si–H side groups along the chain. A dehydrocoupling reaction between Si–H and C–OH groups occurred in presence of Karstedt's catalyst, leading to the formation of Si–O–C bond, as proved by FTIR spectra, thus crosslinking the cellulose derivative. The networks were processed as films by casting before the end of the reaction and were investigated by different techniques to emphasize the morphology, thermal, dielectric and surface properties developed in correlation with the ratio between the two involved components (cellulose and siloxane derivatives). A decrease of the dielectric constant values of cellulose acetate was noticed throughout the studied frequency and temperature range as a result of crosslinking.

Introduction

Cellulose and silicones are two well-known materials, each of them having specific application fields. The major difference between their chemical structures makes some of their properties totally opposed.

Siloxanes are polymeric materials which, as a consequence of their characteristics [1] (high flexibility of the polymeric chain, low dielectric constant, stability towards atomic oxygen, permeability for different gases, hydrophobic and anti-adhesive behaviour, physiological and chemical inertness, etc.), are being used on large scale in many different fields—coatings [2–4], building industry, biomaterials and materials for medical applications [5–8], cosmetics, sensors and optical materials [9, 10], etc. Cellulose acetate is a chemical derivative of cellulose obtained from a renewable resource (natural cellulose fibres), which has the ability to form films with high mechanical resistance [11] and is used on large scale in different applications in fibres, plastics and coatings [12]. The modification of cellulose is necessary in certain applications, such as electronics, sensors, packaging, in order to control and decrease cellulose hydrophilicity and thus avoid the excessive swelling when it comes into contact with environmental humidity [13, 14]. In spite of the clear polarity difference between the carbohydrates (strong polar compounds) and the siloxane derivatives (highly non-polar), the coexistence of these two types of chemical compounds in the same material can induce a new combination of properties to the material [15–18].

For this purpose, an easily soluble cellulose derivative (cellulose acetate) was treated with a siloxane derivative, poly[dimethyl(methyl-H)siloxane], using acetone/DMF mixture as a solvent. Besides a decrease of cellulose hydrophilic nature which would lead to the modification of surface properties, we expected to achieve other effects determined by the presence of the siloxane, i.e. increased flexibility, improvement of thermal-oxidative stability, antifouling, resistance to UV radiations, change in dielectric properties, etc. Some of these properties were investigated for the materials prepared and processed as films described in this paper.

G. Stiubianu (✉) · C. Racles · M. Cazacu · B. C. Simionescu
"Petru Poni" Institute of Macromolecular Chemistry,
Aleea Gr. Ghica Voda 41A, 700487 Iasi, Romania
e-mail: george.stiubianu@icmpp.ro

B. C. Simionescu
"Gh. Asachi" Technical University, 700040 Iasi, Romania

Experimental

Materials

Cellulose acetate, $C_6H_{7.5}O_{2.5}(OCOCH_3)_{2.5}$, CA, was supplied by Fluka; characteristics: DS = 2.5; $d_4^{20} = 0.996$; purity > 99%.

Poly[dimethyl(methyl-H)siloxane], PMHS (Aldrich) with $M_n = 2463$ and 25 mol% Si–H groups along the chain, as estimated based on ^{1}H NMR spectrum, was used as such.

Acetone (Chimopar-Romania) and *N*,*N*-dimethylformamide (Fluka) were used after drying.

Karstedt's catalyst $Pt_2\{[(CH_2 = CH)Me_2Si]_2O\}_3$ (platinum-divinyltetramethyldisiloxane complex in xylene, 2.1–2.4% platinum) was supplied by ABCR GmbH & Co KG (Germany).

1,3-Divinyltetramethyldisiloxane ($M_n = 186.40$, m.p. = −99 °C, b.p. = 140 °C, $n_D^{20} = 0.809$) was supplied by Aldrich.

Equipments

The FTIR spectra of the samples were recorded in KBr pellets on a Bruker Vertex 70 FT-IR spectrometer.

The ^{1}H NMR spectra were recorded on a BRUKER Avance DRX 400 spectrometer, using $CDCl_3$ as a solvent.

Thermogravimetric analyses (TGA) were performed on a Q-1500D System, in air, in the temperature range 25–750 °C, using a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) measurements were performed on a Diamond Perkin Elmer equipment in the temperature range −150 to +30 °C, with a heating rate of 20 °C/min, in nitrogen flow. The glass transition temperature was determined as the midpoint of thermal capacity change during the second heating scan.

A SOLVER PRO-M, NT-MDT instrument was used to evaluate the surface topography and morphology of the samples by AFM.

Dynamic contact angles (DCA) and contact angle hysteresis were measured by using a KSV Sigma 700 tensiometer system—a modular high performance computer controlled surface tension/contact angle meter. Water was used as a measure liquid. The DCA runs were performed on samples processed as rectangular plates. The average values of three measurements were taken into consideration.

Dielectric spectroscopy was performed using the Novocontrol "Concept 40" broadband dielectric spectrometer (Hundsangen, Germany). The samples were subsequently mounted between gold platens and positioned in the Novocontrol Quatro Cryosystem. The first dielectric experiment was carried out keeping the frequency fixed but sweeping the temperature. A heating rate of 5 °C/min over the −120 to 100 °C temperature range was used, and six decades (log scale) of frequency, i.e. 1–100000 Hz, were scanned. In a second experiment, the dielectric constant (ε') and losses (ε'') were recorded in the frequency domain (1 Hz–1 MHz) at constant temperatures (−100, 0, 100 °C).

The measurements for dynamic vapour sorption and sorption hysteresis were performed with an IGAsorp Dynamic Vapour Sorption apparatus with the following characteristics: minimum gas pressure, 2 bar; resolution of 0.1 µg for 100 mg and sample containers made out of stainless steel micron size mesh. Before sorption measurements, the samples were dried at 25 °C in a flow of dry nitrogen (250 mL/min) until the weight of the sample was in equilibrium at a relative humidity (RH) less than 1%.

The silicon content was determined according to a known procedure [19], i.e. disintegration with sulphuric acid and calcination at 900 °C to constant weight.

Procedure

Poly[dimethyl(methyl-H)siloxane] was added under stirring to a 3 wt% cellulose acetate solution in acetone/DMF (33:1) mixture. Two different ratios between the two components were used (CA/PMHS = 75/25 and 56/44).

Karstedt's catalyst (0.15 µL/mol Si–H group) was added and the mixture was stirred at room temperature. The emission of gas was observed immediately after catalyst addition, but this effect was diminished up to disappearance in about ½ h. After 1 h, the reaction mixture was poured in a Petri dish, partially covered for slow solvent evaporation. 24 h later the films were already formed. However, the samples were kept in air about a week and then vacuumed in an oven for 24 h at 70 °C to remove solvent traces.

Two reference samples were also prepared. The first was composed of CA only. The second was based on PMHS crosslinked with 1,3-divinyltetramethyldisiloxane (molar ratio: 1:4.5) by hydrosilylation in presence of Karstedt's catalyst and using acetone as a solvent, at reagents' concentration of 4 w/v%. The mixture was stirred for 1 h and then processed as described above.

Results and discussion

Commercial poly[dimethyl(methyl-H)siloxane] containing 25 mol% Si–H side groups along the molecular backbone (as verified by ^{1}H NMR spectrum, based on the proton peak intensity ratio of dimethylsiloxane and Si–H groups), was used as crosslinking agent for cellulose. Cellulose acetate with a substitution degree DS = 2.5 was chosen due to its good solubility. Two different ratios between

Table 1 Spectral and compositional data for the prepared materials

Sample	Feed mass ratio, CA/PMHS	IR absorption intensity ratio of the relevant bands		Silicon content, wt% found/calc.[a]
		A_{801}/A_{1239} CH_3Si/ν C–O	A_{857}/A_{801} Si–O–C/CH_3Si	
HS1	100/0	–	–	–
HS2	75/25	0.9098	0.3125	10.39/9.81
HS3	56/44	1.2308	0.3707	17.90/17.66
HS4	0/100	–	–	37.00/37.42

[a] Calculated based on initial reaction reagents

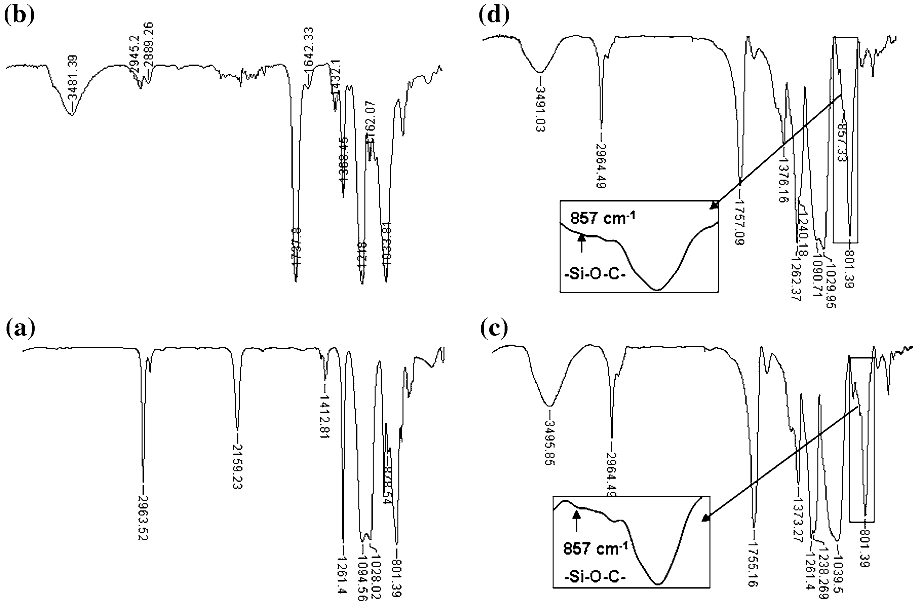


Fig. 1 Comparative FTIR spectra for the reactants and crosslinked products: **a** PMHS, **b** HS1, **c** HS2, **d** HS3

these two components were used (Table 1). For comparison, a model crosslinked polysiloxane was prepared by Karstedt's catalyzed hydrosilylation of divinyltetramethyldisiloxane with the same PMHS, using acetone as solvent.

Analysing the FTIR spectra (Fig. 1) of the starting compounds and of the crosslinked ones, the following conclusions can be drawn: the absorption band at 2159 cm^{-1}, assigned to Si–H bond in PMHS, disappears in the crosslinked compounds; instead, the 1752 cm^{-1} band attributed to –O–C=O group from cellulose acetate remains practically unmodified both as intensity and as position, this leading to the conclusion that the –O–C=O group does not participate in the reaction.

Actually, in the described reaction conditions a dehydrogenative coupling reaction takes place and not a hydrosilylation. In the presence of platinum catalyst a hydrogen molecule is eliminated between the polysiloxane Si–H group and the C–OH group from cellulose acetate. This statement is supported by experimental observation of gas bubbles being produced when mixing the reagents with the catalyst. At the same time, literature data show that in specific conditions the reaction may take place this way [17]. The reaction products are not soluble in usual solvents (DMSO, heptane, chloroform, toluene, acetone, water). In the spectra of the products, absorption bands characteristic for the siloxane component are also present, i.e. at 2964 cm^{-1} (C–H), 1261 and 801 cm^{-1} (Si–CH_3). The siloxane band at 1029–1090 cm^{-1} is overlapped by the bands corresponding to C–O–C bond from cellulose at 1036 cm^{-1} as well as by the band assigned to the expected new Si–O–C bond at about 1010–1095 cm^{-1}. However, the siloxane band being stronger, the bands corresponding to the later two groups cannot be identified in this frequency range. Instead, a shoulder, assigned to the newly formed Si–O–C bond (Fig. 1c, d) [20] is developed at 857 cm^{-1}. Such a signal is not visible in reactant's spectra (Fig. 1a, b). As expected, the relative intensities ratio of the bands specific for siloxane (Si–CH_3 at 801 cm^{-1}) and cellulose acetate (ν C–O at 1236 cm^{-1}) increases with the siloxane content in the reaction mixture. The higher siloxane content in the HS3 sample as compared with HS2 sample was confirmed with silicon content analysis (Table 1). However, the intensities ratio corresponding to the newly created Si–O–C bond (857 cm^{-1}) and Si–CH_3 (801 cm^{-1}) from the siloxane increases only slightly with the increase of the siloxane addition in the reaction mixture from 25% in HS2 to 44% in HS3 (Table 1). Considering, in addition, the absence of Si–H groups in the IR spectra of the products, one can accept that Si–H groups are involved in other reactions beside the one with cellulose C–OH groups. Such undesired reactions could be the hydrolysis or self-condensation in the presence of water traces, resulting in silanol groups or crosslinked polysiloxane interconnected with the crosslinked cellulose derivative.

Based on the above-mentioned results, the structure given in Scheme 1 is proposed for the reaction product.

As expected, the thermogravimetric data (Table 2; Fig. 2) show the reference sample HS4 made with siloxane as possessing the best thermal properties. The HS1 sample film made of cellulose acetate is degraded at the lowest temperature and has the smallest amount of residue. The other samples show an increased resistance against thermo-oxidative degradation and this process yields a larger amount of residue with increasing siloxane content.

As highly flexible siloxane is present in the materials, the thermal investigation in the negative temperature range is of interest. DSC analysis emphasized glass transitions for the two hybrid films: −106 °C for sample HS2 and −113 °C for sample HS3.

Based on the examination of DSC data, the following observations can be noticed:

- by incorporating 25 wt% siloxane in the reaction mixture with cellulose acetate (sample HS2), a transition can be identified at about $T_g = -106$ °C. It is known that polymethyl-H-siloxane has the lowest T_g values among silicones (−138 °C). The higher value observed for sample HS2 is determined by the crosslinked structure (and implicitly by the disappearance of the methyl-H-siloxane units) and by the good mixing of the phases.

Table 2 The main parameters of the thermogravimetric curves

Sample	T_{10}[a]	T_{40}[a]	T_f[b]	Residue (wt%)
HS1	247	340	500	2.0
HS2	313	350	655	23.0
HS3	310	350	650	33.5
HS4	358	–	563	71.5

[a] The temperature corresponding for a mass loss of 10 and 40%, respectively

[b] Final decomposition temperature

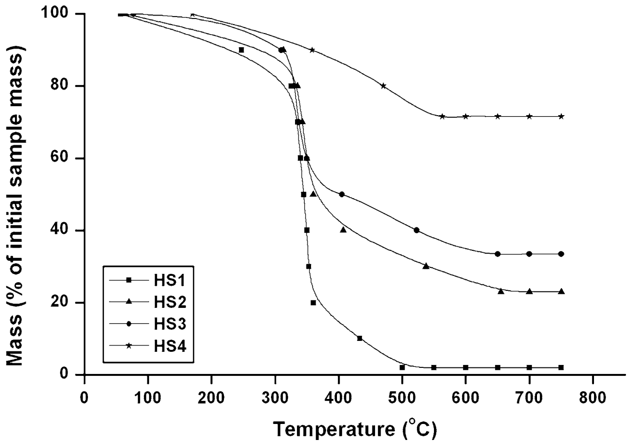
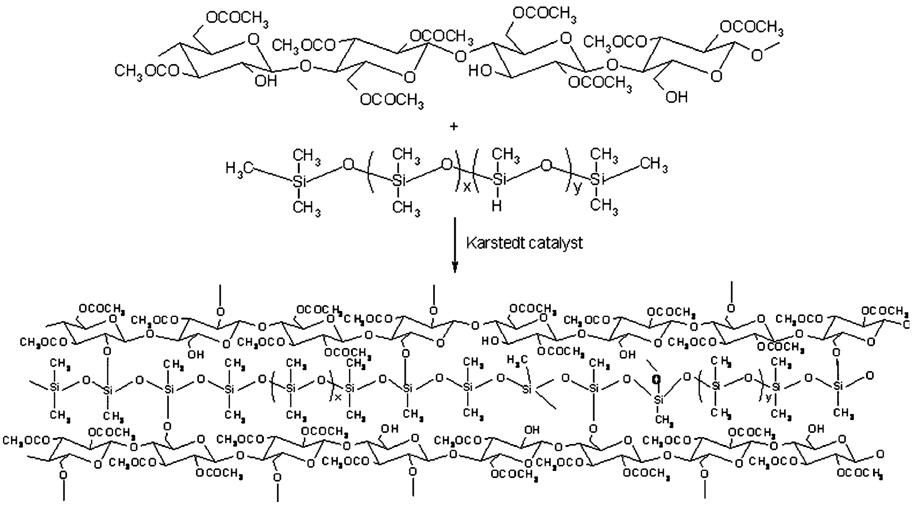


Fig. 2 TGA data for the prepared model and hybrid samples presented in Table 1

- by increasing the added siloxane to 44 wt%, the T_g value lowers to −113 °C, in agreement with the presence of a higher content of polysiloxane. On the other hand, the absence of an additional T_g, corresponding to the self-crosslinked polysiloxane (which would be expected at a lower value) indicates a good mixing between the two crosslinked polymers. This

Scheme 1 The presumed reaction path for the crosslinking of cellulose acetate by PMHS



could be explained through the interconnection of the siloxane network with cellulose acetate, which impedes the phase separation.

The tensiometric method was used for measuring water dynamic contact angles by Wilhelmy plate technique. The values obtained for advancing and receding contact angles for both reference and hybrid samples are presented in Table 3. The difference between the maximum advancing and minimum receding contact angle values, known as contact angle hysteresis and representing a measure of surface heterogeneity and roughness, has been also calculated.

As expected the obtained contact angles values indicate a hydrophilic surface for cellulose acetate, which is significantly modified by the crosslinking with polysiloxane. The advancing contact angle value reaches 100° in crosslinked samples, which indicates a hydrophobic surface. As known, the low surface energy of the siloxanes provides a thermodynamic driving force for their migration to the material-air interface. The same value has been obtained for the advancing contact angle (100°) for the two modified cellulose samples, very close to the value obtained for the reference crosslinked polysiloxane, HS4 (104°). This result suggests that by using 25% siloxane in the synthesis the maximum surface hydrophobicity for such a combination is ensured, a further increase of siloxane content leading to minor changes of this characteristic.

Table 3 The water dynamic contact angles

Sample	Water dynamic angles		Hysteresis H^c
	θ_a[a]	θ_r[b]	
HS1	84	65	19
HS2	100	51	49
HS3	100	55	45
HS4	103	70	33

[a] Maximum advancing contact angle value

[b] Minimum receding contact angle value

[c] $H = \theta_a - \theta_r$

The increased hysteresis of the hybrid films as compared to reference samples was assigned to the co-existence of the hydrophobic and hydrophilic domains on the surface. The slight increase in receding contact angle value and, as a result, the slightly lower hysteresis indicates a more homogeneous surface in HS3 than in HS2. This can be explained by a more uniform coating of the surface with increasing the siloxane content.

Indeed, the AFM images (Fig. 3) reveal a smoother surface of the HS3 sample, even as compared to the HS1 reference sample. The migration of the siloxane present in HS3 to the surface explains this observation.

Water sorption is another property of the cellulose derivative expected to be modified by the siloxane presence. The water vapour uptake capacity at 25 °C, in the relative humidity range RH 0–90%, was investigated by using the IGAsorp equipment. The vapour pressure was increased in 10% humidity steps, each one having a pre-established equilibrium time between 70 and 80 min (minimum time and time out, respectively). The cycle was ended by decreasing the vapour pressure in steps to also obtain the desorption isotherms. The drying of the samples was carried out before sorption measurements, at 25 °C in dry nitrogen flow (250 mL/min) until the weight of the sample reached an equilibrium at RH < 1%.

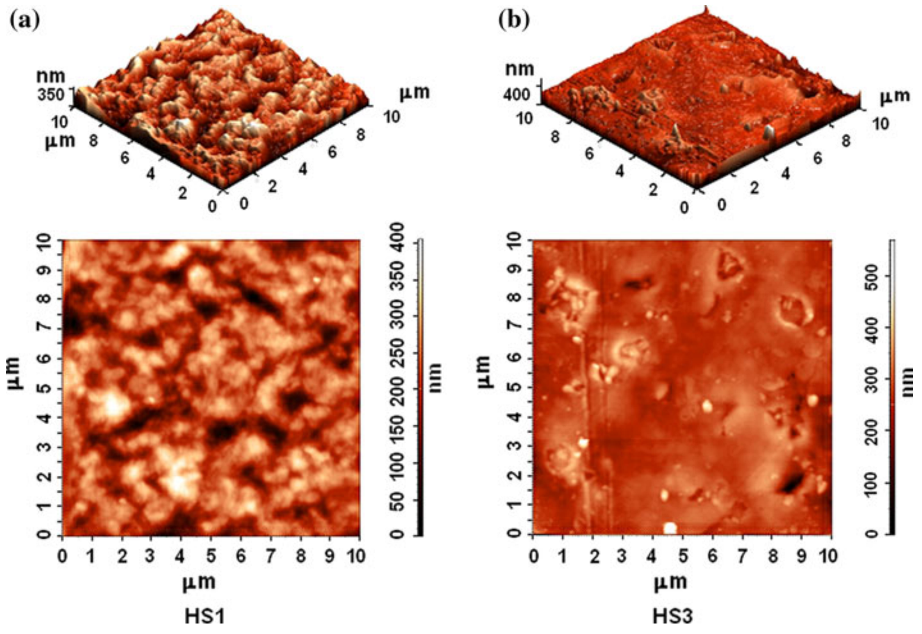


Fig. 3 AFM images of the samples HS1 (**a**) and HS3 (**b**)

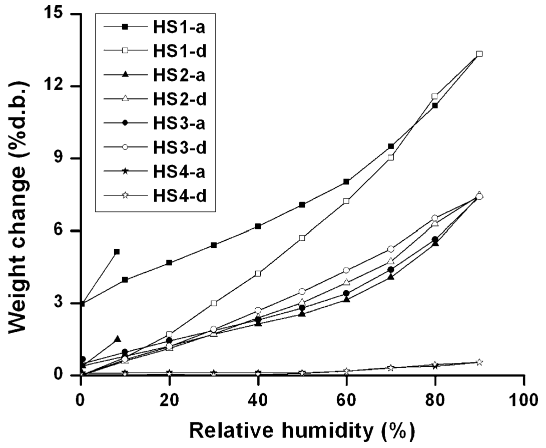


Fig. 4 Rapid water vapours sorption isotherms

Table 4 Maximum water vapour sorption values

Sample	Total water sorption, wt% (d.b) at RH = 90%, T = 25 °C
HS1	13.33
HS2	7.4705
HS3	7.4034
HS4	0.5448

The sorption/desorption isotherms for the hybrid samples as compared to those for a pure crosslinked polydimethylsiloxane are presented in Fig. 4. The obtained total water vapour sorption capacity values are summarized in Table 4.

As can be observed in Table 4, the reference sample HS1 presents the highest water absorption, while the HS4 reference sample has the lowest water vapour uptake. These are logical results taking into account the nature of the two reference samples. By insertion of the siloxane as a crosslinker in cellulose acetate, the water sorption capacity decreases (e.g. sample HS2). However, the subsequent increasing of the siloxane addition (sample HS3) does not change significantly the isotherms shape (Fig. 4) and the maximum sorption capacity. This can be explained in the same manner as in the case of the water dynamic contact angle: 25 wt% siloxane added to cellulose in the crosslinked structure determines the maximum hydrophobic effect and a further increase of the siloxane content (as in sample HS3) does not affect the surface properties. In addition, the estimated crosslinking degrees are quite close.

While for cellulose acetate (HS1) desorption occurs slowly and is not complete—the sample holding a large amount of water at the end of this process—this behaviour disappears once the siloxane chain is inserted in the material. This behaviour can be explained both by the presence of the hydrophobic siloxane and by the consumption of hydrophilic C–OH groups in the dehydrogenative coupling reaction. For all other samples (HS2, HS3, HS4), the hysteresis is insignificant.

Analyzing the shapes of the isotherms, it appears that for sample HS1 sorption is governed by the Langmuir equation [21, 22], as explained by the presence of the polar groups in the structure of cellulose acetate. Such a shape can be also identified on the isotherms of samples HS2 and HS3 at low relative humidity. At high humidity the shape of the curves slightly changes, and it is presumed that a volume sorption process consisting in a non-specific dissolution of water in the polymer matrix (Henry's law) occurs. Such a process is presumed to occur in the case of the HS4 sample within all humidity range.

Cellulose and cellulose derivatives are used as dielectric materials in microelectronics. However, its high moisture sorption can lead to the instability of some parameters, also including dimensional changes [23]. These drawbacks can be reduced through the insertion of siloxane polymer chains. Thus, sorption can be reduced, as already proved by the results presented in Table 3. The effect of the siloxane on electrical insulating properties was evaluated based on the dielectric constant and dielectric loss and their variation with frequency and temperature within the 1 Hz–1 MHz and −120 to +100 °C ranges, respectively. Figure 5 shows the dependence of real and imaginary parts of complex permittivity on temperature at two frequencies. It can be noticed that, generally speaking, there is an increase of ε' and ε'' values with temperature, more significant in the case of sample HS1, possibly due to the influence of cellulose polar groups. In graph d (Fig. 5), two relaxations can be seen at high frequencies (10 kHz) with increasing temperatures: the first is due to siloxane segmental relaxation (−120 to −100 °C) and the second is due to α segmental relaxation of cellulose. With the incorporation of polysiloxane in cellulose acetate and their crosslinking, a decrease of the two component materials permittivity occurs on the entire studied temperature range. This could be explained by the presence of siloxane which increases the material's hydrophobic nature and decreases the humidity absorption, thus decreasing the dielectric constant. In addition, with siloxane incorporation, chain packing is less efficient, free volume increases and the volume concentration of polar groups' decreases. However, sample HS3, with higher siloxane content, shows an increased dielectric constant as compared to sample HS2. An explanation for this overturning could be the increase in the crosslinking degree that reduces the free volume resulting, yielding to an increase of the dielectric constant value [24].

The dielectric constant ε' value varies with temperature and frequency. For reference sample HS1, ε' increases with temperature from 4.59 at −100 °C to 14 at 100 °C at 1 Hz. The crosslinked sample HS2 possesses a smaller value of ε'

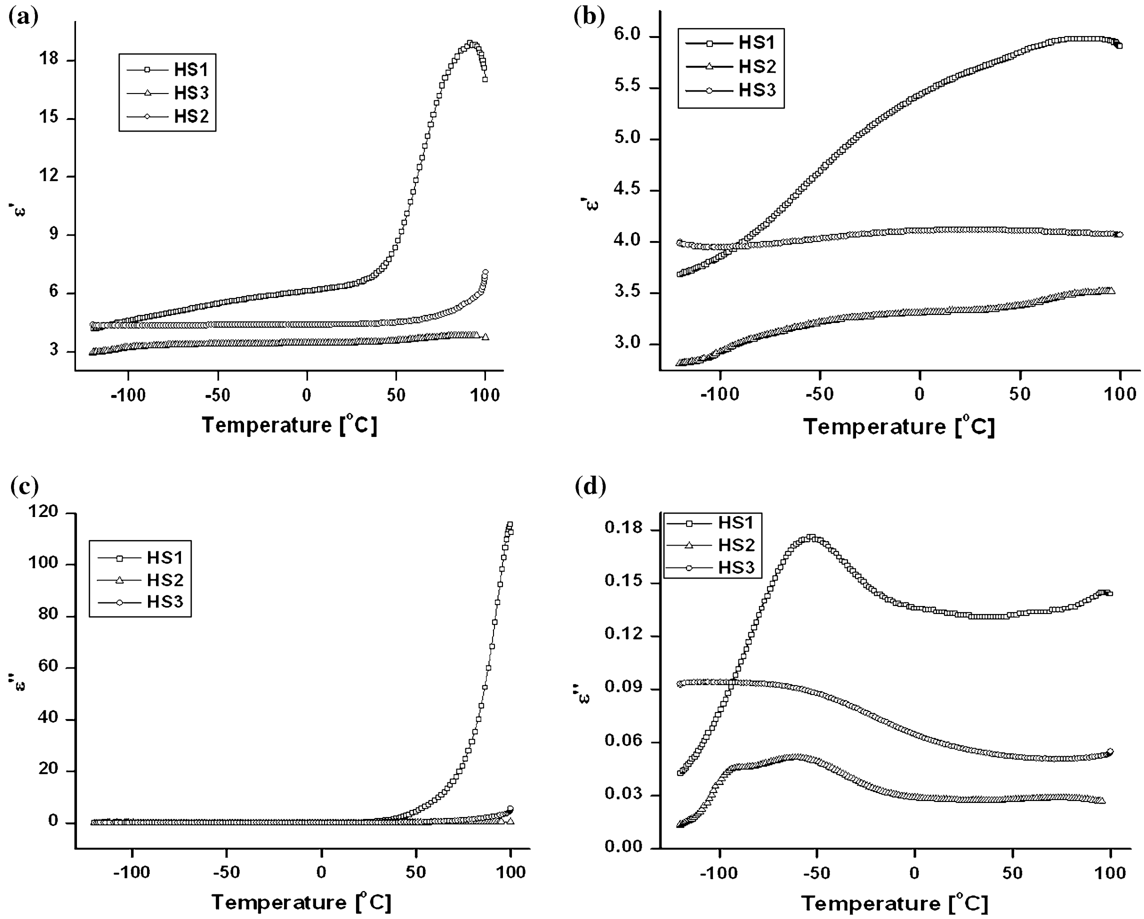


Fig. 5 The dependence of real and imaginary parts of complex permittivity as function of temperature, at two frequencies: **a** ε' 1 Hz, **b** ε'' 1 Hz, **c** ε' 10 kHz, **d** ε'' 10 kHz

and shows a small variation with temperature: for a frequency of 1 Hz, the value of ε' is 3.73 at −100 °C and 3.92 at 100 °C. For sample HS3, with a greater degree of crosslinking as compared to sample HS2, i.e. a smaller free volume, the values of ε' are slightly larger than the ones corresponding to HS2: 4.37 at −100 °C and 7.52 at 100 °C.

In the second type of dielectric measurements, dielectric constant ε' and dielectric loss ε'' were recorded when sweeping the frequency domain (1 Hz–1 MHz) at fixed temperatures: −100, 0 and 100 °C, respectively (Fig. 6). At 0 °C there are no relaxations in this frequency range. At 100 °C, ε'' decreases at low frequencies and this behaviour is owed to the conductivity value which increases at higher temperatures.

The representation of dielectric loss as a function of frequency and temperature (Fig. 7) shows a siloxane relaxation at −120 to −100 °C and a large increase of ε'' value at higher temperatures (50–100 °C) at low frequencies due to cellulose segmental relaxation.

However, generally speaking, the influence of the frequency and temperature on the dielectric parameters is reduced in the case of the hybrid films as compared to that on cellulose acetate film. This is a positive effect for practical applications, dielectric materials with stable dielectric constant and dissipation factor values across large frequency and temperature ranges being highly preferred.

Conclusions

The combination of cellulose and siloxane derivatives in the same system represents a challenge and a promising pathway for obtaining new materials with interesting and tailored properties, especially surface properties. By reacting cellulose acetate with poly[dimethyl(methyl-H)siloxane], a dehydrocoupling reaction occurs in the presence of Karstedt's catalyst yielding crosslinked materials. The properties depend on both the ratio between the two involved components and on crosslinking efficiency. Significant modifications were obtained in the thermal

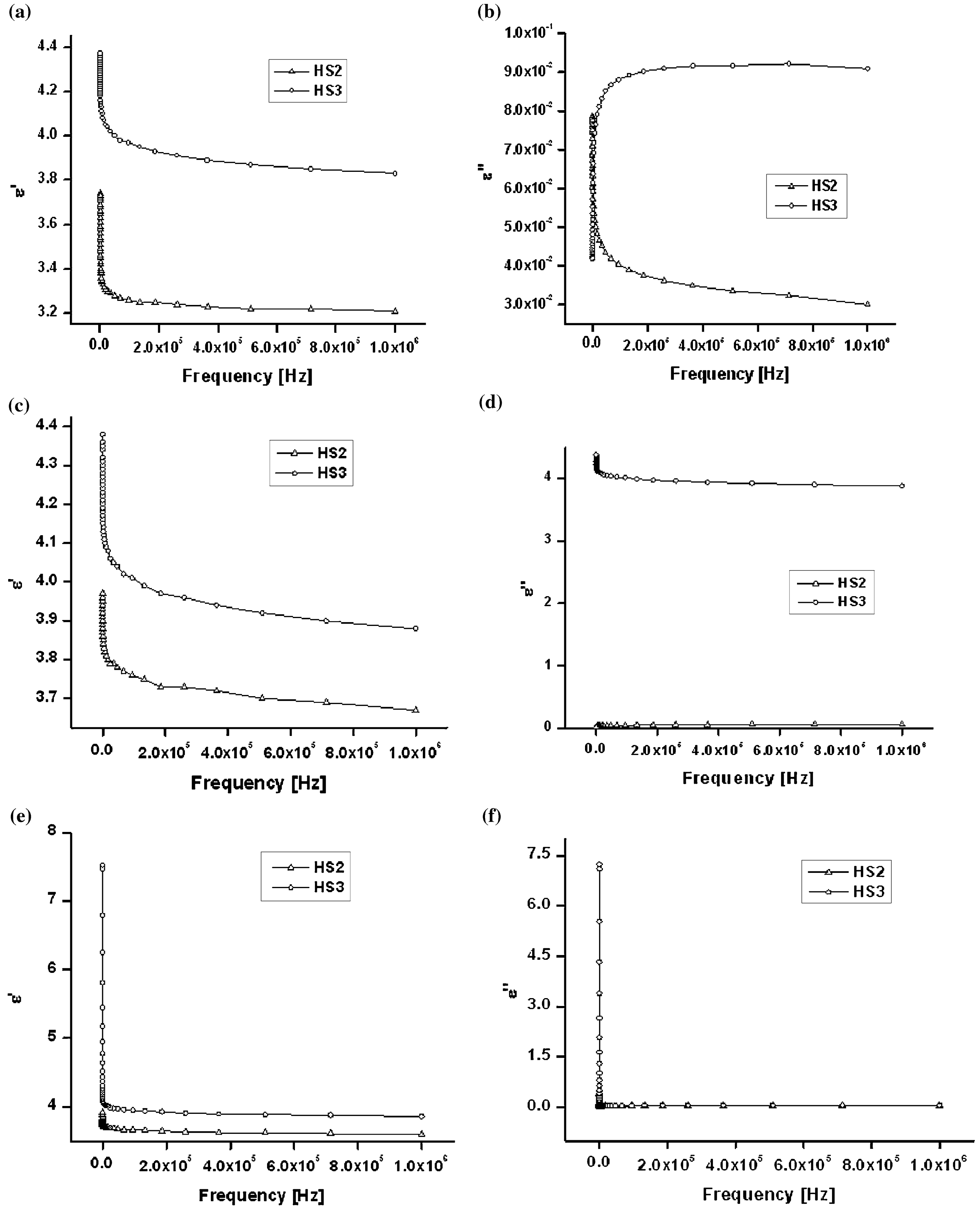


Fig. 6 The dependence of real (**a**, **c**, **e**) and imaginary (**b**, **d**, **f**) parts of complex permittivity as function of frequency, at three temperatures: **a**, **b** −100 °C; **c**, **d** 0 °C; **e**, **f** +100 °C

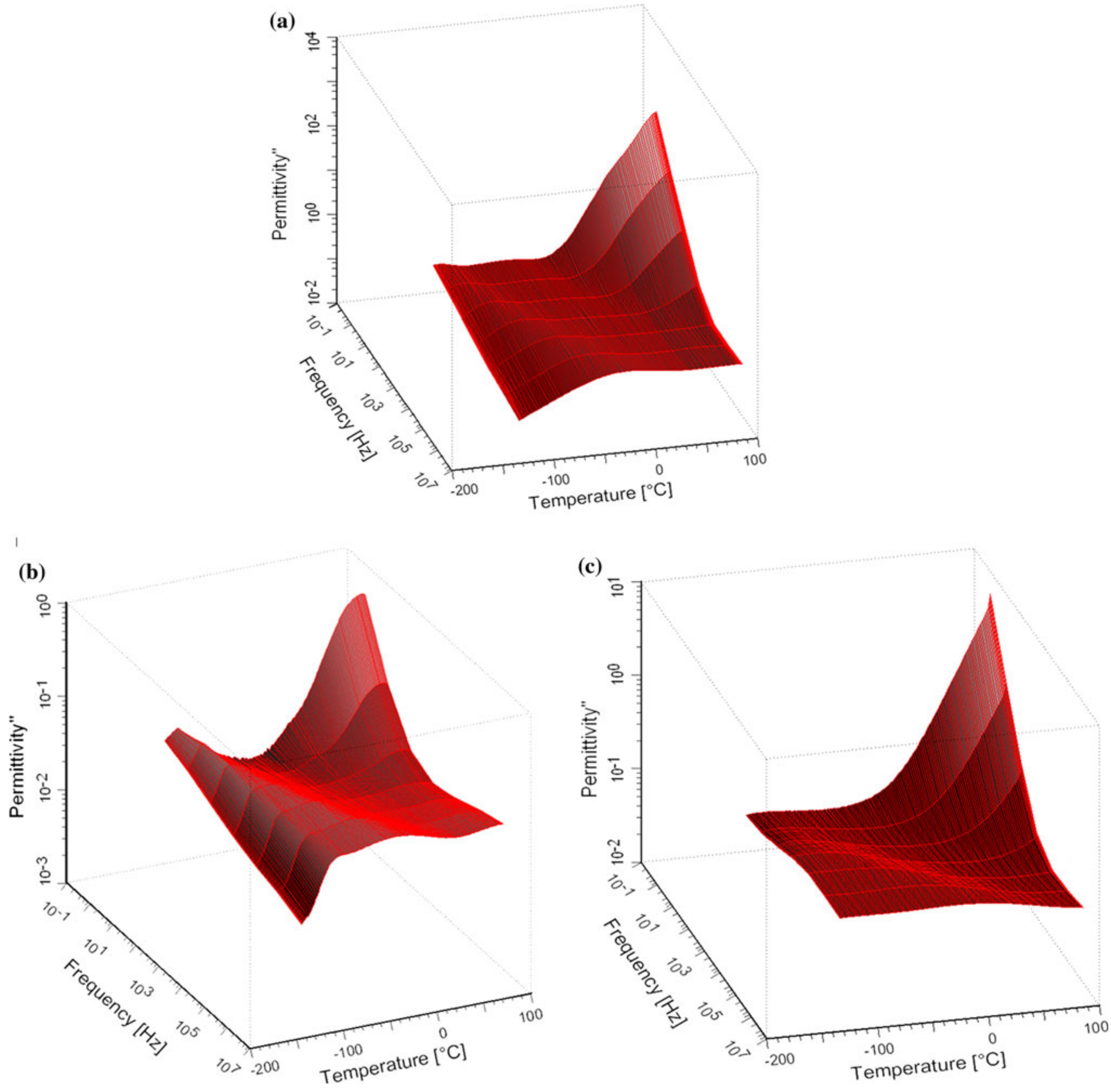


Fig. 7 Dielectric loss variation with temperature and frequency for: **a** HS1, **b** HS2, **c** HS3

(thermo-oxidative stability and thermal transitions) and surface properties (contact angle, water vapour sorption and surface roughness) depending on the two parameters. Slightly lower values of dielectric constant and dissipation factor across large frequency and temperature range resulted by crosslinking the cellulose acetate with polysiloxane.

Acknowledgements This work was supported by CNCSIS – UEFISCSU, project number PNII – IDEI 233/2007.

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