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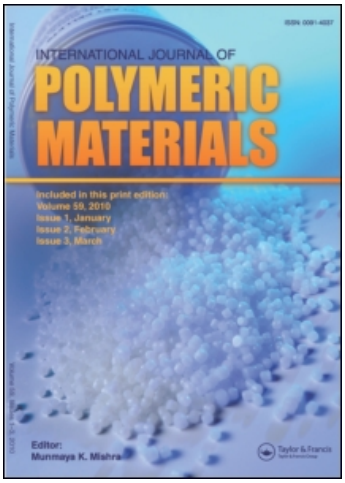

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BIOARTIFICIAL POLYMER MATERIALS BASED ON PVC/NATURAL POLYMER BLENDS: BINARY PVC/HYDROLYZED COLLAGEN BLENDSv

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Compatibility and biocompatibility of the binary blends of plasticized poly (vinyl chloride) and hydrolyzed collagen have been studied. The following investigation methods have been used: differential scanning calorimetry, thermogravimetry, contact angle measurements, and to assess the biocompatibility, "in vitro" cell growth test. The results indicate that these materials behave as relatively homogeneous systems and that the surface polarity increases by collagen incorporation. Polyvinyl chloride interacts with hydrolyzed collagen through either hydrogen or chemical bonds. A better substrate for cell growth in comparison with pure components has been obtained.

The main effects of the combination of these polymers are, on the one hand, the improvement of hydrophylicity and thermal stability of PVC, and on the other hand, the rapid dissolution is avoided of the collagen-based materials when in contact with biological fluids, which means a better biological stability in terms of resistance to enzymatic digestion.

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Keywords: poly(vinyl chloride), collagen, biomaterials, biocompatibility, surface, thermal properties

1. INTRODUCTION

Blends of synthetic and natural polymers have been used in recent years to develop some bioartificial polymeric materials. Their capacity of combining good physical and mechanical properties with suitable biocompatibility characteristics was studied with the view of obtaining new materials for biomedical applications [1,2,3,4].

Poly(vinyl chloride) (PVC) is one of the materials mostly used in medical applications. It has many desirable properties, such as flexibility, kink resistance, toughness, chemical and biological resistance, and suitability for sterilization (with no discoloration) by ethylene oxide, gamma radiation or autoclaving. More than that, PVC surface presents the lowest adhesion to bacterial cells, among other different plastic materials (including polyethylene and silicone) [5]. Plasticized PVC is a widely used plastic material with an excellent price/performance ratio. The PVC plasticized with phthalates is one of the materials that is able to ensure all the in-service qualities required by healthcare professionals while remaining affordable [6].

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PVC properties can be varied by blending. Usually, the polyvinyl chloride (PVC) films satisfy some requirements imposed by medical applications, such as chemical inertness, biocompatibility, ease of design and lower cost of the existing technologies [7,8]. An increased concentration of plasticizer significantly reduces the yellowness index of materials after gamma sterilization [9]. Such films are used in biological and medical applications in storage of substances (e.g. blood and blood products, drugs and injectables), for catheters with antithrombogenic activity, or as filtration membranes [10,11]; flexible PVC materials are used in neurosurgical implants [12] and others [13,14].

Such applications require materials whose morphology, chemical composition, and surface polarity should not affect the biological environment; additionally, all these characteristics should be stable in time.

Dumitrascu et al. [15,16] have applied corona discharge treatments to plasticized PVC in order to improve these characteristics but, commonly, plasma–treated surfaces are not stable enough in time.

A new solution – i.e., preparation of plasticized PVC/natural polymer blends – is proposed here for improving the adhesion and biocompatibility with various biological media. The authors also consider that by combining the PVC properties with those of hydrolyzed

collagen (HC), each component's properties will be enhanced. On the one hand, an improvement of PVC thermal stability, hindering plasticizer's migration and realization of a better substrate for cell growth in comparison with pure components, are expected. On the other hand, the rapid dissolution of the collagen-based materials in contact with biological fluids will be avoided, which means a better biological stability in terms of resistance of enzymatic digestion.

2. EXPERIMENTAL

2.1 Materials

Polyvinyl chloride (PVC) of medical quality was supplied by Oltchim, Râmnicu Vâlcea, Romania. It is a suspension-polymerization type with the following characteristics: Kw = 70, plasticizer absorption 112 wt%, oxide-reducing substances expressed as milliliters of 0.01 N $KMnO_4$/ 100 mL of aqueous extract − 3 ml, water and volatile substances 0.1 wt%, ash 0 wt%, granulation 0.05−0.25 mesh, residual vinyl chloride monomer of <5 ppm. It was plasticized with 55 phr di- (2-ethylhexyl) phthalate (DEHP) with respect to dried, powdered PVC and stabilized with Ca/Zn stearate system; soy oil has been also incorporated as a processing aid.

The collagen, supplied by the National Institute of Research and Development for Biological Science, Bucharest, Romania, had been obtained by acid hydrolysis of bovine derma. The powdered sample was obtained by a spray-drying process with a BÜCHI 190 Mini Spray Dryer. It is a type I and type III collagen consisting of a mass of peptides with the following elemental composition: 42.7% C, 10.8 % H, 12.2% N and 34.3% O; the number-average molecular weight determined by GPC on solution in dimethylformamide is 99,000 daltons and polydispersity was 1.66. It is thermally resistant up to 180°C. The hydrolyzed collagen (HC) is a highly hydrophilic polymer.

2.2 Compounds' Preparation

Binary blends of plasticized PVC and HC were prepared by successive operations of open-roll mixing, and pressing or extrusion/granulation operation. The mixing temperature was 80−110°C, temperature profile in extrusion/granulation was 110, 125, 100, 90°C, rotation speed was of 45−70 rpm. Pressing was achieved at a pressure of 300 kgf/cm^2 and a temperature of 120°C, with removal of sheets at 50°C. The content of hydrolyzed collagen in the blends varies between 5 and 60 phr with respect to powdered PVC (without plasticizer).

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Processing behavior was followed by means of a Brabender plastograph (Duisburg, Germany). After 10−minute mixing, the mixing energy time was of 5.5 kgf.m for most of the binary blends, increasing slightly with the increase of the HC content. In the torque-time curves of the blends containing 50 and 60 phr HC, a clear maximum appears at $\sim$2 minutes mixing time.

2.3 Investigation Methods

The thermal and surface properties of films based on blends of soluble collagen and polyvinyl chloride were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), IR spectroscopy and contact angle measurements.

DSC measurements were performed on a Mettler DSC12 instrument in the following conditions: heating rate 10°C min.$^{-1}$, nitrogen flow 50 mL min.$^{-1}$, sample mass 6.7−13.5 mg, temperature range 20−250°C. Prior to the DSC curve recording, the samples were dried in high vacuum at 25°C for at least 48 h.

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The thermogravimetric (TG) curves were recorded on a Paulik-Paulik-Erdey type Derivatograph, Mom, Budapest, under the following operational conditions: heating rate (β) 12°C min^{-1}, temperature range 25−600°C, film sample mass 50 mg, platinum crucibles, 30 cm^3 min^{-1} air flow. Two curves were recorded for each sample. The actual (β) values were evaluated from the temperature-time curve, and the calculated (β) values were further employed in the evaluation of the kinetic parameters. Three or four repeated readings (temperature and weight loss) were performed on the same TG curve, each of them having at least 15 points.

Kinetic analysis of the TG data was carried out on a single curve using both integral Coats-Redfern [17] (CR) and Reich−Levi [18], and differential Swaminathan-Madhavan [19] (SM) methods. The subscript of the overall kinetic parameters—activation energy (E), preexponential factor (A) and reaction order (n)—indicates the evaluation method.

With the last method the general expression of the conversion function was considered:

$$\beta \, d\alpha/dT = Ae^{-E/RT}[\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p] \quad (1)$$

where $\alpha = w_t/w_\infty$ is the conversion degree (ratio of the weight loss at time "t" and at the end of process); T is temperature in K, A is the preexponential coefficient, E is the activation energy, R is the gas constant, n is the reaction order, while m and p are other exponents of the

conversion function; $f(\alpha) = [\alpha^m\ (1-\alpha)^n\ [-\ln(1-\alpha)]^p$ is the differential form of the conversion function. Exponents m, n, p may take different values with respect to either the reaction mechanism or physical processes occurring during decomposition. From a mathematical viewpoint, both the positive and the negative values of A, E or of the exponents can describe with sufficient accuracy the TG or DTG curves, yet not all values have a kinetic significance. The positive values of the kinetic parameters, A and E, must be used as a selection criterion for "the most probable kinetic parameters." As additional criteria used in our studies, we could mention the good reproducibility of kinetic parameters obtained from different readings of TG data, the maximum values of the correlation coefficient or the minimum values of average square errors for each experimental point of the DTG or TG curves, with respect to the calculated ones using the obtained kinetic parameters, etc.

Infrared (IR) spectra of the blends, in KBr tablets, were recorded using a Perkin-Elmer 577 Spectrometer.

Contact angles of the blend films were determined by the sessile drop method at 20°C within 30 sec, after placing drops of liquids of 1 μL on the film surface. This time is high enough for the drop to reach an equilibrium contact angle, yet sufficiently short to neglect the losses by evaporation [20]. The diameter of the base and the height of the liquid drop are measured, thus obtaining the corresponding contact angle.

Thermodynamic work of a liquid adhesion on a solid surface has been calculated by means of Young's complete equation [21]

$$W_{SL} = (1+\cos\theta)\gamma_L = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{+}\gamma_L^{-}} + \sqrt{\gamma_S^{-}\gamma_L^{+}}\right) \qquad (2)$$

where ${\gamma_{S.L}}^{+}$, ${\gamma_{S.L}}^{-}$ represent the electron acceptor and, respectively, the electron donor parameters of the free surface energy corresponding to the solid (S)/liquid (L) and ${\gamma_{S.L}}^{LW}$ – Lifshitz-van de Waals component of the free surface energy for the solid/liquid:

$$\gamma_S = {\gamma_S}^{LW} + {\gamma_S}^{-} + {\gamma_S}^{+} = {\gamma_S}^{LW} + {\gamma_S}^{ab} \qquad (3)$$

Three pure liquids, from which at least two should to be polar, are used, namely [22] doubly distilled water ($\gamma_w = 72.8$ mN/m), formamide ($\gamma_f = 57.2$ mN/m), and α-bromonaphthalene ($\gamma_{bn} = 44.8$ mN/m). The Lifshitz Van der Waals (${\gamma_S}^{LW}$), electron donor parameter (${\gamma_S}^{-}$), electron acceptor parameter (${\gamma_S}^{+}$), as well as the acid-base component (${\gamma_S}^{ab}$) of the free surface energy (γ_S), were evaluated.

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The biological properties in terms of cytotoxicity and cytocompatibility have been studied through in vitro tests based on the cell culture method [23,24]. The 20×5 mm-sized samples were sterilized by exposure to ^{60}Co gamma radiation at a dose of 15 KGy. The biocompatibility was tested in vitro on epithelial cell cultures of veal kidney. Five pieces of samples have been introduced in each culture dish. Incubation took place at 37°C for 5 days and the cell growth was followed each day by microscopical examination. After these periods, the samples were examinated using an optical microscope with a maginification of 160X, 250X and 400X. Optical examination of the film samples was performed by means of a microscope from IOR, Bucharest, Romania.

A Dumen culture medium with 10% bovine fetal serum was employed; coloration was by the Gieson method [25]. Three reference samples of cell suspension were used.

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3. RESULTS AND DISCUSSION

3.1 DSC and IR – Spectroscopy Results

The plasticized PVC exhibits a glass transition temperature (Tg) at approximately 56°C and HC has a second order transition temperature, probably water–induced, of 74°C. The Tg values of all blends depend on blend composition, increasing with HC content with a maximum at 40 phr HC (Figure 1). The behavior is different than that expected for binary incompatible blends with non-interacting components.

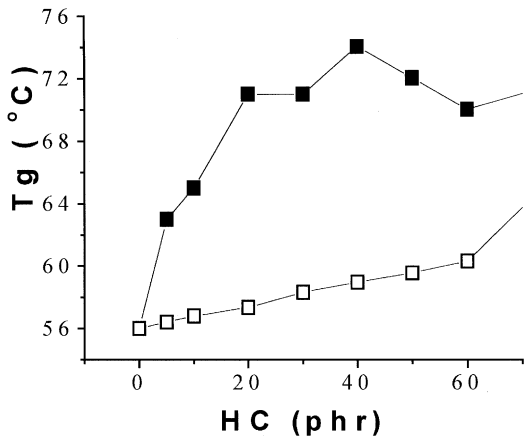

FIGURE 1 Variation of glass transition temperature with HC content of PVC/HC blends (■) experimental.

The positive deviation of the experimental Tg values with respect to that of PVC or that evaluated with Fox relation [26] may be explained by interactions between the components of the blends and by blends' good homogeneity, as well.

A comparison of the IR spectra of the blends (not shown here) shows in all of them the characteristic bands of the components, the intensity of which depends on the components' mixing ratio. Slight modifications appear in the IR spectra of the components in the fingerprint region. The bands at 740 cm^{-1} assigned to the C−Cl from PVC and primary NH_2 from HC decrease by increasing the HC content of the blends. The band at 1050 cm^{-1} (assigned to the phenyl and ethyl or propyl groups from the plasticizer) and the band at 1475 cm^{-1} (phenyl from the plasticizer) decrease by increasing the HC content in blends [27]. The differences are evident in the 3000−3500 cm^{-1}, 1400−1600 cm^{-1}, 1100−1400 cm^{-1}, 650−800 cm^{-1} region. The ratio between the height of the bands at 700 and 790 cm^{-1} is different from that of PVC. The absorption bands in this last region of wave numbers are assigned to the C−Cl and C−H groups, which could interact with the −OH and NH groups (3000−3500 cm^{-1}, 1400−1600 cm^{-1}) of hydrolyzed collagen [28,29,30]. This possible interaction could explain the increase in glass transition values.

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3.2 Thermogravimetry

For each TG stage, the following thermal characteristics have been determined: onset temperature (T_1); temperature corresponding to the maximum mass loss (T_M), and to the end of stage (T_f), respectively; (errors in temperature determination are of $\pm 2°C$), mass loss (Δw, error $\pm 1\%$) and overall kinetic parameters as activation energy (E_n, error of determination $\pm 10-15$ kJ/mol); pre-exponential factor (A) and reaction order (n) (Table 1 and 2).

By comparing the TG/DTG curves (not shown here) and thermogravimetric data of Table 1, one notes that the two components of the blends exhibit different thermooxidative behavior. While the curves of the blends are similar over a wide range of composition, their main TG stage occurs within the same temperature range, and it generally follows the curves corresponding to PVC, even if the contents of hydrolyzed collagen (HC) or content of DEHP are relatively high. Neither DTG nor TG curves of the blends present inflexion or splitting of the peaks. All blends have a similar behavior independent of the mixing ratio of the components and different from that of the components. The T_1 values are higher than those of the blends components, therefore the thermal stability of PVC is slightly increased. These

TABLE 1 Thermogravimetric Data Corresponding to the First Step of Decomposition of Plasticized PVC, HC and Binary Plasticized PVC/HC Blends

Sample composition (in phr of HC with respect to powdered PVC)	Characteristic temperatures (°C)								
	T_1 (°C)	T_m (°C)	T_f (°C)	ΔW (%)	E_{CR} (kJ/mol)	n_{CR}	E_{SM} (kJ/mol)	Ln A_{SM}	n_{SM}
Plasticized PVC	169	299	382	62.5	163.5	1.8	187.4	39.7	1.76
5HC	196	267.5	372	68.5	152.2	1.2	137.6	22.34	1.3
20HC	187	266.5	380.5	62.0	167.9	1.4	162.1	32.46	3.6
30HC	185	265	388	60	167.1	2.4	186.6	39.4	3.9
40HC	188	261	390	58.5	146.5	2.4	131.2	29.9	2.6
50HC	197	266	396	61	143.2	2.4	117.9	25.9	2.5
60HC	187	268	399	59.5	147.8	2.4	126.8	28.0	2.6
HC	158	300	424	53.5	74.15	1.7	88.4	17.41	2.0

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variations suggest the existence of certain interactions between components, which could lead to their compatibility.

One may easily observe that collagen absorbs a high quantity of water (~5–6 wt%). Both PVC and binary PVC/HC blends do not absorb water. Hydrolyzed collagen incorporation increases the initial thermal stability of plasticized PVC. The Tm values are lower than those of the components (Figure 2a). It is possible that, in the first moments of degradation, a cross-reaction takes place between components. The variation of the characteristic temperatures of the

TABLE 2 Thermogravimetric Data Corresponding to the Second Step of Decomposition of Plasticized PVC, HC and Binary Plasticized PVC/HC Blends

Sample composition (in phr of HC with respect to powdered PVC)	Characteristic temperatures (°C)					
	T_i (°C)	T_m (°C)	T_f (°C)	ΔW (%)	E_{CR} (kJ/mol)	n_{CR}
Plasticized PVC	382	437	494	13	230.4	1.8
5HC	372	435	493	12.5	152.2	1.2
20HC	392	433	495	12.75	178.9	1.35
30HC	390	450	503	13.25	172.4	1.2
40HC	390	438	493	12.5	178.5	1.0
50HC	394	438	492	13.75	176.5	1.3
60HC	400	448	502	13.25	186.5	1.2
HC	424	540.5	–	25.2	–	–

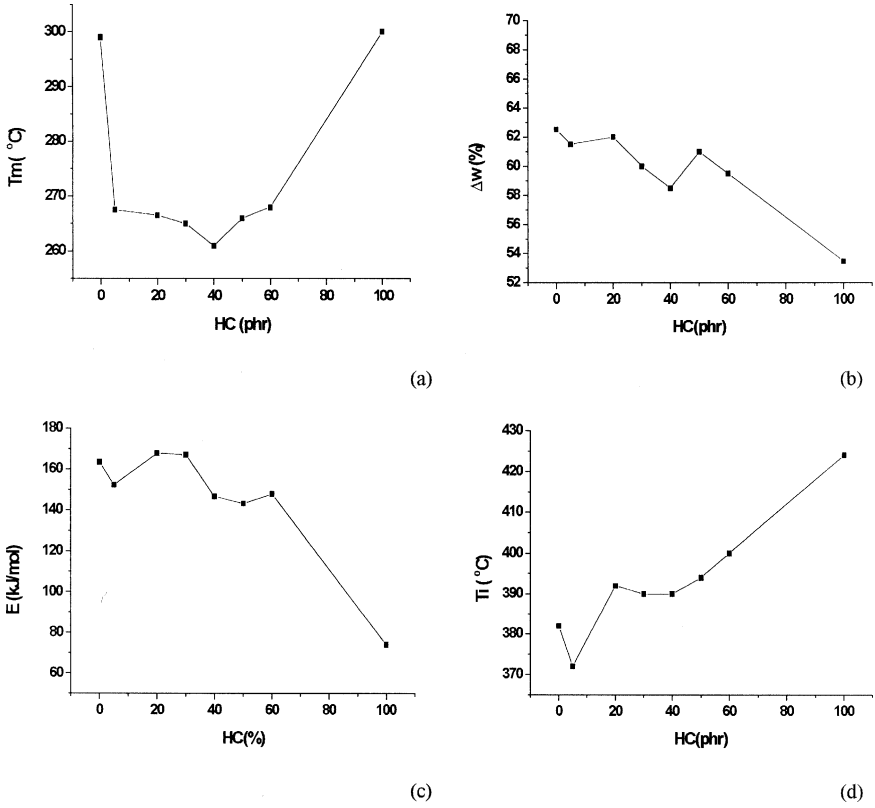

FIGURE 2 (a–c). Thermal characteristics versus HC content of the first step of decomposition of binary PVC/collagen blends. d). Onset decomposition temperature (Ti) for the second thermogravimetric step of decomposition of binary PVC/collagen blends.

second peak versus the blend composition is different, they are almost similar to those obtained by the additivity rule (Figure 2d).

The blends weight losses take intermediate values between those of the components, with the exception of blends containing 50 and 60 phr HC, which exhibit higher mass losses than those corresponding to the additivity rule (Figure 2b).

The overall activation energies of the main thermogravimetric step are higher for the blends than the values evaluated by the additivity rule (Figure 2c). This variation may be due to components' interaction during heating since, in the beginning of decomposition, the overall kinetic parameter values are close for all studied samples. The differences increase with increase, the conversion degree (Figure 3a) and

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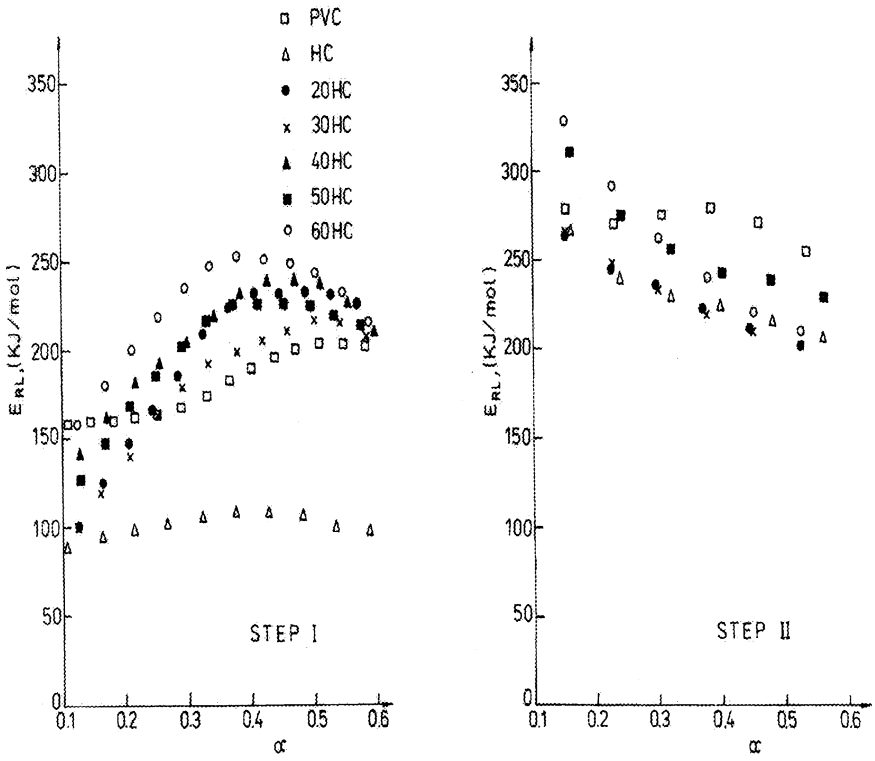

FIGURE 3 Overall activation energy vs. the conversion degree for the first and the second step of decomposition of PVC/collagen blends.

HC content. Increase of the activation energy with the conversion degree may be explained by interaction of blends partners and also by overlapping of the process of volatilization/decomposition of the plasticizer (DEHP) with that of PVC dehydrochlorination. It is known that the former is characterized by low values of the kinetic parameters [31]. The variation of the overall activation energy with the conversion degree for the second thermogravimetric step has also shown the increasing difference with respect to the values of blends' partners with increasing the HC content. However, the values are now close to those of HC and higher at low conversion degrees.

3.3 Surface Properties of the PVC/HC Blends

Collagen is widely used as a basic material in a variety of applications. Numerous studies have demonstrated its general biocompatibility and

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biodegradability, so it provides a valuble alternative to improve the biocompatibility of synthetic polymers such as poly (vinyl chloride) (PVC) used in medical applications. One of its advantages is the significant improvement of surface properties. In its turn, this component of the blend influences the surface properties as well, because it usually contains functional polar groups.

The contact angle between the surface of the binary polymer blends and twice-distilled water increases by HC incorporation, from 89.59 degrees, a value corresponding to plasticized PVC, to 96.2 degrees for 5 wt% HC and to 93.98 degrees for 20 wt% HC [32], respectively (Table 3).

It can be concluded that the surface free energy may be controlled by variation of the collagen content.

Generally, the contact angles between water and the α-bromonaphthalene film surface of the binary blends decrease comparatively with the corresponding value of PVC, while the contact angles with formamide increase (with a few exceptions). The HC incorporation into PVC matrix increases the acid-base component (γ_S^{ab}) of the free surface energy for all studied blends with respect to that of PVC (Figure 4a). This behavior is due to the strong hydrophilic character of HC. Increase of the acid-base component ($\gamma_S^{ab} = \gamma_S^+ + \gamma_S^-$) is mainly due to the increase of the electron-donor parameter (γ_S^-) (Figure 4b), and also to the superior values of the electron-acceptor parameter (γ_S^+) with respect to that of PVC (Figure 4c). In the case of binary blends (PVC/HC), increase of the acid-base component takes place with increasing the HC content and reaches a maximum value of approximately 125 mN/m, for 30% incorporated HC; for a higher quantity of HC, γ_S^{ab} decreases and tends to reach the value corresponding to PVC (Figure 4d).

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TABLE 3 Contact Angles Between Water (θ_{water}), Formamide ($\theta_{formamide}$) and α-bromonaphtalene ($\theta_{\alpha\text{-bromonaphtalene}}$) and Surface of the Film of Binary PVC/HC Blends

Sample composition (in phr of HC with respect to powdered PVC)	θ_{water} (degrees)	$\theta_{formamide}$ (grade)	$\theta_{\alpha\text{-bromonaphtalene}}$ (degrees)
Plasticized PVC	89.59	77.11	38.56
5 HC	96.2	82.07	35.2
20 HC	93.98	86.92	37.55
30 HC	70.88	84.70	39.89
40 HC	83.97	84.84	24.89
50 HC	85.57	72.98	36.28

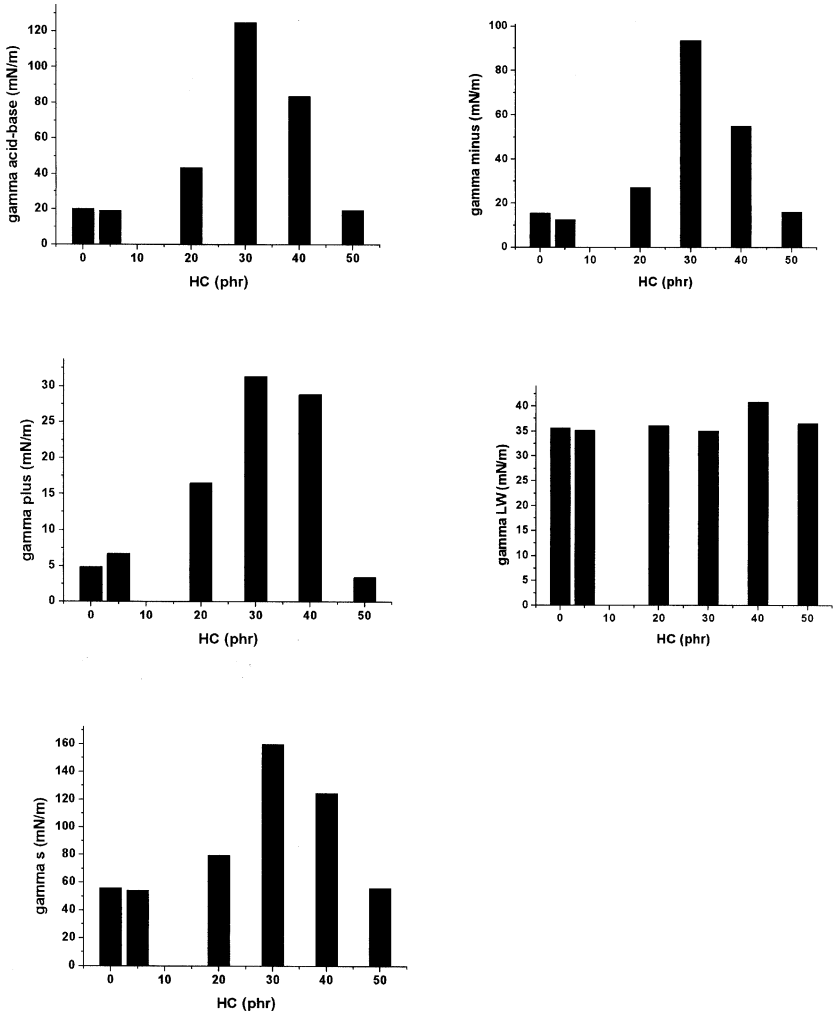

FIGURE 4 Variation of: a) acid-base component (γs^{nb}); b) electron donor parameter (γs^{-} c) electron acceptor parameter (γs^{+}); d) Lifshitz-van-der Waals component (γs^{LW}) of the free surface energy. and e) total free surface energy (γs) with hydrolyzed collagen content for the binary blends PVC/HC.

The variation of the total free surface energy is similar to that of the acid-base component (Figure 4e).

Based on these values, the interfacial blood-polymer tension of the material has been determined (Figure 5). It can be easily observed

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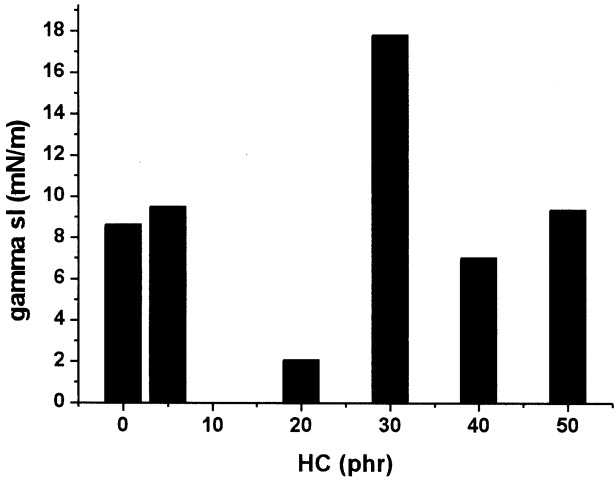

FIGURE 5 Interfacial tension blood-material versus HC content in binary blends of PVC/HC.

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that this lies within the biocompatibility range of (1–3 mN/m) for binary blends containing up to PVC/20% HC ($\gamma_{SL} = 2$ mN/m for 20 wt% HC).

3.4 Biocompatibility Test

As to the behavior during the *in vitro* biocompatibility test, the following observations were evident (Figure 6). The samples of binary blends show no cytotoxic effect on the epithelial cell culture; moreover, the cells show good adherence to the samples surface, which is not evident on PVC samples (Figure 6a). After 96 h culture on the 100PVC/20HC blend sample, the cells form a monolayer that is still expanding (Figure 6b). On the surface there are both agglomerated and isolated cells. From a morphological point of view, both flattened and merging cells occur. The nuclei are round or oval with granular chromatin and with 1 or 2 distinct nucleons. Some cells present vacuolized cytoplasm (Figure 6c), while other are in division (Figure 6d).

Some explants (compact masses of cells), from which the cells migrate and lie as monolayer, are also present (Figure 6a).

CONCLUSIONS

The results obtained indicate that these blends behave as homogeneous systems and that the surface polarity increases by hydrolyzed

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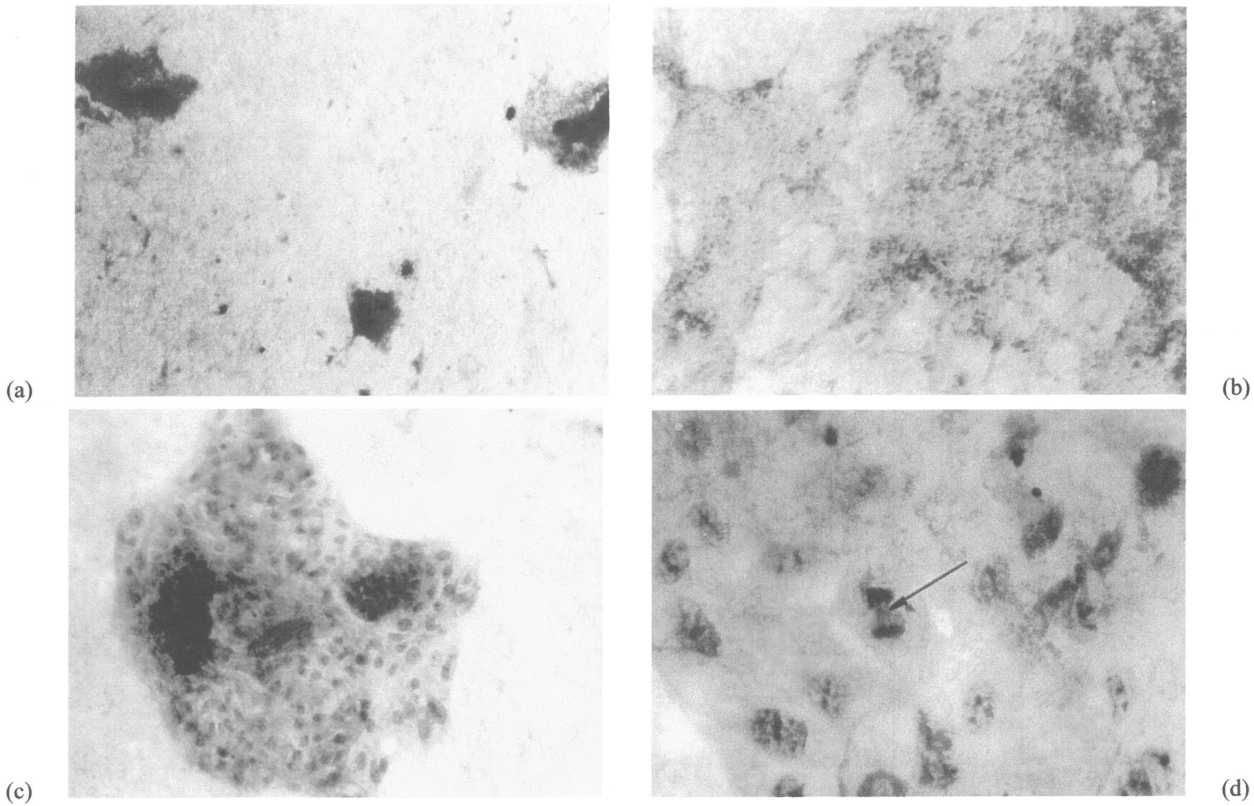

FIGURE 6 Optical microscopy images of surface plasticized PVC and binary blend PVC/20 HC maintained in cells culture for 96 hours: a) plasticized PVC; b) binary blend PVC/20 HC with cells migration as monolayer; c) cells in expansion; and d) cells in division.

collagen incorporation. A most suitable substrate for cell growth, in comparison with that of plasticized PVC, has been obtained. The physico-mechanical indices are only slightly varied ($\pm 5\%$) with increasing HC content; therefore enhanced properties are obtained without affecting other plasticized PVC characteristics.

Polyvinyl chloride could interact with collagen through either hydrogen or chemical bonds. Hydrolyzed collagen (HC) incorporation into the PVC matrix increases the polar components of the free surface energy, therefore HC imparts a hydrophilic character to PVC and materials with controllable properties can be obtained. Increase of the acid-base component reaches a maximum for HC content of 30%.

For HC content of 20% in binary PVC/HC blends, the interfacial energy with blood takes values in the biocompatibility domain (between 1 and 3 mN/m), which means a good compatibility with biological media. This blend composition is suitable for medical applications. A very good agreement was found with the results of the *in vitro* biocompatibility test, as the number of cells is maximum and adherence is optimum for the same blend composition.

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