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Preparation and study of novel biodegradable blends based on gelatinized starch and 1,4-trans-polyisoprene (gutta percha) for food packaging or biomedical applications

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The gas and water vapour permeability coefficients of novel biodegradable films based on 1,4-trans-polyisoprene and gelatinized starch were determined. The glass transitions, indirectly determined from gas permeability measurements, were compared to those obtained from thermal measurements (differential thermal analysis and dynamic mechanical thermal analysis). Incorporation of a low plasticizer amount in the blend was attempted in order to improve the mechanical properties of the blends. Some initial biodegradability experiments showed that these novel blends are biodegradable. This is primarily due to the presence of starch. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

Although in the past synthetic polymers were extensively used for multi-purpose applications because of their satisfactory mechanical and thermal properties, their lack of biodegradability has recently complicated and hindered their use (Wool, 1989; Peanasky *et al.*, 1991; Albertsson & Karlsson, 1994; Griffin, 1994; Wool, 1995). On the other hand, natural polymers, though usually endowed with inherent biodegradability, have inferior mechanical properties and present processability problems that hold them back from widespread use (Kumar, 1987; Krochta *et al.*, 1994; Andrady, 1994).

One way to overcome this problem is to resort to blending of natural polymers. Polymer blending is a well-used technique whenever modification of properties is required because it has an easy and straightforward procedure and it is low cost (Tadmor & Gogos, 1979). The usual target for preparing a novel blend of two or more polymers is not to change the properties of the components drastically but to capitalize on the maximum possible performance of the blend. On several occasions the initial dispersion of the blend components is further promoted by crosslinking, creation of interpenetrating networks, mechanical interlocking of components and use of 'compatiblizing agents' in order to ensure that no demixing will occur at a later stage (Bergen, 1967; Tadmor & Gogos, 1979; Griffin, 1994).

Gutta percha, or 1,4-trans-polyisoprene (TPIP), is a natural polymer that has through time found several applications, one of the most important being as an endodontic filling material (Arvanitoyannis *et al.*, 1992a, b, c; Kolokuris *et al.*, 1992a, b; Arvanitoyannis *et al.*, 1993). Starch is one of the most promising natural polymers because of its inherent biodegradability, its overwhelming abundance and its annual renewal (Blanshard, 1987). This paper deals with the preparation of blends in which the components are mixed to an adequate degree of dispersion by thermal pressing. A series of novel blends

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of TPIP with gelatinized starch (GS), with or without plasticizers (glycerol) or 'compatibilizers' such as ethylene acrylic acid (EAA), was prepared in an attempt to preserve the excellent biocompatibility of gutta percha (essential for biomedical applications) and to impart biodegradability for eventual food packaging applications.

EXPERIMENTAL

Materials

Potato starch and 1,4-TPIP were purchased by Wako Chemicals (Japan). Sorbitol, glycerol and ethylene acrylic acid (EAA) were also purchased from Wako Chemicals (Japan).

Extrusion

TPIP and potato starch, after having been thoroughly mixed, were extruded, in the presence of 15–20% water content, using a twin-screw extruder (Ikegai Co. Ltd PCM-30, Japan). The extrusion conditions were as follows: temperature zones 120, 120, 120 and 110°C (slot die); L/D, 500/30; feed motor and mix motor 2.0 and 50 rpm, respectively. The extrudates were subsequently hot pressed (110°C, 15 min, 3.5 MPa) to prepare specimens for measurements of mechanical properties.

Preparation of blends for gas permeability measurements

Potato starch (starch/water 30% w/w) was made amorphous by gelatinizing and roller drying (one process) at 140°C: roller drier speed, 10 rev min^{-1}: pressure, 32 psi (221 kPa); gap, 1 mm; diameter, 165 mm; width, 150 mm. Mixtures of TPIP and gelatinized potato starch were passed through the roller drier to obtain blends of appropriate composition. Preparation of films of TPIP with potato starch for permeability measurements was carried out by pressing the samples at 110–120°C for 15 min (Arvanitoyannis *et al.*, 1992a, b; Arvanitoyannis & Blanshard, 1993; Arvanitoyannis *et al.*, 1994). Conditioning of samples at different relative humidities was carried out as previously described (Arvanitoyannis *et al.*, 1994).

Preparation of samples for dynamic mechanical thermal analysis (DMTA)

Preparation of samples of TPIP/gelatinized potato starch (with 25% water) was carried out by pressing the samples (3.5 MPa) at temperatures of 120 to 130°C for 15–20 min. Conditioning of samples at different relative humidities was carried out as previously described (Arvanitoyannis *et al.*, 1994).

DMTA measurements

The dynamic mechanical thermal analyzer (DMTA, Mark II, Polymer Laboratories, UK) with a heating rate of 2°C/min and a single cantilever bending mode at 1 Hz was calibrated each day and measurements were taken of at least five samples.

The glass transition was defined as the peak in loss modulus (E″) and the peak in tanδ (tan$\delta = E''/E'$, where E'' is the loss modulus and E′ is the elastic modulus). This procedure normally gave values varying within a range of 5°C.

Differential thermal analysis (DTA) measurements.

DTA measurements were taken using a Shimadzu differential thermal analyzer equipped with a liquid N_2 cooling accessory and connected to an IBM PC and a Hewlett Packard plotter. Hermetically sealed aluminum pans were used with an empty aluminum pan as reference. The sample size for DTA was approximately 10 mg. Temperature calibration was carried out with cyclohexane, dodecane and octane. Heat flow calibration was carried out by reference to the known melting enthalpy of indium metal (purity 99.9%) from Goodfellows Metals. The purge gases used were dry helium and dry nitrogen. The T_gs were determined from the second run after melting, quenching with liquid nitrogen and reheating at a heating rate of 2°C/min. The percentage crystallinity with DTA was calculated according to Gidley (Gidley, 1992).

Wide-angle X-ray (WAXR) measurements

X-ray diffraction measurements of TPIP/GS blends at various moisture contents were carried out using a Shimadzu (Japan) diffractometer from 5 to 40° (2θ). The crystallinity was determined as previously reported (Marsh, 1986).

Measurements of permeability

The measurements of gas permeability were carried out using a Davenport apparatus connected to an IBM PC in accordance with ASTM D1434-66 (1966). Thickness was measured with a micrometer at five or six locations on the film.

Assuming that a unidirectional diffusion through a flat membrane occurs, then diffusion can be expressed as:

$$J_i = -D_{i(ci)} \frac{dC_i}{dx} \quad (1)$$

where J_i is the flux, $D_{i(ci)}$ signifies that the diffusion coefficient is dependent on the composition of penetrant and C_i refers to the local gas or penetrant concentration.

The formula for the determination of the diffusion constant is:

$$D = \frac{d^2}{6\theta} \tag{2}$$

where d is the thickness of the film and θ is the time lag of the permeation. The lag is related to the time required by the gas to pass through the film and establish an equilibrium with an originally gas-free chamber. The extrapolation of the pressure–time curve to the zero axis will produce the time lag (θ) (Amerongen, 1947; Amerongen, 1949). The quantity of gas (Q) that will then pass through the film is directly proportional to the difference in the pressure exerted by the gas on each face of the film ($p_1 - p_2$) and is inversely proportional to thickness (x). It is also directly proportional to the area exposed (A) and the time (t) for which permeation occurs according to the following relationship:

$$Q = \frac{PAt(p_1 - p_2)}{x} \tag{3}$$

where P has a constant value for a specific combination of gas and polymer at a given temperature and is known as the transmission factor or the permeability factor/constant/coefficient (van Krevelen, 1990).

Water vapour transmission rate (WVTR) measurements

The WVTR measurements were carried out as previously reported (Martin-Polo *et al.*, 1992).

Mechanical properties: tensile strength and percentage elongation

Tensile strenth and percentage elongation were measured on dumbbells, after their equilibration at various relative humidities, using an Instron Universal Testing Instrument (model 1122) operated according to ASTM D828-88 (1989). Measurement conditions and calculations of tensile strength and percentage elongation were made as previously described (Arvanitoyannis & Psomiadou, 1994; Arvanitoyannis *et al.*, 1995).

Biodegradability experiments

Mass changes

A Sartorius balance was used for measuring the film masses to 0.01 mg accuracy. The films were weighed both prior to and after burial. In the latter case the films were first rinsed with distilled water after they were removed from the burial site (burial time was up to 180 days) and then dried at 60°C for 48 h prior to their weighing.

Simple hydrolysis

1 g of film consisting of TPIP/GS and 20 ml distilled water was added to three test tubes. The tubes were kept in a water bath at 70°C. Weight measurements were taken every 3 h in order to record the weight losses versus time.

Alkali hydrolysis

A similar procedure to that of simple hydrolysis was followed except that 0.1 N NaOH solution was used instead of distilled water.

RESULTS AND DISCUSSION

Thermal and thermal mechanical properties

In binary systems, the presence of an amorphous polymer has been shown to affect the crystallinity character of the other semi-crystalline polymer substantially (Arvanitoyannis *et al.*, 1998; Arvanitoyannis *et al.*, 1997; Psomiadou *et al.*, 1998). Some representative WAXR diffraction patterns (WAXDP) are given in Fig. 1, in which it can be seen that the TPIP contribution, though lessened, continues to be present even at a ratio of TPIP/GS of 25/75 w/w. The blend preparation process involves heating (100°C), pressing (3.5 MPa) and then cooling the blends down to room temperature. This is a rather

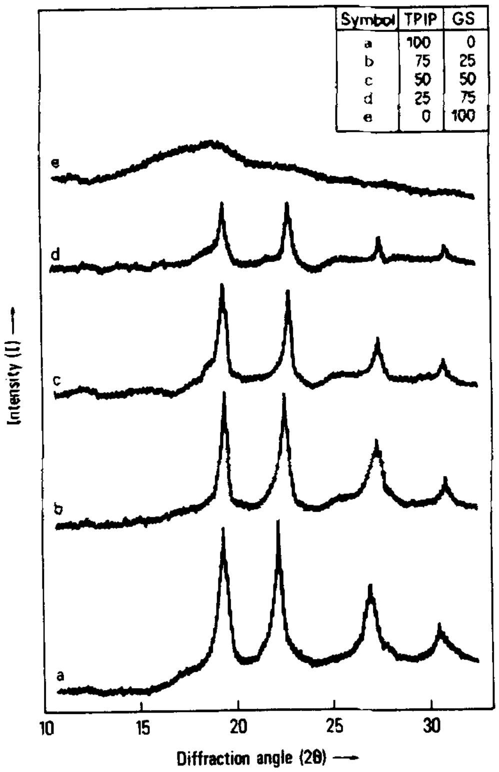

Fig. 1. Wide angle X-ray diffraction patterns of TPIP/GS blends.

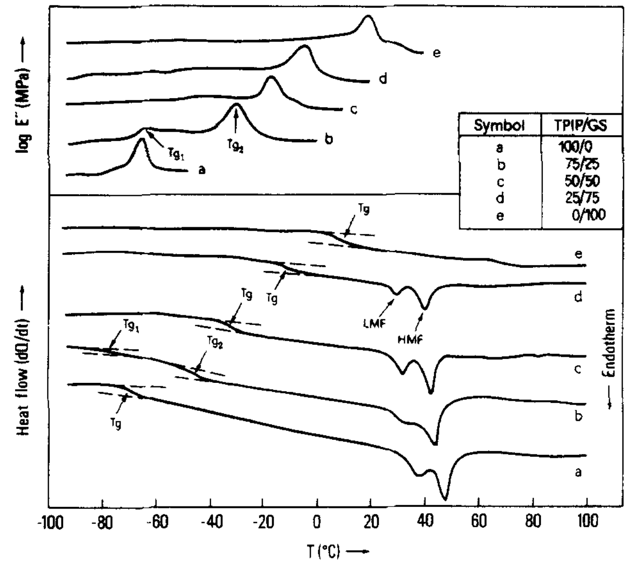

Fig. 2. First run DTA and DMTA traces of TPIP/GS samples with 18% moisture content.

slow process that hardly bears any resemblance to quenching. Therefore, the cooling process should be visualized as an annealing experiment which results in TPIP of both low melting form (LMF) and high melting form (HMF). The presence of LMF and HMF was confirmed by DTA. The melting points of the two isomorphous forms of TPIP (44 and 55°C, respectively, Fig. 2) are in satisfactory agreement with values obtained elsewhere (Cooper & Vaughan, 1963; Davies & Long, 1979; Chaturvedi, 1987a, b; Boochathum *et al.*, 1993a, b).

The recrystallization that occurred was thought to be the result of alignment after melting of stress-distorted crystallites formed during rapid cooling (Bunn, 1955; Keeper and Schlesinger quoted by Cooper & Vaughan, 1963; Takahashi *et al.*, 1973). Previous publications have stressed the importance of erasing any thermal history by heating the TPIP at temperatures higher than 80°C, which is the melting temperature of the last persisting nuclei (Chaturvedi, 1987a). Therefore, our adopted protocol ensures heating at $\theta > 100°C$ so that no nuclei will remain in the melt. The effect of dilution, due to the presence of an amorphous polymer, in the bulk of the semi-crystalline polymer is a quite complicated phenomenon, which has not been clarified yet (Arvanitoyannis *et al.*, 1992b). From the thermodynamic point of view, a polymer melt containing a diluent will necessarily have higher entropy than the non-diluted one, thus leading to even higher energy requirements for the crystallization of TPIP from blends. The presence of a diluent such as starch, in our case, in the TPIP melt decreases the inter- and intramolecular interactions substantially. Thus, it has been occasionally claimed, although without being able to provide concrete evidence, that nucleation mode might be subject to changes from intermolecular, for undiluted TPIP, to intramolecular interactions at high dilutions (Cooper & Vaughan, 1963). Therefore, in our TPIP/GS system, being an intermediate case, both nucleation mechanisms should be involved and considered. As is obvious from Fig 1 and 2, the more diluted the TPIP melt becomes (higher GS content), the less crystallized material ($\%X_c$) is produced. This happens because the density of the TPIP crystallites (in the diluted system) presumably drops to very low values and the initially formed nuclei are no longer able to influence either the orientation or the organization of amorphous regions, which primarily consist of GS. This assumption is corroborated by previous publications where formation of larger sized spherulites and their further growth and perfection in diluted systems is attributed to decreased interpenetration of molecules (i.e. TPIP and GS) because of a substantial drop in melt viscosity (Keller & Martuscelli, 1972; Chaturvedi, 1987a, b; Boochathum *et al.*, 1993a, b).

Table 1 summarizes the results from WAXDP and differential scanning calorimetry (DSC) measurements. The $\%X_c$ values determined from WAXDP and DSC data were found to be in close agreement. Previous thermodynamic studies revealed that though the LMF and HMF coexist, the LMF is quite metastable and it converts into the HMF by a process of fusion and crystallization (Kent & Swinney, 1966; Keller & Martuscelli, 1972). It is clear that both data series point to the same direction, that is the higher the GS content the lower the $\%X_c$. Therefore, it becomes obvious that the TPIP content in the TPIP/GS blend is of major importance in determining the predominant crystallization mechanism but a detailed and in-depth crystallization study should also involve microscopic analysis of nucleation, and growth and morphological data on a large number of TPIP/GS systems.

The glass transition (T_g) determination was carried out with DTA and DMTA measurements. A linear relationship was established for the T_g versus the feed molar ratio of the two components, TPIP and GS. There is satisfactory agreement between the calculated values from the inverse rule of mixtures equation (equation (4), dotted line, Fig. 3) and the experimentally obtained values (DTA, Fig. 3). The DMTA results and, in particular, the $\log E''$ data, given in Table 2, are in reasonable agreement with the DTA measurements. The occasional occurrence of a second peak (as a shoulder) in $\log E''$ traces for some TPIP/GS samples could be due to phase separation of the two components (Fig. 2b for DTA and DMTA).

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{4}$$

The addition of a plasticizer, such as glycerol or sorbitol, to the TPIP/GS resulted in a lowering of T_g (Table 2) in agreement with previous publications on

Table 1. Thermal and thermomechanical properties of TPIP/GS (1:1)/glycerol, TPIP/GS (1:1)/sorbitol and TPIP/GS (1:1)/EAA blends. The results give the average and standard deviation of at least five measurements for thermal and permeability measurements, respectively

							T_g		
TPIP	GS	Glycerol	Water	$\%X_c$ (DTA)[a]	$\%X_c$ (WAXR)[b]	DTA	DMTA(E'')	DMTA (tanδ)	Permeability (inflection)[c]
47.5	47.5	0	5	38.4±4.1	45.4±3.9	24.9±3.2	22.4±2.5	29. 8±2.1	23.6±2.4
45.0	45.0	5	5	36.5±3.2	40.5±4.0	19.4±1.8	19.0±1.8	25.0±2.2	18.7±2.0
42.5	42.5	10	5	32.1±2.8	35.8±3.2	8.8±0.7	9.1±0.6	13.4±1.0	10.5±0.9
40.0	40.0	15	5	29.0±3.0	32.6±2.9	3.0±0.1	2.4±0.3	6.8±0.7	—
37.5	37.5	20	5	24.8±2.1	28.4±2.5	−4.2±0.2	−3.5±0.4	2.0±0.3	—
34.5	34.5	26	5	20.3±1.6	25.0±2.0	−11.5±0.2	−19.8±0.7	−4.3±0.5	—
TPIP	GS	Sorbitol	Water						
45.5	45.5	4	5	34.0±2.9	39.3±3.0	18.6±1.5	17.8±2.1	24.6±2.0	19.8±1.8
42.5	42.5	10	5	30.3±3.3	35.6±3.3	7.0±0.9	6.1±0.8	11.8±1.2	9.0±0.8
40.5	40.5	14	5	26.8±2.5	31.0±2.6	−1.3±0.3	0.4±0.1	3.9±0.4	—
36.5	36.5	22	5	23.5±1.8	27.2±2.5	−8.8±0.5	−8.5±0.7	−2.5±0.2	—
35.0	35.0	25	5	17.8±1.5	22.4±2.7	−17.5±0.6	−19.3±0.9	−10.6±1.3	—
TPIP	GS	EAA	Water						
44.5	44.5	6	5	35.3±3.6	40.0±3.8	19.0±2.1	18.4±1.6	26.5±2.8	20.8±2.1
42.0	42.0	11	5	31.0±2.5	37.4±2.9	8.2±0.7	7.3±0.8	13.4±1.6	9.4±1.0
39.5	39.5	16	5	28.1±1.9	32.8±3.4	0.4±0.2	0.2±0.03	2.9±0.2	—
37.0	37.0	21	5	25.4±2.6	28.6±3.0	−5.0±0.3	−6.4±0.5	0.1±0.01	—
35.0	35.0	25	5	18.2±2.0	23.0±1.9	−14.6±1.2	−13.8±1.1	−6.9±0.4	—

[a] $\%X_c$ is the average from DTA where 100% crystalline for TPIP equals 12.5 kJ mol^{-1} (van Krevelen, 1990). [b] Average values from wide angle X-ray diffraction measurements. [c] Average values from inflection of O_2, N_2 and CO_2 permeability versus $1/T$.

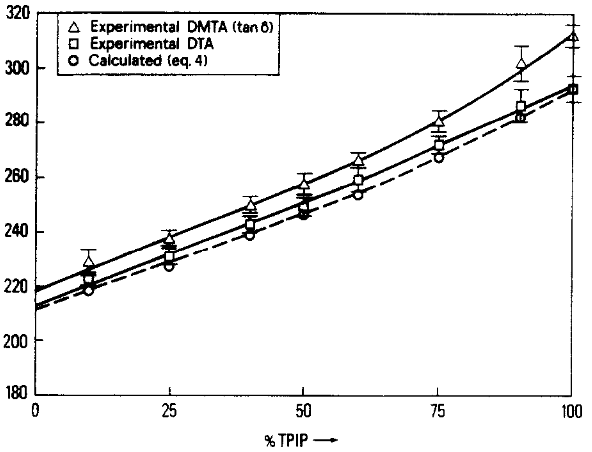

Fig. 3. Glass transition temperatures (T_g) versus composition of TPIP/GS blends.

synthetic and natural polymers (Bazuin & Eisenberg, 1986; Ollet *et al.*, 1991; Kalichevsky *et al.*, 1992; Kalichevsky *et al.*, 1993; Kirby *et al.*, 1993). In contrast, addition of a compatibilizer like EAA hardly had any effect on the thermal properties of the TPIP/GS blend. The interactions of molecules in the TPIP/GS/water and/or polyol systems are primarily due to hydroxyl groups of starch chains, starch–water, starch–polyol, polyol–polyol and water–polyol, whereas TPIP is not involved (Tolstoguzow, 1994). Therefore, in view of the TPIP hydrophobicity, any plasticization occurring in the composite matrix should be mainly attributed to starch/polyol content which, via moisture uptake, results in the creation of highly mobile regions.

Mechanical properties

The tensile strength, tensile modulus and percentage elongation of TPIP/GS/water in the presence or absence of polyols/compatibilizer are summarized in Table 3. Since the blends consist of two components, TPIP and GS, the prediction formulae for their mechanical properties are (Ashby & Jones, 1985):

$$E_{\text{blend}} = V_{\text{GS}}E_{\text{GS}} + (1 - V_{\text{GS}})E_{\text{TPIP}} \qquad (5)$$

$$E_{\text{blend}} = \frac{1}{\frac{V_{\text{GS}}}{E_{\text{GS}}} + \frac{1-V_{\text{GS}}}{E_{\text{TPIP}}}} \qquad (6)$$

Study of tensile strength against storage time showed a gradual increase in embrittlement, probably induced by a phase separation, at least partial, of the two components in the blend. It should be emphasized that when EAA was used, the embrittlement was encountered to a much lesser extent compared to the blends containing a plasticizer (e.g. glycerol or sorbitol). A possible explanation might be that these plasticizers appeal primarily to hydrophilic starch whereas they have no influence whatsoever on TPIP. Apart from the deviations due to experimental errors, other factors responsible for experimental errors, conducive to greater standard deviation, are: (a) considerable differences in percentage crystallinity since both components are semi-crystalline, (b) non-uniform distribution of amorphous/crystalline regions, (c) variations in the crystal packing in view of the coexistence of LMF and HMF and (d) stress localization or 'necking' or 'slipping' of the specimen (Kausch, 1987; Haward, 1987).

Furthermore, starch is by nature heterogeneous, consisting of amylose and amylopectin, having both amorphous and crystalline regions and thereby contributing to the general non-uniformity encountered in this composite matrix. The higher the glycerol and sorbitol content in the TPIP/GS blend, the higher the elongation and the lower the tensile strength, as shown in Table 3.

Water vapour transmission rate

It is well known that the main disadvantage of edible films has been their high WVTR. For this reason it is important either to use a bi/multi-layer or a blend with a hydrophobic polymer (Guilbert, 1986).

Table 2. Glass transition temperatures (T_g in °C) of TPIP and GS blends conditioned at different relative humidities

TPIP (%)	Water(%)	GS(%)	DTA(2nd run)	DMTA(E'')	DMTA(tanδ)
80	20	—	−60.0±3.4	−62.0±3.4	−56.5±2.9
75	20	5	−56.1±2.5	−58.0±3.0	−52.0±3.4
70	20	10	−48.5 + 3.2	−51.9±2.4	−43.2±2.0
60	20	20	−39.0±2.4	−42.8±1.9	−37.4±3.2
54	20	26	−36.9±1.9	−40.0±2.6	−35.0±2.5
50	20	30	−32.3±2.3	−36.8±1.7	−31.4±1.9
42	20	38	−25.0±2.6	−30.5±1.5	−26.3±2.2
34	20	46	−11.2±0.8	−16.1±1.8	−11.1±0.8
47.5	5.0	47.5	10.6±1.7	7.4±0.8	12.2±1.4
45.5	9.0	45.5	3.5±1.9	1.2±0.2	5.0±0.6
42.0	16.0	42.0	−7.4±1.6	−10.1±1.3	−6.2±0.3
40.0	20.0	40.0	−20.5±2.2	−23.0±2.0	−18.4±1.6
37.5	25.0	37.5	−28.0±1.8	−28.2±1.5	−23.6±2.5
34.5	31.0	34.5	−37.2±1.9	−39.6±3.4	−34.0±2.8

Table 3. Mechanical properties and water vapour transmission rate (WVTR) of TPIP/GS (1:1)/glycerol, TPIP/GS (1:1)/sorbitol, and TPIP/GS (1:1)/EAA blends conditioned at different relative humidities. The results give the average and standard deviation of at least eight measurements

TPIP	GS	Glycerol	Water	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation (%)	WVTR (gm^{-1} s^{-1} Pa^{-1}) ×10^{-11}
47.5	47.5	0	5	14.5±1.3	12.0±1.3	6.8±0.6	1.8±0.1
44.5	44.5	6	5	12.8±1.4	10.3±1.4	10.5±1.1	3.0±0.4
42.5	42.5	10	5	10.6±0.9	9.5±0.8	13.9±1.5	4.6±0.3
39.5	39.5	16	5	8.3±0.6	8.0±1.9	18.0±3.0	5.4±0.6
36.5	36.5	22	5	6.1±0.4	7.4±0.8	24.2±2.6	6.8±0.7
32.5	32.5	30	5	3.9±0.2	6.0±0.6	33.1±5.0	9.4±0.8
TPIP	GS	Sorbitol	Water				
45.0	45.0	5	5	11.0±11.1	8.4±0.7	14.3±1.6	4.3±0.5
42.0	42.0	11	5	8.8±0.7	7.0±0.9	18.5±2.0	5.5±0.4
40.0	40.0	15	5	7.4±0.6	5.7±0.6	26.4±2.4	6.2±0.7
36.0	36.0	23	5	5.3±0.7	4.2±05	31.5±3.0	7.6±0.5
33.5	33.5	28	5	3.0±0.4	2.7±0.3	40.4±3.8	10.5±1.1
TPIP	GS	EAA	Water				
45.5	45.5	4	5	17.4±1.5	9.2±0.8	8.4±0.7	1.9±0.3
42.5	42.5	10	5	14.6±0.9	8.3±0.6	15.5+1.4	3.9±0.5
39.5	39.5	16	5	11.2±1.0	6.4±0.5	21.0±2.0	4.5±0.6
37.0	37.0	21	5	8.7±0.7	5.0±0.4	28.5±2.9	5.9±0.5
34.0	34.0	27	5	6.6±0.5	6.3±0.5	36.4±4.1	8.0±0.7

Since TPIP is hydrophobic, the absorbed amount of moisture depends primarily on starch and polyol content (Table 3). It is difficult to find out which of the two components (GS or polyol) has a higher water sorption. However, since the GS contribution is substantially greater in terms of weight content, our main interest should be focused on it. The inherent difficulty for making accurate sorption and transport measurements for water vapour has been repeatedly acknowledged in the past and attributed to its high vaporization heat, low saturation vapour pressure, high solubilization and plasticization of polymeric systems and its clustering tendency (Schult & Paul, 1996). Although the blend being studied here is not an edible one, the presence of GS facilitates the clustering of water molecules in their diffusion through microcavities. Recent studies with computer simulation confirmed the accessibility and availability of amorphous hydrophilic polymers, particularly in the presence of plasticizers (Takeuchi, 1990; Takeuchi & Okazaki, 1990; Takeuchi *et al.*, 1990; Trommsdorff & Tomka, 1995).

Gas permeability

No simplified relationship between polarity, hydrophobicity or hydrophilicity and solubility has been established yet mainly because of the complexity of interactions between the matrix components and, in particular, their non-homogeneous distribution of crystalline/semi-crystalline or amorphous areas and plasticizer(s). Throughout the matrix, the amorphous areas are characterized by high segmental mobility, thus creating the appropriate conditions for gas solubility, diffusion and permeation.

The gas permeability modelling for amorphous synthetic polymers, as proposed by Salame (1986), has been widely accepted and is as follows:

$$N \times \pi = \Pi = (N_i \times \pi_i) \qquad (7)$$

where the so-called polymer permachor (π) is by definition proportional to the negative logarithm of a relative permeability, the product $N \times \pi$ is known as molar permachor (Π), an additive molar function, N = the number of characteristic groups per structural unit and π_i = the increment of the group i.

After the numerical value of π is calculated, the permeability at ambient temperature can be estimated as follows:

$$P_{(298)} = P^*_{(298)} \exp(-s\pi) \qquad (8)$$

where $P_{(298)}$ is the permeability of a standard gas (e.g. N_2) in a standard polymer (rubber was arbitrarily chosen) and s is the scaling factor. By substituting $\log P^*_{(298)} = -12$ and $s = 0.122$ for nitrogen (van Krevelen, 1990), the following equation is obtained:

$$\log P^*_{(298)} = -12 - 0.053\pi \qquad (9)$$

It should be emphasized that this equation is applicable only to amorphous polymers.

In order to apply the above-mentioned equations to semi-crystalline (sc) polymers, where the crystallites impose constraints on the amorphous chains and gathering of chain defects (e.g. chain ends and chain branches) imparts different properties to the amorphous phase of sc polymers, a further modification (Salame, 1986) is required, thus leading to:

$$\pi_{sc} = \pi_\alpha - 18 \ln \alpha = \pi_\alpha - 41.5 \log(1 - X_c) \qquad (10)$$

where α is the amorphous volume fraction and X_c is the crystallinity.

When equations (7) to (9) were applied to starch the obtained values for dry amorphous samples were 6.99×10^{-20} and $2.4 \times 10^{-19}\,\mathrm{cm^2\,s^{-1}\,Pa^{-1}}$ for amylopectin and amylose, respectively. The values of nitrogen permeability for dry starch are significantly lower than the experimental ones (Table 4). Significant discrepancies between empirical and experimental values for TPIP/GS blends have been observed. In general, such discrepancies should be attributed to factors such as non-uniform distribution of microcrystallites/voids, polarity/accessibility of polar groups and strength of water/water or polymer/water bonds (van Krevelen, 1990; Mueller-Plathe, 1991a, b; Mueller-Plathe, 1992).

The water content influences greatly the films containing hydrogen bonding groups and the gas diffusivity increases with water content, as can be seen from Fig. 4. This figure demonstrates how T_g can be determined from permeability measurement, i.e. the inflection of the line from permeability measurements versus the inverse temperature ($1/T$). A possible reason for such a change in the slope is that in the first instance a strong localization of the initially sorbed water occurs over a limited number of sites, whereas at higher water contents the film matrix may swell, thus resulting in an even higher mobility of the sorbed water molecules. At high water contents it is believed that the polymer chains move further apart and the number of intra- and interchain hydrogen bonds decreases considerably (Trommsdorff & Tomka, 1995). The widening of the composite matrix structure due to incorporation of plasticizer molecules would enhance gas permeation (Table 4). Since TPIP is hydrophobic, it is mainly the GS that undergoes plasticization due to water/polyol insertion, resulting in chain separation because of a considerable drop in intra- and interchain bonding. Table 4 shows that the higher the polyol content, the higher the gas permeability.

The thermal dependence of diffusivity on temperature was found to follow the Arrhenius equation satisfactorily:

$$D = D_0 \exp(-E_D/RT) \qquad (11)$$

where D_0 is the diffusion coefficient, E_D is the activation energy of diffusion and R is the universal gas constant.

Table 4. Gas permeability (O_2, N_2 and CO_2 in $cm^2 s^{-1} Pa^{-1}$) of TPIP/GS (1:1)/glycerol, TPIP/GS (1:1)/sorbitol, and TPIP/GS (1:1)/EAA blends conditioned over different relative humidities. The results give the average of at least five measurements at ambient temperature (23±2°C)

TPIP	GS	Glycerol	Water	O_2	N_2	CO_2
47.5	47.5	0	5	$1.3(\pm0.1)\times10^{-14}$	$2.0(\pm0.3)\times10^{-15}$	$0.3(\pm0.01)\times10^{-12}$
44.5	44.5	6	5	$2.9\pm0.2)\times10^{-13}$	$1.5(\pm0.2)\times10^{-14}$	$9.5(\pm1.2)\times10^{-12}$
42.5	42.5	10	5	$2.3(\pm0.2)\times10^{-12}$	$4.1(\pm0.3)\times10^{-13}$	$7.8(\pm0.6)\times10^{-11}$
39.5	39.5	16	5	$9.5(\pm1.5)\times10^{-12}$	$0.7(\pm0.1)\times10^{-12}$	$4.6(\pm0.3)\times10^{-10}$
36.5	36.5	22	5	$5.7(\pm0.4)\times10^{-11}$	$6.1(\pm0.5)\times10^{-12}$	$1.1(\pm0.1)\times10^{-9}$
32.5	32.5	30	5	$3.3(\pm0.3)\times10^{-10}$	$4.5(\pm0.4)\times10^{-11}$	$9.2(\pm0.6)\times10^{-9}$
TPIP	GS	Sorbitol	Water			
45.5	45.5	4	5	$3.1(\pm0.3\times10^{-13}$	$4.0(\pm0.3)\times10^{-14}$	$1.2(\pm0.2)\times10^{-11}$
42.0	42.0	11	5	$4.8(\pm0.5)\times10^{-12}$	$6.2(\pm0.5)\times10^{-13}$	$8.5(\pm0.7)\times10^{-11}$
40.5	40.5	14	5	$1.4(\pm0.2)\times10^{-11}$	$2.3(\pm0.1)\times10^{-12}$	$6.3(\pm0.4)\times10^{-10}$
36.0	36.0	23	5	$9.6(\pm0.6)\times10^{-11}$	$8.0(\pm0.6)\times10^{-12}$	$3.8(\pm0.2)\times10^{-9}$
33.5	33.5	28	5	$4.2(\pm0.5)\times10^{-10}$	$3.1(\pm0.2)\times10^{-11}$	$2.2(\pm0.3)\times10^{-8}$
TPIP	GS	EAA	Water			
45.5	45.5	4	5	$9.7(\pm0.8)\times10^{-14}$	$7.7(\pm0.6)\times10^{-15}$	$7.4(\pm0.6)\times10^{-13}$
42.5	42.5	10	5	$4.8(\pm0.4)\times10^{-13}$	$5.9(\pm0.4)\times10^{-14}$	$4.0(\pm0.3)\times10^{-12}$
39.5	39.5	16	5	$3.6(\pm0.3)\times10^{-12}$	$5.0(\pm0.30\times10^{-13}$	$2.5(\pm0.2)x10^{-11}$
37.0	37.0	21	5	$1.2(\pm0.6)\times10^{-11}$	$2.4(\pm0.5)\times10^{-12}$	$3.7(\pm0.7)\times10^{-10}$

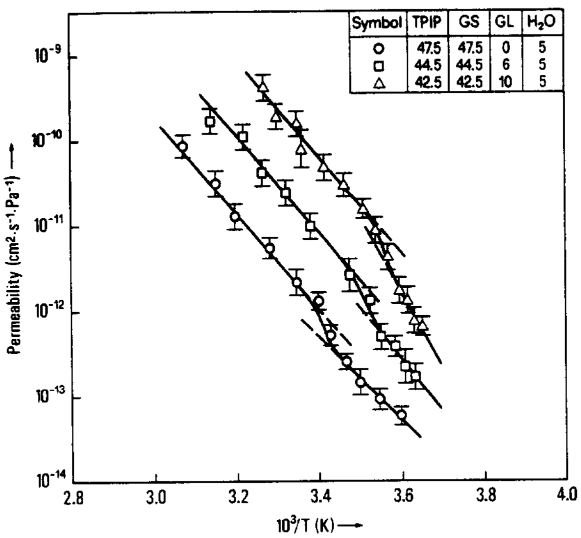

Fig. 4. Permeability of CO_2 in TPIP/GS blends versus the inverse temperature ($10^3/T$). The results give the average and the standard deviation of at least six measurements.

The corresponding logarithmic expression for equation (11) describing diffusivity is:

$$\ln D = \ln D_0 - E_D/RT \qquad (12)$$

Similarly to equation (11), the temperature dependence of permeability can be expressed as:

$$P = P_0 \exp(-E_P/RT) \qquad (13)$$

where E_P is the apparent activation energy of permeation and

$$\ln P = \ln P_0 - E_P/RT \qquad (14)$$

The Arrhenius equation, both in its original and its logarithmic forms (equations (13) and (14)), was found to describe satisfactorily the dependence of gas diffusivity on temperature (Figs 4 and 5). When the gas molecule moves through the polymer substrate along the parallel chains no activation energy is required. However, if this is not the case, the calculated E_D is of primary importance because it is equal to the necessary energy for causing the minimum chain separation in order to permit passage of the gas molecule (Pace & Datyner, 1979a, b, c). When plasticizing molecules are introduced in the network it becomes considerably more flexible than before. Furthermore, it was found that the larger the diameter of the gas molecule, the greater the required hole size and the higher the diffusion activation energy, as previously reported (Arvanitoyannis *et al.*, 1992a; Arvanitoyannis *et al.*, 1994).

Figures 4 and 5 show that the gas diffusion within the composite polymer matrix could be distinguished between lower than T_g and higher than T_g regions. In the former it is accepted that gas molecules are trapped in small sized voids as a result of their oscillations, whereas in the latter, because of higher segmental

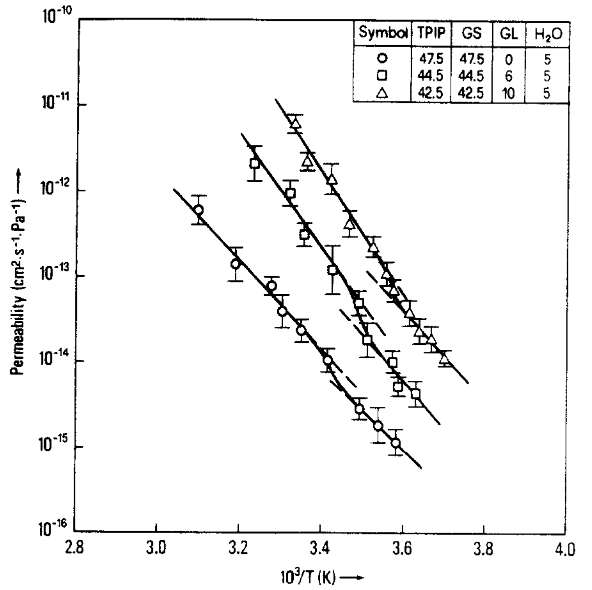

Fig. 5. Permeability of O_2 in TPIP/GS blends versus the inverse temperature ($10^3/T$). The results give the average and the standard deviation of at least six measurements.

mobility, interconnecting channels annihilate the original cavities, which are replaced by new ones (Gelin, 1994).

The activation energies for diffusion and permeation, calculated from equations (12) and (14), varied from 4 to 21 kJ mol^{-1} depending on the gas (O_2, N_2 or CO_2), temperature and the blend composition. E_D and E_p for the same blend composition fell in the following order: $O_2 > N_2 > CO_2$. At higher than T_g temperatures E_D and E_P were considerably lower than at temperatures below T_g. When there was water or a polyol in the blend both E_D and E_P decreased substantially because of plasticization of the matrix. On the other hand, the presence of EAA increased the required E_D and E_P.

Biodegradability studies

Several methods are usually applied for assessing the biodegradability of novel materials. Some of the classical methods are burial in soil, exposure to sea water, enzymatic hydrolysis, simple water hydrolysis (exposure to water at pH≈7.0) and accelerated alkali hydrolysis.

The weight losses from simple and alkali-accelerated hydrolysis and soil burial are summarized in Table 5. Accelerated alkali hydrolysis resulted in greater weight losses for the polymer blends than simple hydrolysis, presumably because of the NaOH presence, which enhances the solubilization of GS in the polymer blend.

The soil burial method is well known to be a slow process mainly because of the low percolation rate (Peanasky *et al.*, 1991; Goheen & Wool, 1991). However, it is noteworthy that the burial soil test reflects more than any other test the real-life conditions, though soil composition usually varies from place to place. Although after 15 days soil burial testing indicated lower losses than those determined by both types of hydrolysis testing, at the end of 120 days (4 months) the measured losses almost equalled the losses of the samples subjected to hydrolysis for 7 days. It is obvious that the entire amount of starch content is not removed during the biodegradability experiments. A possible explanation might be that starch inclusions in some areas of blend are well protected, especially if the sample is thick, and not easily accessible to water or to microbial/bacterial action. However, gradually both starch and plasticizer are removed and 8–10% of TPIP (probably LMP) is also removed. The removal of the latter might be attributed to solubilization of the lower molecular weight component but this assumption requires a more detailed study with gel permeation chromatography so that the molecular weight distribution is compared before and after biodegradation.

Table 5. Weight losses (W_f%) of TPIP and GS blends plasticized with water and glycerol or sorbitol or EAA after their exposure to simple hydrolysis (80°C), alkali hydrolysis (10% NaOH, 70°C) and burial in soil. The results give the average and standard deviation of five measurements

		Simple hydrolysis		Alkali hydrolysis			Burial in soil	
TPIP	GS	2d	7d	2d	7d	15d	60d	120d
100	0	3.6±0.4	7.9±0.6	4.5±0.3	9.3±0.8	2.8±0.3	6.5±0.5	8.8±0.7
95	5	6.9±0.7	11.0 + 1.2	8.6±0.5	13.5±1.2	5.8±0.4	8.9 + 0.7	12.0±1.1
85	15	10.5 + 1.0	16.3±1.4	12.7±1.2	18.9±1.5	7.0±0.3	12.5±1.1	19.5±1.3
70	30	18.8±1.2	25.9±1.8	21.0±0.9	28.2±2.2	9.5±0.8	18.3±1.6	26.1±2.0
60	40	28.0±1.4	39.0±2.0	30.5±1.8	43.7±3.5	12.3±1.1	26.0±0.9	40.3±3.2
50	50	35.7±2.2	44.8±1.7	38.0±2.3	46.3±2.8	14.5±1.2	35.6±2.5	45.8±4.0
40	60	43.6±2.6	57.7±2.8	47.8±3.5	54.0±4.3	18.0±0.9	41.5±3.3	51.9±4.5
30	70	52.0±4.1	60.5±3.9	57.1±4.4	66.8±3.9	21.4±2.0	51.0±4.2	66.0±4.8
TPIP/GS	Glycerol							
35/35	30	51.2±4.2	68.3±5.0	60.0±4.8	74.3±6.3	48.0±3.9	62.5±5.2	71.1±5.9
TPIP/GS	Sorbitol							
35/35	30	53.8±4.5	72.0 + 6.3	64.6 + 5.9	77.0±6.5	51.3±4.8	65.1±6.0	73.2±5.8
TPIP/GS	EAA							
35/35	30	17.3±1.5	44.0±2.0	22.1±2.0	49.4±2.3	8.9±0.8	27.0±1.5	45.9±22

CONCLUSIONS

Novel binary biodegradable blends based on TPIP and GS with or without plasticizers (water or glycerol/sorbitol) or compatibilizer (EAA) were studied with regard to their thermal mechanical properties and gas/water permeability. The plasticizers increased the percentage elongation considerably whereas they decreased the tensile strength, glass transition and melting points of the composite matrix. The determined gas and water permeability values of the blend were intermediate values of the two components. Initial biodegradability experiments (simple hydrolysis or alkali hydrolysis of matrix) showed that this binary blend constitutes a promising biodegradable composite polymeric matrix for further exploitation.

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