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# Environmentally degradable plastics: thermal behavior of polymer blends based on waste gelatin

**Summary** — Blends, based on waste gelatin (WG) and poly(vinyl alcohol) (PVA), formulated for agroindustrial applications are currently under investigation. In the present contribution their characterization by thermogravimetry (TG) and differential scanning calorimetry (DSC) is reported. The results obtained are compared with those of analogous blends based on "virgin" gelatin (VG). Whereas these last tended to phase segregate, those based on WG resulted compatible due to the presence of glycerol in WG and its inherent destructurization caused by former thermal and mechanical treatment.

**Key words**: Environmentally biodegradable plastics, gelatin, poly(vinyl alcohol), thermal analysis, mulching films, hybrid blends plastic waste.

Synthetic polymers displaced metals, glasses, ceramics, and wood as raw materials in the manufacturing of many durable products. However, once these have completed their life cycle and are discarded, they tend to persist in the environment due to their structural recalcitrance to environmental degradation. This fact creates a multitude of ecological and safety concerns [1]. Since plastic waste has caused serious, even though often emotionally exaggerated environmental concern, there are nowadays increasing demands to develop environmentally acceptable polymeric materials that may disintegrate and eventually experience a final harmless microbial mineralization [2—5].

The interest for environmentally degradable polymeric materials has been growing in connection with waste management problems and novel exploratory outlets [6—11]. Among the biodegradable polymers, starch and gelatin hold a particular position since these biopolymers have no adverse impact on human health or environment [12—14]. Gelatin is currently used in food processing and pharmaceutical formulations. However, gelatin scraps generated in the different manufacturing processes constitute a special waste to be properly disposed in spite of its yet valuable energy context.

The use of plastic films for agricultural mulching has increased rapidly due to the advantages that such a practice is offering in terms of product quality and economical returns [15, 16]. However, conventional mulching films based on polyolefins need a post-consume costly care for their removal from the field at the end of each fruiting season since they do not decompose in the soil and hence have to be treated as a special waste. The application of degradable mulching films would abundantly reduce the estimated 100—120 US $ cost/acre required to remove conventional mulching films [17] and would reduce deleterious environmental effects caused by illegal burning or burial practices of non environmentally degradable plastics [15].

As a part of a continuing interest in the investigation and promotion of environmentally degradable polymers and plastics for sound applications in agroindustrial and biomedical-pharmaceutical fields [18—21], an investigation has been undertaken on the utilization of pharmaceutical grade waste gelatin (WG) in the formulation of films for sustainable mulching and solarization applications provided of a self-fertilizing potential.

In the materials processing there are several variables that influence the ultimate properties of the products. Among them the thermal characteristics and thermal history experienced by the materials often hold a crucial position. In the case of gelatin, depending on its source, different transitions temperature can be found due to the effect of water amount, drying process and primary structure (composition and sequencing of amino and imino acids residues along the peptide backbone) [22—25].

In the present contribution, we report on the thermal analysis of films based on virgin gelatin (VG), waste

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gelatin (WG) and blends with PVA either treated or not with a crosslinking agent. The work is stemming from an action undertaken almost three years ago by the International Centre for Science and High Technology of Trieste — Italy under umbrella of the United Nations Industrial Development Organization (UNIDO) for the diffusion of awareness in Environmentally Degradable Plastics as a option to Environmental Protection and implementation of a more rational use of natural renewable resources and agroindustrial waste.

## EXPERIMENTAL

### Materials

Materials used in this study were either waste gelatin [WG — consists of scraps derived from pharmaceutical process of soft capsules which contain pigments and glycerol (*ca.* 8%) as additives from original formulation and was used as received, $M_w$ = 75 000] or parent "virgin" gelatin (VG, $M_w$ = 83 000). Both WG and VG were kindly supplied by Rp Scherer Co., Egypt. The elemental micro-analysis gave: 42.43 wt. % of C, 14.77 wt. % of N, 6.32 wt. % of H and 0.02 wt. % of P for VG and 43.55 wt. % of C, 11.62 wt. % of N, 6.59 wt. % of H and 0.02 wt. % of P, for WG.

Poly(vinyl alcohol) (PVAL, $M_w$ = 67 000) with a degree of hydrolysis of 88% was supplied by Idroplast SpA, Altopascio (Lucca) — Italy and was used without further purification.

Glutaraldehyde was Aldrich product commercialized as 50 wt. % aqueous solution and was used as crosslinking agent in various weight proportions without any further purification treatment.

### Film fabrication

WG was suspended in water at 50°C after stirring for 30 min. For blends preparation a 10 wt. % of PVA water solution was introduced into a 10 wt. % of WG water suspension and the resulting mixture was stirred at 70°C for 20 min. For crosslinked samples the desired amount of glutaraldehyde water solution was introduced into a WG water suspension and the mixture was stirred for 5 min at room temperature. Films were obtained by casting of the solutions in teflonated aluminium trays.

### Methods

Thermogravimetric analyses (TG) were performed by means of a Mettler TA 4000 System equipped with the TG50/M3 thermobalance. Samples of about 20 mg were scanned at 10°C · min$^{-1}$ from 25 to 600°C under nitrogen atmosphere with a flow rate of 200 ml · min$^{-1}$.

The thermodynamic characterisation of the samples was carried out by using the DSC 30 cell of the same equipment. Samples of 10—15 mg were scanned under nitrogen flow of *ca.* 80 ml · min$^{-1}$. Different procedures were carried out and will be described herein in detail. For statistical analysis of the results, some samples were measured at least three times with different sampling.

## RESULTS AND DISCUSSION

### Thermogravimetry

TG experiments were aimed at defining the limits of thermal stability of the starting components and relevant blends and at estimating the amount of volatile compounds eventually present that may act as plasticizers for waste gelatin (WG) and poly(vinyl alcohol) (PVAL).

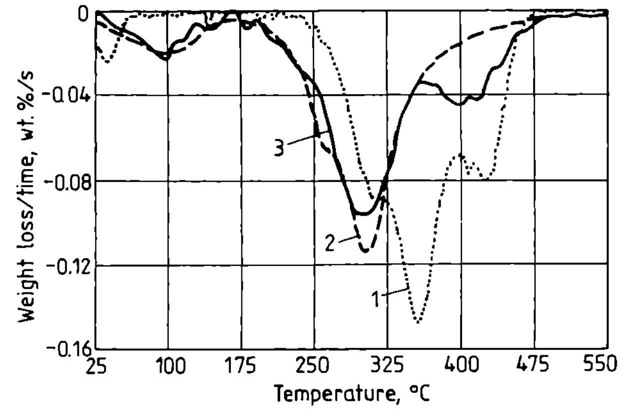

*Fig. 1. Differential thermogravimetric (DTG) traces for PVAL (1), WG (2) and the blend WG/PVAL (3) at 50 wt. %*

Figure 1 shows typical differential thermogravimetric (DTG) traces for WG, PVAL and the 50 wt. % WG/PVAL blend conditioned at ambient conditions. Analogous profiles were found for VG and its corresponding blends with PVAL. Two principal steps of weight loss could be identified for both VG and WG. The first step corresponding to water or water-glycerol overlapped evaporation from VG and WG, respectively. The second and third steps represent thermal decomposition. For the blends the second step is correlated to gelatin and third one is related to PVAL.

Characteristic TG parameters are collected in Table 1. Calculations were made by defining the limits with the aid of differential traces due to the difficulty found on integral traces to attribute the relative contributions of the blend components to the overlapped weight losses. VG showed to be more stable than WG by about 32°C considering both $T_1$ (temperature at which 1% weight loss decomposition is observed, taken as reference temperature at which no weight loss related to any evaporation process is occurring) and $T_d$ (onset decomposition temperature corresponding to temperature taken in correspondence of the crossover of tangents drawn on both side of the decomposition trace). $T_1$ value for WG was 201°C and 232°C for $T_d$.

**Table 1. Thermogravimetric data for virgin gelatin (VG), waste gelatin (WG) and their blends with PVAL**

| Sample | $T_1$[a], °C | $T_d$[a], °C | Volatiles[b] wt. % | Residue[c] wt. % |
|---|---|---|---|---|
| VG | 232.5 | 260.5 | 15.6 | 21.9 |
| VG/PVAL (50/50 wt. %) | 226.0 | 257.3 | 11.5 | 17.3 |
| WG | 201.0 | 232.0 | 10.8 | 20.9 |
| WG/PVAL (50/50 wt. %) | 159.7 | 250.0 | 8.1 | 14.0 |
| PVAL | 254.7 | 279.4 | 0.0 | 1.1 |
| Glycerol | 102.5[d] | 163.2[d] | 100.0 | 0.0 |

[a] $T_1$ — temperature at which 1 wt. % neat weight loss occurs; $T_d$ — onset decomposition temperature at the tangent crossover drawn on both side of the decomposition trace. [b] Water in samples containing VG and water + glycerol in those based on WG. [c] At 580°C. [d] Related to evaporation considering that boiling with decomposition occurs at 290°C [26].

By considering that PVAL is more thermally stable than VG and WG, the decomposition temperatures of the blends would be therefore governed by the gelatin component. On the basis of the recorded $T_1$ values, it can be observed that both VG/PVAL and WG/PVAL blends resulted less stable than VG and WG, respectively. $T_1$ decreasing was about 6°C and 42°C for formulations based on VG and WG, respectively. On the other hand, the behavior of $T_d$ showed to be different. In this case, VG/PVAL blend $T_d$ is not significantly different from that of the parent VG. However, WG/PVAL blend is about 20°C more stable than the parent WG. The method to obtain the onset decomposition temperatures is dependent upon the slope of high side limit temperature and, consequently, of the decomposition rate. Therefore, this decomposition temperature can be often overestimated depending on the position of the TG trace one take the limit of the onset calculation [27]. This observed discrepancy between decomposition temperatures ($T_1$ and $T_d$) of the WG based materials suggests a development of chemical and/or physical changes during blend preparation.

The water content in the blends investigated and residue values reported in Table 1 are related to the total sample weights and are corresponding to those expected on the basis of gelatin content in the blends.

Table 2 shows thermogravimetric data for crosslinked waste gelatin as a function of glutaraldehyde concentration conditioned at ambient conditions. For $T_d$ there are no significant differences in thermal stability of samples with different crosslinking degree. This result further substantiates the working hypothesis on the effect of decomposition rate taking into account that the mechanism for these samples is the same. On the other hand, $T_1$ values indicate that crosslinking slightly lowers decomposition temperature of WG. However, no direct correlation can be drawn between the crosslinking extent and the thermal stability of the analyzed samples. Mean value of 190±9.3°C at a confidence level of 95% can be taken for the crosslinked WGs.

**Table 2. Thermogravimetric data for crosslinked waste gelatin as a function of glutaraldehyde (GA) concentration**

| WG:GA, wt:wt | $T_1$, °C | $T_d$, °C | Volatile[a] wt. % | Residue[b] wt. % |
|---|---|---|---|---|
| 100:0.00 | 201.0 | 232.0 | 10.9 | 20.9 |
| 100:0.25 | 186.0 | 235.8 | 11.0 | 20.0 |
| 100:1.00 | 195.0 | 234.0 | 10.2 | 25.1 |
| 100:2.50 | 194.0 | 231.2 | 11.0 | 19.7 |
| 100:5.00 | 183.2 | 233.2 | 10.3 | 19.8 |

[a] Volatile corresponds to water + glycerol. [b] At 580°C.

## Differential scanning calorimetry

### Thermal characteristics of gelatins

Virgin gelatin (VG) supplied by Rp Scherer Co. that was used as source of WG consists of a mixture of yellow and white granules. After a separate physical collection and lyophilization, only a slight difference was however detected in the thermal properties of the two separated samples (Table 3). In both cases, in fact, the glass transition takes place in a broad temperature range included between 70 to 180°C. The average of inflection point $T_g$ values showed in Table 3 was 124.9±6.3°C for the yellow fraction and 118.9±17.5°C for the white one at a confidence level of 95%. A whole average $T_g$ value for VG could be taken as 121.9±8.1°C. The broadness of the transition can be tentatively attributed to a contribution of a series of relaxation modes very close one to another. The mean change on heat capacity at $T_g$ was 1.42±0.06 $J \cdot g^{-1} \cdot K^{-1}$ (95% of confidence). This is a fairly high value indicating that after lyophilization by 24 h, the amount of water (about 8 wt. %) in VG is sufficient to intensify chain mobility.

**Table 3. Thermodynamic properties of virgin gelatin (VG) lyophilized for 24 h**

| Colour | $T_g$, °C | $\Delta C_p$, $J \cdot g^{-1} \cdot K^{-1}$ | $T_m$, °C | Water, wt. % |
|---|---|---|---|---|
| White | 114.4 | 1.37 | 206.9 | 8.1 |
| White | 123.5 | 1.42 | 208.2 | 7.8 |
| Yellow | 125.4 | 1.46 | 214.2 | 8.0 |
| Yellow | 124.4 | 1.45 | 218.2 | 7.5 |

The melting peak temperature of lyophilised VG resulted in an average value of 211.9±8.4°C (from Table 3) corresponding to the melting of imperfect crystals [24]. Decomposition reaction occurred at the end of melting transition. The heterogeneity of the VG composition can be the factor responsible for the dispersions in the collected data as was observed by Thomas *et al.* [25].

Figure 2 reports on a comparison between TG and DSC traces of both VG and WG. No first order transition for WG was detected and it appears to decompose with mechanism different from that related to VG.

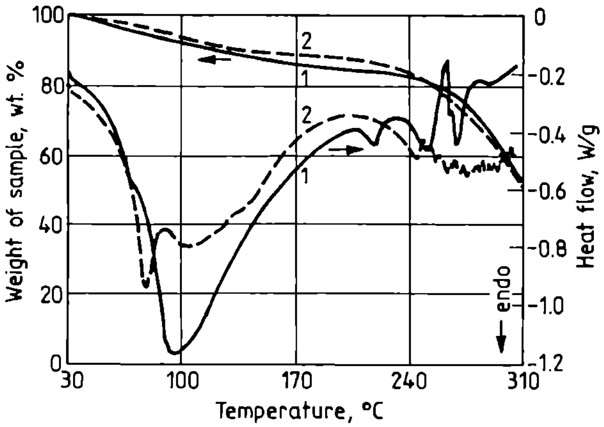

*Fig. 2. DSC and TG traces of VG (1) and WG (2)*

The temperature of 200°C was taken as the end limit for DSC treatment protocol (cyclic heating and cooling — see below) to avoid structural changes due to decomposition (Fig. 2; Table 1). Figure 3 shows DSC traces for VG as conditioned at ambient temperature (first heating) and that of a second heating as recorded by the following treatment protocol (Mode I): 1) first heating at 10°C · min$^{-1}$ from 25 to 200°C; 2) first cooling at 10°C · min$^{-1}$ from 200 to -20°C; and 3) second heating at 10°C · min$^{-1}$ from -20 to 200°C.

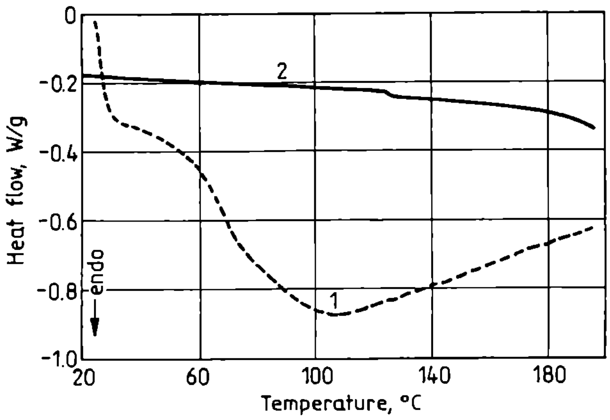

*Fig. 3. Water plasticizing effect on VG glass transition temperature: 1 — first heating, 2 — second heating; water content about 16 wt. % (from TG) (Mode I — see text)*

After water evaporation during first heating and thermal treatment (first heating and cooling), VG presented an increase on its apparent glass transition of about 57°C; this means that the inflection point of baseline shift changed from 67.4°C to 124.6°C. This value for $T_g$ is in accordance with that observed by Fraga *et al.* [22] for fish gelatin as prepared according to the Yannas' procedure [24]. The water evaporation after the first heating was 12.4±0.1 wt. %. So, at the second heating the transitions detected would correspond to a sample with about 4 wt. % of water. Yannas and Tobolsky [28] verified that 1 wt. % of water depresses the $T_g$ of gelatin nearly of 5°C. Taking into account this observation it can be said that the analyzed VG should have a "dry" $T_g$ of *ca.* 145°C which is 30°C lower than that previously obtained by them [28].

The results by Fraga *et al.* [22] showed that no significant difference was observed for the two dehydration processes used in the materials with low level of water without crosslink (exhaustive dehydration of gelatin by any method induces irreversible crosslinks [29]. However, it can be noted that only the first $T_g$ did not changed for both treatments but apparently the second one seems to occur only for one treatment. The first $T_g$ (120°C) was narrow with enthalpy relaxation, on both dehydration methods applied. This $T_g$ was attributed to "soft blocks" constituted by loose α-aminoacid residues. The second $T_g$, broad and less clear, occurred at about 180°C and was attributed to "rigid blocks" composed of imino acids such as proline and hydroxyproline. In both tripeptide sequences of "soft and rigid blocks" glycine appears at every third position.

In general, the difference in heat capacity ($\Delta C_p$) at $T_g$ of gelatin is not commented in thermal analysis studies. However, Tseretely *et al.* [23] studying thermal transitions of gelatin by DSC concluded that $\Delta C_p$ has a value of 0.50±0.05 J · g$^{-1}$ · K$^{-1}$ (estimated on the basis of dry gelatin weight) for samples with 14 wt. % of 'bound water'. Besides, $\Delta C_p$ was practically constant for samples with bound water between 5—30 wt. %. In the present work, it was observed that, contrary to the results attained by Tseretely *et al.* [23], $\Delta C_p$ at $T_g$ is a function of both heat treatment and water content. Results from adopted Mode I, showed a $\Delta C_p$ value for VG of 0.88 J · g$^{-1}$ · K$^{-1}$ (0.77 J · g$^{-1}$ · K$^{-1}$ on dry basis) from first heating run, changing to 0.10 J · g$^{-1}$ · K$^{-1}$ in the second heating run, indicating a significant variation in chain mobility after a water loss of about 12 wt. %.

By considering the previously discussed observations, the effect of annealing at three temperatures was investigated, by taking as reference temperature 110°C (temperature at which a maximum on water evaporation rate was observed — Fig. 3). Table 4 comprises the results obtained for VG after the second heating of the following treatment protocol (Mode II): 1) first heating from 25 to $T_{an}$ at 10°C · min$^{-1}$; 2) isotherm at $T_{an}$ by 10, 20, 30, 40 and 60 min; 3) first cooling from $T_{an}$ to 0°C at 10°C · min$^{-1}$; and 4) second heating from 0 to 200°C at 10°C · min$^{-1}$; $T_{an}$ is the annealing temperature equal to 90, 110, 120°C, respectively.

**Table 4. Effect of annealing on VG conditioned at ambient conditions**

| Temperature[a)], °C | Time min | $T_{g1}$ °C | $\Delta C_{p1}$ $J \cdot g^{-1} \cdot K^{-1}$ | $T_{g2}$ °C | $\Delta C_{p2}$ $J \cdot g^{-1} \cdot K^{-1}$ |
|---|---|---|---|---|---|
| 90 | 10 | 111.2 | 1.79 | nd[b)] | nd |
| 90 | 20 | 117.9 | 1.58 | nd | nd |
| 90 | 30 | 122.2 | 1.40 | nd | nd |
| 90 | 40 | 128.7 | 1.14 | 171.0 | 0.05 |
| 90 | 60 | 128.8 | 0.51 | 146.2 | 0.27 |
| 110 | 10 | nd | nd | 124.6 | 1.39 |
| 110 | 20 | 118.0 | 0.28 | 139.5 | 0.45 |
| 110 | 30 | 120.6 | 0.26 | 138.0 | 0.20 |
| 110 | 40 | 123.9 | 0.22 | 149.6 | 0.32 |
| 110 | 60 | 134.7 | 0.17 | 153.8 | 0.11 |
| 120 | 10 | 118.0 | 0.31 | 137.0 | 0.34 |
| 120 | 20 | 119.0 | 0.29 | 147.2 | 0.34 |
| 120 | 30 | 122.3 | 0.29 | 148.0 | 0.25 |
| 120 | 40 | 128.2 | 0.22 | 163.0 | 0.20 |
| 120 | 60 | 134.8 | 0.31 | 166.4 | 0.18 |

[a)] Different sampling for each annealing treatment. [b)] nd = Not detected.

Figure 4 exemplifies characteristic traces of the two glass transitions temperatures observed as a function of annealing time for 10 and 60 min compared with that obtained on second heating of Mode I.

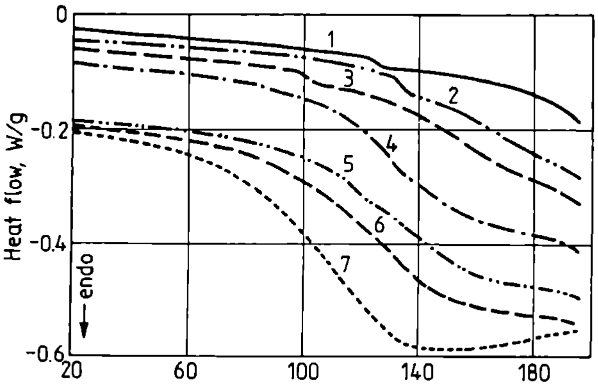

*Fig. 4. DSC traces after annealing at differential temperatures and times (Mode II — see text) of VG: 1 — second heating performed according to Mode I; 2 — after 1 h at 120°C; 3 — after 1 h at 110°C; 4 — after 1 h at 90°C; 5 — after 10 min at 120°C; 6 — after 10 min at 110°C; 7 — after 10 min at 90°C*

Samples treated at 90°C presented only one broad transition up to a 30 min treatment. For longer annealing time, the samples indicated the presence of a second transition at a higher temperature which was clearly detectable in the differential thermal profile. The first glass transition ($T_{g1}$) increased and its $\Delta C_{p1}$ decreased when the time of annealing increased. For the second one ($T_{g2}$) it was not possible to find any correlation. This may be due to its poor definition. The present behavior corresponds to the expected effect of plasticized samples. The $T_{g1}$ was 111°C for a treatment time of 10 min and the higher one was 129°C after 60 min (see Table 4).

Thermal treatments at 110°C and 120°C generally presented two baseline shifts for samples treated at times included between 10 to 60 min, that corresponds to different temporal kinds of structural organizations into samples. The first transition ($T_{g1}$) began to be noted after a treatment of 20 min at 110°C and it was present at any annealing times at 120°C. This transition agree with that observed in VG after the second heating of Mode I, which occurs in a narrow temperature range (Fig. 4). For these two annealing temperatures, their $T_{g1}$ values are analogue to those observed for samples treated at 90°C. For both annealing temperatures, $T_{g1}$ increased from 118°C to 135°C within the time interval comprised between 10 and 60 min. Moreover, the related $\Delta C_{p1}$ values presented a different behavior. For samples treated at 110°C, $\Delta C_{p1}$ decrease from 0.28 $J \cdot g^{-1} \cdot K^{-1}$ to 0.17 $J \cdot g^{-1} \cdot K^{-1}$ with increase of annealing time, while $\Delta C_{p1}$ for samples treated at 120°C seems to be constant with the average value 0.28±0.05 $J \cdot g^{-1} \cdot K^{-1}$ (95% of confidence).

The second glass transition temperature ($T_{g2}$) and corresponding $\Delta C_{p2}$ values for treatments at 110 and 120°C presented the same behavior observed for $T_{g1}$ and $\Delta C_{p1}$. In correspondence of an increase of $T_{g2}$ a decrease was recorded for $\Delta C_{p2}$. However, this second transition occurs in a broad temperature range and $\Delta C_{p2}$ values are of the same magnitude of $\Delta C_{p1}$ values. For samples treated at 110°C, $T_{g2}$ changed from about 125°C after annealing by 10 min to 154°C after 60 min; the $\Delta C_{p2}$ changed from 1.39 to 0.11 $J \cdot g^{-1} \cdot K^{-1}$, respectively. Also, samples after a treatment at 120°C by 10 min presented a $T_{g2}$ of 137°C with a $\Delta C_{p2}$ of 0.34 $J \cdot g^{-1} \cdot K^{-1}$ that changed to 166°C and 0.18 $J \cdot g^{-1} \cdot K^{-1}$ after 60 min of annealing.

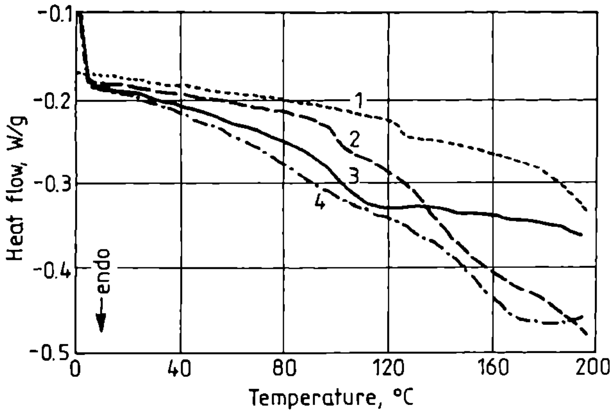

*Fig. 5. DSC traces as a function of thermal treatment: 1 — second heating of VG performed according to Mode I; 2 — VG after 30 min at 110°C; 3 — second heating of WG performed according to Mode I; 4 — WG after 30 min at 110°C*

**Table 5. Effect of annealing on waste gelatin (WG) conditioned at ambient conditions**

| Time at 110°C[a)], min | $T_{g1}$ °C | $\Delta C_{p1}$, J · g$^{-1}$ · K$^{-1}$ | $T_{g2}$ °C | $\Delta C_{p2}$, J · g$^{-1}$ · K$^{-1}$ |
|---|---|---|---|---|
| 0[b)] | nd[c)] | nd | 103.0 | 0.50 |
| 30 | 83.0 | 0.36 | 155.4 | 0.55 |

[a)] Mode II. [b)] Second heating of Mode I. [c)] nd — Not detected.

Figure 5 displays the annealing effect on WG transitions (table 5) compared with that on VG at 110°C by 30 min. The main difference was detected on the first transition temperature ($T_{g1}$) which is lower for WG submitted to treatments carried out in Modes I and II. In addition, both heat capacities differences ($\Delta C_p$) and transition temperature ranges are higher for WG than VG. Probably, these differences are due to the glycerol present in waste gelatin that acts as a plasticizer component in addition to water.

### Thermal characteristics of blends

Gelatins modified by blending with PVA or crosslinking with glutaraldehyde were characterized under controlled conditions. By convenience, a temperature of 30°C, a relative humidity (RH) [30] of 75% and conditioning time of 42 h were selected. The samples were loaded in pre-weighted aluminum pans. After the conditioning time the sample pans were immediately closed, weighed and a hole was made on pan covers only immediately before transferring the samples to the holder. The following treatment protocol (Mode III) was adopted: 1) first heating from -10°C to 200°C at 10°C · min$^{-1}$; 2) natural cooling and re-weighing of sample when returned at 25°C; and 3) second heating from -10°C to 200°C at 10°C · min$^{-1}$.

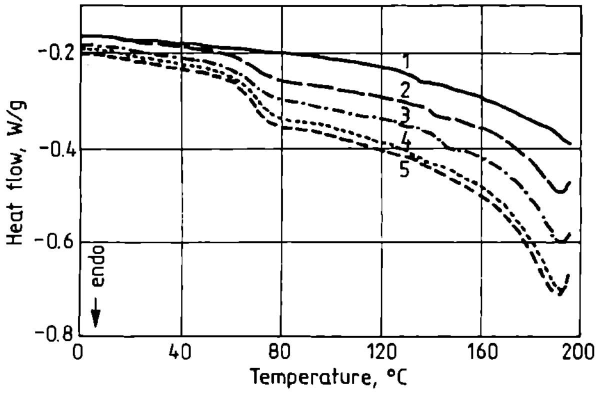

*Fig. 6. DSC traces of VG, PVAL and their blends; samples conditioned at 30°C and 75% RH for 42 h; second heating (Mode III — see text): 1 — 100% VG, 2 — 50% VG + 50% PVAL, 3 — 30% VG + 70% PVAL, 4 — 5% VG + 95% PVAL, 5 — 100% PVAL*

**VG/PVAL blends.** Figure 6 presents the second heating traces of conditioned VG/PVAL blends after Mode III. The first change on heat capacity corresponds to the $T_g$ of PVAL, the second one to the $T_g$ of VG and the incomplete first order transition to the melting of PVAL. Transitions temperatures did not show any appreciable changes in the range of the compositions studied. This corresponds to a typical behavior of incompatible systems [31]. Thermodynamic characteristics for both heating scans and water loss after the first heating are collected in Table 6.

**Table 6. Thermodynamic characteristics of VG, PVAL and VG/PVAL blends[a)]**

| VG/PVAL[b)] wt:wt | $T_{g1}$ °C | $\Delta C_{p1}$ J · g$^{-1}$ · K$^{-1}$ | $T_{mPVAL}$ °C | $T_{g2}$ °C | $\Delta C_{p2}$ J · g$^{-1}$ · K$^{-1}$ | $T_{mPVAL}$ °C | Water loss wt. % |
|---|---|---|---|---|---|---|---|
| 0:100 | 55.8 | 0.52 | 191.7 | 69.7 | 0.60 | 190.9 | 12.1 |
| 50:50 | | | | | | | |
| PVAL | 56.6 | 0.90 | nd[e)] | 68.0 | 0.48 | 191.1 | — |
| VG | 75.4 | 2.20 | — | 142.1 | 0.24 | — | 16.3 |
| 30:70 | | | | | | | |
| PVAL | 56.4 | 0.82 | 191.6 | 68.8 | 0.51 | 192.5 | — |
| VG | 77.7 | 2.57 | — | 144.5 | 0.53 | — | 14.3 |
| 05:95 | | | | | | | |
| PVAL | 53.2 | 0.47 | 193.2 | 71.2 | 0.56 | 191.6 | — |
| VG | 78.8 | 6.44 | — | 133.6 | 0.12 | — | 13.0 |
| 100:0[c)] | 70.5[d)] | 2.75 | — | 132.6 | 0.08 | — | 21.9 |

[a)] $T_{g1}$, $T_{g2}$ — glass transition temperatures on first and second heating, respectively; $\Delta C_{p1}$ and $\Delta C_{p2}$ are the difference on heat capacity calculated on dry weight basis of each component; $T_{mPVAL}$ is a temperature corresponding to the melting peak of PVAL. [b)] Samples conditioned 42 h at 30°C and 75% RH [30]. [c)] At first heating, trace presents a peak at about 150°C overlapped with water evaporation peak. [d)] Glass transition with endothermic relaxation. [e)] nd — Not detected.

Considering that the PVAL $T_g$ values are basically independent on composition, the average value from all compositions at first heating would be 55.5±2.9°C and that for the second heating 69.4±1.5°C. On the other hand, $T_{g1}$ values of VG in the blends are higher than the values recorded for the single material and increase with decrease of VG concentration. At the second heating cycle no systematic trends took place. These results suggest that the $T_g$ values do not change appreciably with blend compositions. The average $T_g$ value for VG would be 142.7±5.6°C for the second heating cycle. The $T_g$ values variation detected for VG and PVAL and water loss value, suggest that water plasticizing effect is more significant on VG than PVAL.

The melting peak temperatures of PVAL in the blend did not showed to be influenced by blend composition. The average value would be 191.7±2.2°C.

**WG/PVAL blends.** The DSC traces for the system WG/PVAL are displayed in Figure 7 whereas in Table 7 there are reported the transition temperatures as a function of the blend compositions including water loss after first heating cycle carried out under Mode III. In the blends of correspondent composition, the $T_{g1}$ values for

**Table 7. Thermodynamic characteristics of WG, PVAL and WG/PVAL blends[a]**

| VG/PVAL[b] wt:wt | $T_{g1}$ °C | $\Delta C_{p1}$ $J \cdot g^{-1} \cdot K^{-1}$ | $T_{mPVAL}$ °C | $T_{g2}$ °C | $\Delta C_{p2}$ $J \cdot g^{-1} \cdot K^{-1}$ | $T_{mPVAL}$ °C | Water loss wt. % |
|---|---|---|---|---|---|---|---|
| 0:100 | 55.8 | 0.52 | 191.7 | 69.7 | 0.60 | 190.9 | 12.1 |
| 5:95 | | | | | | | |
| PVAL | 53.0 | 0.54 | 191.3 | 66.1 | 0.52 | 191.3 | 12.7 |
| WG | nd[d] | nd | — | nd | nd | — | — |
| 30:70 | | | | | | | |
| PVAL | 56.6 | 1.17 | 185.9 | 54.7 | 0.63 | 188.5 | 15.1 |
| WG | 64.8 | 0.55 | — | 148.7 | 0.20 | — | — |
| 50:50 | | | | | | | |
| PVAL | 57.7 | 1.79 | 184.2 | 53.0 | 0.78 | 187.2 | 16.0 |
| WG | 63.8[c] | 1.29 | — | 135.4 | 0.12 | — | — |
| 70:30 | | | | | | | |
| PVAL | 58.0[c] | 1.86 | 178.6 | 46.8 | 1.18 | 181.8 | 17.9 |
| WG | nd | nd | — | 130.5 | 0.33 | — | — |
| 95:5 | | | | | | | |
| PVAL | 56.3[c] | 2.21 | — | 33.5 | 2.59 | 172.9 | 21.0 |
| WG | nd | nd | — | 106.7 | 0.37 | — | — |
| 100:0 | 71.3[c] | 3.85 | — | 129.8 | 0.07 | — | 19.8 |

[a] and [b] as in Table 6. [c] Glass transition with endotherm relaxation. [d] nd — Not detected.

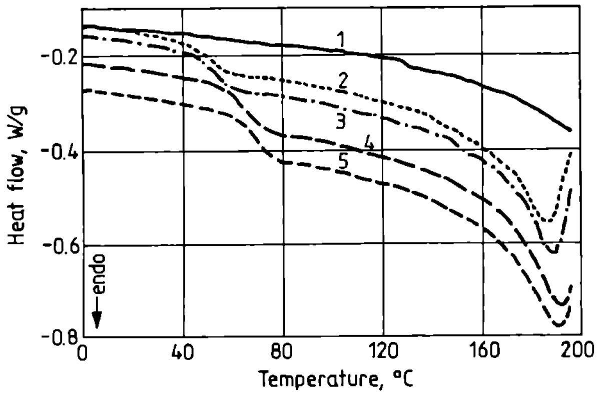

*Fig. 7. DSC traces of WG, PVAL and their blends; samples conditioned at 30°C and 75% RH for 42 h; second heating (Mode III — see text): 1 — 100% WG, 2 — 50% WG + 50% PVAL, 3 — 30% WG + 70% PVAL, 4 — 5% WG + 95% PVAL, 5 — 100% PVAL*

WG were followed by an endothermic relaxation which increased by increasing the WG content. Basically, the $T_{g1}$ values of PVAL are equal to those obtained for VG/PVAL blends. However, for WG the behavior was different where its $T_g$ values were detected only at comparable contents of the two components and with a value lower than WG alone. At second heating, $T_g$ values of both PVAL and WG as well as $T_m$ for PVAL decreased with increasing WG content. Contrary to VG/PVAL system, the results for WG/PVAL blends suggest a compatibility between the two components as most likely mediated by the glycerol originally present in WG. If PVAL-glycerol interactions dominate, this effect will be more significant at lower WG content by increasing the $T_g$ of WG. On the other hand, the decrease of the extent of WG-glycerol interactions facilitates WG-WG contacts that can result in crosslinking formation [24, 29].

**Table 8. Thermodynamic parameters of WG as a function of glutaraldehyde (GA) content[a]**

| WG/GA, wt:wt | $T_{g1}$[b] °C | $\Delta C_{p1}$ $J \cdot g^{-1} \cdot K^{-1}$ | $T_{g2,1}$ °C | $\Delta C_{p2,1}$ $J \cdot g^{-1} \cdot K^{-1}$ | $T_{g2,2}$ °C | $\Delta C_{p2,2}$ $J \cdot g^{-1} \cdot K^{-1}$ | Water loss wt. % |
|---|---|---|---|---|---|---|---|
| 100:0.00 | 71.3 | 3.85 | nd[d] | nd | 129.8 | 0.07 | 19.8 |
| 100:0.25 | 51.1[c] | 1.05 | 98.8 | 0.38 | nd | nd | 20.2 |
| 100:1.00 | 61.3 | 0.96 | 97.9 | 0.44 | 137.0 | 0.08 | 20.6 |
| 100:2.50 | 63.0 | 0.90 | 102.9 | 0.37 | 136.2 | 0.06 | 20.2 |
| 100:5.00 | 57.2 | 0.65 | 95.4 | 0.40 | 137.8 | 0.06 | 21.2 |

[a] Samples conditioned 42 h at 30°C and 75% [30]. [b] $T_{g1}$, $T_{g2}$ — glass transition temperatures recorded on first and second heating respectively; $\Delta C_p$ values are the difference on heat capacity calculated on dry weight basis of each component. [c] Glass transition with endothermic relaxation. [d] nd — Not detected peak.

**Crosslinked WG/PVAL blends.** In Table 8 there are collected the thermodynamic parameters of WG crosslinked with glutaraldehyde (GA). Transitions temperatures on both heating scans do not indicate any specific trend influenced by GA concentration. On the other hand, $\Delta C_{p1}$ from first heating, where samples are more plasticised by water, presented values that decrease with increase of crosslinking agent content, as expected on the basis of chain mobility reduction. However, it was expected also that the $T_g$ increased with concentration of crosslinking agent. This behavior was observed for the glass transition recorded after second heating of the crosslinked samples and of uncrosslinked WG whose values are about 137°C and 130°C, respectively. As $\Delta C_p$ provides indication about chain mobility, it is possible that the observed single transition on first scan may be the result of the overlapping of two kinds of segmental movements. At the same time, one of $T_g$ values can be hidden by the transition connected to water evaporation. As the calculation for a single transition was made on the basis of the total dry weight, the resulted values are overestimated. On the second heating, two glass transitions were observed. A possible explanation for the absence of a systematic change of $T_g$ with GA content in the blends can be associated with the occurrence of competitive phenomena giving rise to a leveled effect for the conditions of sample preparation and analysis.

The values of the mean thermodynamic parameters for some WG/PVAL blends crosslinked with GA are presented in Table 9. These results were analyzed statistically using the hypothesis testing [32] at a 95% of confidence. Data from the second heating were compared by maintaining the crosslinking agent content constant and changing blend compositions or *vice-versa*. At constant crosslinking agent contents (WG/PVAL/GA —

**T a b l e 9. Thermodynamic parameters of WG/PVAL blends crosslinked with glutaraldehyde (GA)[a)]**

| WG/PVAL/GA[b)] wt:wt:wt | $T_{g1}$[b)] °C | $\Delta C_{p1}$ $J \cdot g^{-1} \cdot K^{-1}$ | $T_{g2}$ °C | $\Delta C_{p2}$ $J \cdot g^{-1} \cdot K^{-1}$ | $T_{mPVAL}$ °C | Water loss wt. % |
|---|---|---|---|---|---|---|
| 0:100:0.25 | 56 | 0.5 | 68 | 0.5 | 192 | 12 |
| 100:0:0.25 | 57[c)] | 1.3 | 99 | 0.4 | — | 20 |
| 80:20:0.50 | | | | | | |
| PVAL | 56±1 | 0.7±0.1 | 38±3 | 1.4±0.8 | 178±2 | 19±1 |
| WG | nd[d)] | nd | 134±1 | 0.3±0.0 | — | — |
| 50:50:0.50 | | | | | | |
| PVAL | 59±1 | 0.6±0.0 | 45±1 | 0.7±0.0 | 185±0 | 16±0 |
| WG | nd | nd | 114±3 | 0.1±0.0 | — | — |
| 50:50:1.00 | | | | | | |
| PVAL | 57±1 | 0.7±0.0 | 46±0 | 0.7±0.0 | 186±0 | 17±0 |
| WG | nd | nd | 122±6 | 0.1±0.0 | — | — |
| WG | nd | nd | 144±4 | 0.2±0.0 | — | — |

[a), b), c), d)] as in Table 8. $T_{mPVAL}$ — temperature corresponding to the melting peak of PVAL

80/20/0.5 and 50/50/0.5 systems) the three transitions are substantially different. As a consequence, the blend composition can be considered as an important variable in crosslinked blend formulations. On the other hand, by maintaining constant blend composition and varying the crosslinking agent content (50:50:0.50 and 50:50:1.00) no significant difference of glass transition temperatures of the major components was detected. This is rather surprising and against any perspective founded on the effect of the crosslinking on the segmental motion. However, it could be observed an influence of the crosslinking agent content on the PVAL crystallisation as demonstrated by the null hypothesis.

## CONCLUSIONS

Samples of waste gelatin (WG) and their blends with poly(vinyl alcohol) (PVAL) either in the presence or absence of glutaraldehydedehyde (GA) as crosslinking agent were prepared. Virgin gelatin (VG) was also analyzed as a reference standard valuable for a better understanding of the characteristics of WG and relevant blends with PVAL in the presence or absence of GA.

WG presented a decrease of thermal stability of about 32°C in relation to VG and when blended with PVAL resulted to decompose at a temperature of 232°C that is 20°C higher than WG alone. However, if we consider the temperature at which 1 wt. % on net weight loss occurs ($T_1$) an opposite behavior appears to hold. The temperature of the thermal decomposition of WG alone is 201°C and decreases to about 160°C when WG is blended with PVAL. On the other hand, both temperatures of VG/PVAL blends decreased but in a lesser extent in comparison with the system WG/PVAL.

Thermal treatment and water content are variables that can promote changes of gelatin structure leading to one or two glass transitions detectable by DSC analysis. The presence of glycerol in WG has a small effect in lowering its $T_g$ values in relation to VG. WG and VG conditioned at 30°C, 75% RH for 42 h presented a water content of about 20 wt. %. Under those conditions, the $T_{g1}$ for WG was equivalent to that of VG: $T_g$ values of 71.3°C and 70.5°C were recorded, respectively. Re-heating after a scan until 200°C and cooling, did not lead to a substantial differentiation in $T_{g2}$ behavior (values of 129.8°C and 132.6°C were, respectively, recorded).

Blends of VG with PVAL resulted to be incompatible; $T_g$ values do not indicate any changes with composition, but increase slightly in relation to the gelatin alone. In this case, PVAL acts as a kind of organic filler of VG. On the other hand, the presence of glycerol in WG and presumable destructurization of gelatin during processing generating WG lead to a different behavior of WG/PVAL blends. The $T_g$ values of PVAL and WG and $T_m$ values of PVAL on second heating decreased by increasing WG content. This behavior can be interpreted as due to a different partition coefficient of glycerol in relation to both WG and PVAL in the blend. The content of glycerol in each phase could influence filler characteristics of PVAL and auto-crosslinking of gelatin which can be a concurrent phenomenon.

No systematic effect of GA content (up to 4.8 wt. %) on $T_g$ values of crosslinked WG was observed. As a working hypothesis it was proposed that competitive phenomena related to the sample preparation and thermal analysis methodology play an important role.

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