Thermal and mechanical characterisation of films from Nylon 6/EVOH blends

P. Russo, D. Acierno*, L. Di Maio, G. Demma

Department of Chemical and Food Engineering, University of Salerno, Via Ponte don Melillo, 84084 Fisciano (Salerno), Italy

Abstract

Blown films from blends of dispersed ethylene-co-vinyl alcohol copolymer in a Nylon 6 matrix were characterised thermally and mechanically in humid laboratory conditions. Preliminary evaluations in terms of tensile tests revealed a non-equilibrium state for all the prepared Nylon 6/EVOH ratio based systems. Dynamic mechanical tests on films from blends appeared to indicate the occurrence of a single glass transition temperature (T_g) located between the T_g of the two homopolymers. However the T_g composition trend did not follow a monotonic path showing a maximum for EVOH contents close to 25% by weight. At this composition, the highest environmental ageing and the minimum of static tensile properties of blown films were also evident. Thermogravimetric analysis of all the investigated samples revealed an equilibrium water up-take close to 2% by weight with a maximum of 2.6% by weight for pure polyamide films. © 1999 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Nowadays, plastic films for packaging is showing constant development due to their good quality/service/prices ratio, lightness and flexibility in adapting to a broad range of packaging types. Especially for food applications, severe and precise law requirements considerably restrict materials which can be used for this scope. In fact plastics employed for this purpose have to avoid contact between food and any kind of contaminants through good and specific barrier properties. Packaging must not release harmful substances over the shelf life of foods and have to show fairly good mechanical properties in order to guarantee handy applications.

Usually, employed polymers for film production are polyolefins (PE, PP), polystyrene and technopolymers such as PET, polyamides and PVC. Moreover, huge amounts of scraps generated during the production of films and recently, ever more restrictive environmental

laws, have caused an enormous interest in the recyclability of commercialised films.

Plastic sheets for food packaging are often produced by expensive co-extrusion processes such as blown or cast film having a multi-layer structure in which two or more layers of different polymers are faced together, each of them with specific properties. Usual incompatibility between polymeric materials often makes it necessary to use opportune tie-layers [1] to assure a sufficient interfacial adhesion and good mechanical performance of the final product.

Recently, the difficulties to perform and control co-extrusion processes, on one hand, and the poor recyclability of packaging obtained, on the other, have changed the research interest towards the production of multiphase mono-layer structure films [2–7]. As is well known from the literature [8–10], the morphology of blends is determined by local stress level, interfacial tension, mixing history, composition and material properties like viscosity and melt elasticity of the components. As a consequence, the optimisation of technology could allow the production of films from polymeric blends with lamellar structures in which

---

* Corresponding author. Fax: 089 964 057.

lamellae of an impermeable component are dispersed in a cheap matrix with good mechanical strength.

In this work, blown films from blends of poly (ethylene-co-vinyl) alcohol (EVOH) dispersed in Nylon 6 were accurately characterised in terms of thermal and mechanical properties. Preliminary results confirmed interesting, but not immediate, perspectives in packaging fields, as already stated by some patents [11, 12], especially for films containing an amount of EVOH close to 25% by weight.

2. Experimental

2.1. Materials

Polymeric materials used in this study were a film grade polyamide Nylon 6 supplied from SNIA Tecnopolimeri under the code Ny6F34L (ηrel = 3.4 at 20°C in sulphuric acid) and an excellent barrier polymer ethylene-co-vinyl alcohol (EVOH) produced by Nippon Gohsey and containing about 29% by volume of ethylene. Due to their hygroscopic nature, before use, both polymers were dried overnight in a vacuum oven at 80°C.

2.2. Blend preparation and film blowing

Blends were prepared in a Brabender extruder ($L/D = 400/20$) linked to a head with a rectangular 20 mm-wide flat die operating at a screw speed of 20 R.P.M., a take-up speed of 0.65 m/min and a temperature profile of 230–240–240°C from the hopper to the head. Ny6/EVOH ratios are summarised in Table 1. For comparison, this same procedure was also applied on pure constituents. The extruded strips of material were ground in a laboratory Retsch Mill and vacuum re-dried for successive film-blowing processes.

Films were produced by using the same extruder employed in the mixing step fitted with a 20 mm annular blown film die and a Haake take-up system. The extrusion was carried out at 20 R.P.M. with different thermal profiles for each investigated system as also

Table 1
Composition and thermal profiles in film blowing extrusion for investigated systems

Ny6	EVOH	Thermal profile (°C)
100	0	255–260–250 (head)
90	10	255–255–250 (head)
75	25	250–250–250 (head)
50	50	250–250–250 (head)
0	100	255–240–240 (head)

indicated in Table 1. The blow up ratio and the draw ratio were fixed at values of 3 and 10, respectively.

2.3. Techniques

The presence of amide and -OH groups on the molecular structure of Ny6 and EVOH, respectively, make these polymers and their relative blends very hygroscopic with substantial effects on mechanical properties. In this work, if not otherwise specified, all the films were characterised at room conditions (humid) in order to monitor the real properties of materials during their use.

Apparently, it was soon clear that an initial time-dependence of tensile properties was related to their moisture sensitivity. Thus, data were collected on samples environmentally aged for at least two months after their production and results were compared with data coming from homologous dried samples.

Calorimetric measurements were carried out using a DSC Mettler TC11. Film samples of 10–20 mg were closed in aluminium pans and subjected to the following thermal history with a scanning rate of 20°C/min under nitrogen flux:

- heating from −20 to 260°C and holding at this last temperature for 2 min;
- cooling from 260 to −20°C;
- second heating from −20 to 260°C followed by uncontrolled cooling of sample.

Apparent entalphies of fusion were calculated from the area of the endothermic peak. The weight percent crystallinity of Ny6 was evaluated using the following equation:

$$\% Crystallinity = \frac{\Delta H_f}{\Delta H_f^0} \cdot 100$$

where ΔH_f is the heat of fusion of Ny6 in the blend and ΔH_f^0 is the heat of fusion of 100% crystalline Ny6 taken as 45.6 cal/g from the literature [13].

Mechanical tensile tests were performed by an Instron 4301 equipped with a 100 N cell. Rectangular specimens 10 mm wide and at least 120 mm long were cut from dried and aged films and tested in the film-blowing machine direction.

Drying protocol, applied in this case, was conducted by placing rectangular samples in a vacuum oven at room temperature for about 2 h. Reported results for each system are always averaged on at least ten specimens.

Dynamic mechanical measurements at 1 Hz were made in tensile mode with a zero starting deformation using a Polymer Laboratories dynamic mechanical thermal analyser MKIII apparatus. Tests were carried out at 4°C/min (heating rate) from −100 to 200°C, in

dry nitrogen with a strain amplitude equal to 16 μm. Rectangular specimens 6 mm wide and 8 mm long were used.

Finally, water equilibrium up-takes of humid films were evaluated by a thermogravimetric analysis with a TG209 Netzsch apparatus heating each sample at 5°C/min in air on a thermal range from room temperature to 200°C.

3. Results and discussion

3.1. Calorimetric analysis

Typical DSC thermograms are reported in Figs. 1–3. A rapid glance of the first thermal traces (see Fig. 1) evidently shows the occurrence, in all cases, of an extra endothermic signal preceding melting peaks. This extra peak, totally absent in second heating traces, is surely due to the evaporation of absorbed water in tested samples. In Figs. 2 and 3, comparisons of cooling and second heating traces are reported, respectively.

A close examination of these thermograms clearly indicates that inclusion of EVOH copolymer in the polyamide matrix slightly reduces both heat of fusion (Fig. 4) and melting temperature (Fig. 5) of both components. In other words, taking into account that Ny6 and EVOH form separate crystalline phases and that the intrinsic chemical structure of the two considered polymers is responsible for specific hydrogen interactions at the blend interface, as demonstrated by Venkatesh et al. [14] by FTIR investigations, it is suggested that blending reduces the amount and perfection of crystals formed and alters these latter interactions. The former effect, evaluated quantitatively for Ny6, is quantitatively reported as a function of EVOH
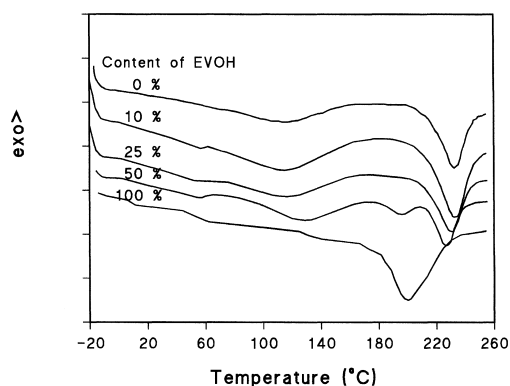

Fig. 2. DSC thermograms of materials investigated from cooling of film samples on the thermal range 260–−20°C and parametrized in function of EVOH content. Heating rate 20°C/min. For the sake of clarity, the thermograms are mutually shifted in the vertical direction.
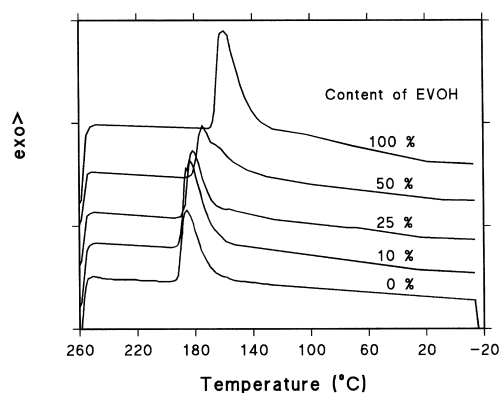
content in Fig. 6 showing a maximum reduction of crystallinity close to 5% corresponding to 50% by weight of dispersed phase.

Furthermore, from the comparison of DSC curves, it is always evident that there is a gap of at least 40–50° between the crystallisation, during cooling, and melting temperature peak, during heating, respectively. This effect, likely due to the complex crystallinity of both phases, is expected to be enhanced for strongly interacting blends.

3.2. Static–mechanical analysis

Tensile test results are summarised in Table 2. This table also collects modulus data of samples vacuum dried at room temperature. Moreover, modulus–com-
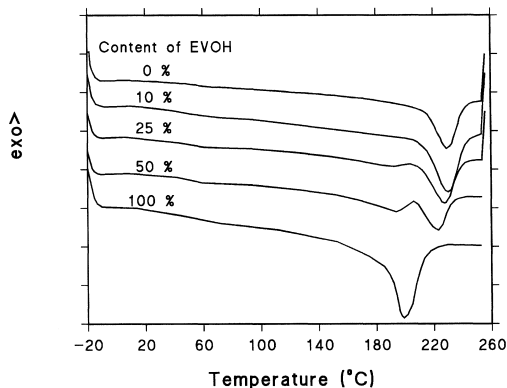

Fig. 1. DSC thermograms of materials investigated from 1st heating of film samples on the thermal range −20–260°C and parametrized in function of EVOH content. Heating rate 20°C/min. For the sake of clarity, the thermograms are mutually shifted in the vertical direction.

Fig. 3. DSC thermograms of materials investigated from 2nd heating of film samples on the thermal range −20–260°C and parametrized in function of EVOH content. Heating rate 20°C/min. For the sake of clarity, the thermograms are mutually shifted the in vertical direction.
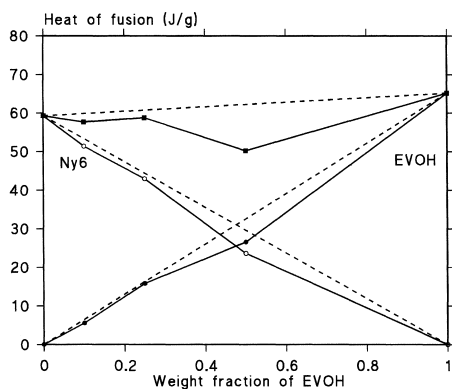
Fig. 4. Total heat of fusion (J/g) of blends investigated (■) and relative contributions from homopolymers Ny6 (○) and EVOH (●) vs weight fraction of EVOH.

Fig. 6. Percent of Ny6 crystallinity in binary blends studied vs weight fraction of EVOH.

position relationships are depicted in Fig. 7 for dried and humid samples.

Dispersions of EVOH in a Nylon 6 matrix always involves a reduction of modulus especially in the presence of 25% of the dispersed phase exhibiting a negative deviation blend behaviour from the simple additive rule (NDB). For dried specimens, instead, the trend is just reversed (PDB behaviour).

This observation could be explained by taking into account that polymers like Ny6 [15, 16] and PET [15, 17] may develop a three phase structure: crystalline, amorphous and para-crystalline or n-phases [18, 19]. These latter, characterised by a not well-defined unit cell, generally come at the expense of oriented amorphous phases and also evolve at room temperature.

Looking at the crystalline phase, it is widely reported that polyamides are characterised by a low degree of crystallisation which, in turn, shows a poor structural order and thus are difficult to investigate [17–21]. Moreover, nylon crystals may be classified in two forms best known as α and γ, the latter being the less
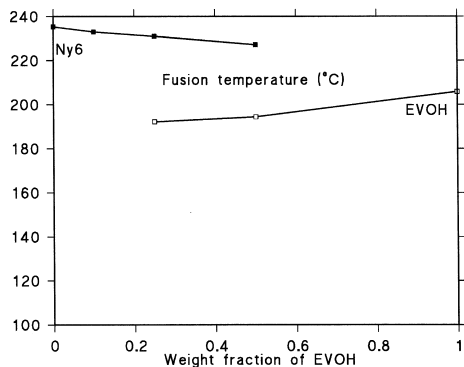

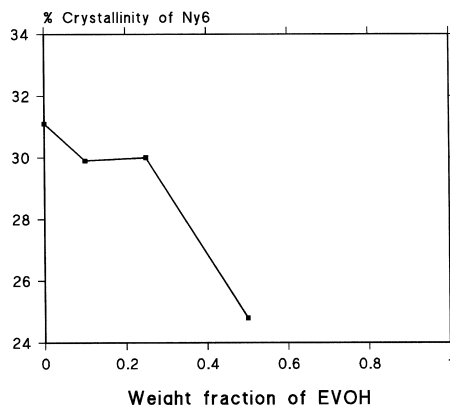Fig. 5. Fusion temperatures (°C) of homopolymers Ny6 and EVOH vs weight fraction of EVOH.

stable and occurring only in particular conditions such as fast cooling of melts.

In this work, thermal and mechanical analysis of nylon 6/EVOH based films allows the distinguishing of:

● two crystalline structures of Ny6 and EVOH, respectively;
● para-crystalline forms from Ny6 (see successive dynamic-mechanical results); and
● two finely dispersed amorphous phases (see dynamic–mechanical data again), with strong interactions between them.

Actually, the ultimate morphology could be complicated by the spontaneous conversion from the γ- to the α-form of the crystal structure of Ny6 [21–24].

In light of these considerations, the above cited time-dependence of film samples as produced could be easily understood and, for practical purposes, work is in progress to attenuate these structural variations by addition of small amounts of a compatibilizer such as functionalised EVOH. In fact, additions of compatibilizers, among other effects, is expected to reduce the interface mobility partially preventing further structural modifications, at least at room temperature. Preliminary results have been already reported in the literature by De Petris et al. [25].

In other words, it is known that modulus as well as yielding properties characterise material behaviour at low levels of strain and depend essentially on their internal structure. Consequently, negative deviations manifested by humid film sample moduli were ascribed partially to the already proved poor crystallisation degree of both polymers and, on the other side, to the expected simultaneous reduction of potential free H-bond sites by saturation with absorbed water molecules. Attempts to confirm these conclusions with

Table 2
Static mechanical properties of investigated systems

| Material | | Ny6/EVOH | Ny6/EVOH | Ny6/EVOH | |
Property	Ny6	90/10	75/25	50/50	EVOH
Modulus dried samples[a] E (Mpa)	1002.0	1266.0	1563.0	1777.0	2430.0
Modulus E (Mpa)	811.0	505.8	460.0	684.9	2398.0
Yield stress σ_y (Mpa)	26.57	15.99	13.16	17.41	37.34
Yield strain ε_y (%)	12.38	10.29	11.05	10.42	2.60
Break stress σ_b (Mpa)	38.25	21.14	19.87	22.40	40.15
Break strain ε_b (%)	240.1	191.20	199.9	209.9	46.16

[a] Dried samples in a vacuum oven at room temperature for about 2 h.

more appropriate techniques, like FTIR spectroscopy and X-ray diffraction, are in course.

Positive deviations of dried specimen moduli, instead, could be attributed to the largely claimed interactions occurring between Nylon 6 and EVOH dispersed domains.

The vacuum drying protocol applied on tensile specimens at room temperature was selected to prevent concurrent structural modifications that are especially activated at higher temperatures, following the above considerations.

Furthermore, analogous considerations have been used to explain that inclusions of EVOH copolymer in the polyamide matrix always appeared to reduce the equilibrium values for stress and strain both at yield and at break conditions.

3.3. Dynamic–mechanical analysis

Dynamic–mechanical tests revealed that, for all the studied formulations, inclusions of EVOH phase in the
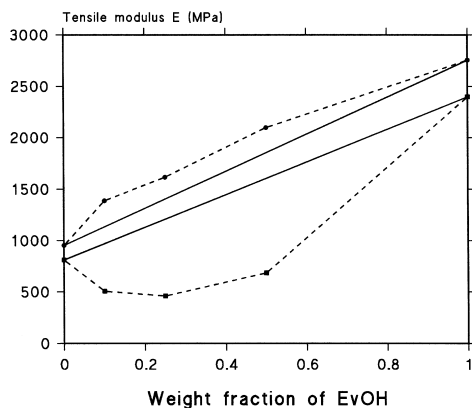
Fig. 7. Tensile modulus of film samples as a function of the weight fraction of EVOH (● specimens vacuum pre-dried at room temperature—upper curve, ■ specimens at laboratory conditions—lower curve).

Nylon 6 matrix increase the polyamide storage modulus, at least in the glassy region.

Loss modulus spectra, instead, showed broad signals emphasising the concomitant occurrence of more relaxation phenomena. For this purpose, from the literature [15–17], with particular interest in relaxations occurring at temperatures higher than 0°C, it is known that the loss signal for polyamides generally involves at least two relaxation events:

- the first relative to the amorphous phase and so representing the classical glass–rubber transition; and
- the second due to the relaxation of the above mentioned *para*-crystalline structures.

Following these observations, each spectrum was deconvolved by a suitable software as reported in Fig. 8(a)–(e). In particular, given the main experimental damping peak, assuming a mixed Gaussian and Lorentz profile of the spectroscopic signals and keeping in mind the presence of only two significant subsignals as above suggested, the deconvolution procedure located the two peaks that best represented the whole primitive signal. Results in terms of temperature peaks and width at medium height (WMH) of the first signal and area of the second one are numerically collected in Table 3 as a function of composition.

Regarding the EVOH copolymer, the considered deconvolution of its loss modulus peak in two sub-signals is not supported by a clear literature interpretation but a hypothesis may also be advanced assuming that the amorphous phase relaxation is likely coincident with the second temperature sub-peak.

According to the latter aspects, we always observed a single relaxation signal situated between the T_g of the two homopolymers over the range of EVOH content investigated. This behaviour, commonly attributed to a fine dispersion in the amorphous state between the two polymers mixed together, is not unambiguous evidence of their mutual miscibility, particularly for polymers having very close T_g. Thus, in this context,
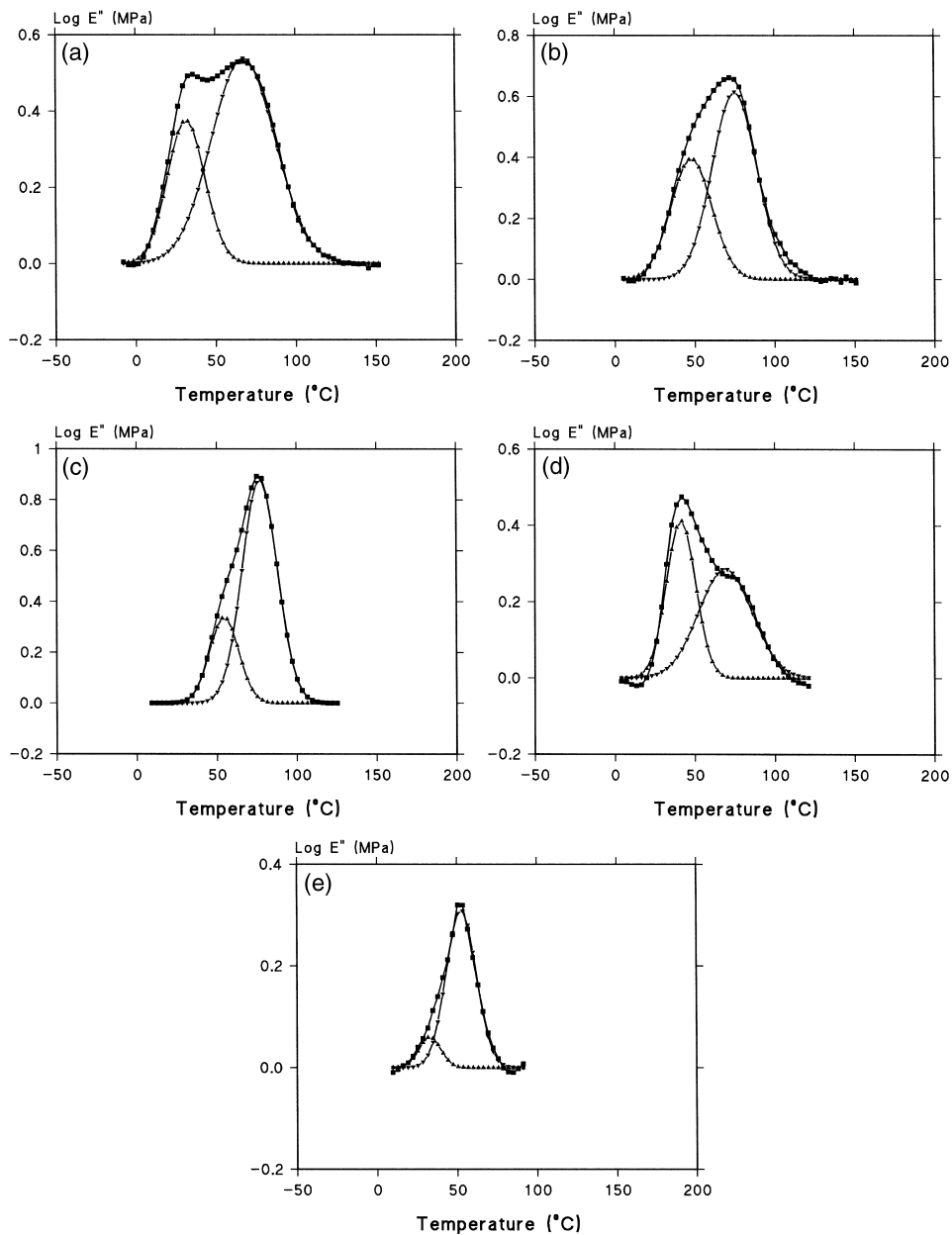
Fig. 8. (a) Deconvolution of loss modulus E'' signal for Nylon 6 film on the thermal range −50–200°C. Tensile mode, frequency 1 Hz, zero initial deformation, strain amplitude 16 μm. (b) Deconvolution of loss modulus E'' signal for Ny6/EVOH 90/10 w/w system on the thermal range −50–200°C. Tensile mode, frequency 1 Hz, zero initial deformation, strain amplitude 16 μm. (c) Deconvolution of loss modulus E'' signal for Ny6/EVOH 75/25 w/w system on the thermal range −50–200°C. Tensile mode, frequency 1 Hz, zero initial deformation, strain amplitude 16 μm. (d) Deconvolution of loss modulus E'' signal for Ny6/EVOH 50/50 w/w system on the thermal range −50–200°C. Tensile mode, frequency 1 Hz, zero initial deformation, strain amplitude 16 μm. (e) Deconvolution of loss modulus E'' signal for EVOH film on the thermal range −50–200°C. Tensile mode, frequency 1 Hz, zero initial deformation, strain amplitude 16 μm.

Table 3
Peak temperature (T_g) and width at medium height (WMH) of first sub-peak and area of second sub-peak from deconvolution of loss modulus signal for investigated systems

Ny6	EVOH	T_{g_1} (°C)	WMH$_1$ (°C)	Area$_2$
100	0	32.8	34.4	26.3
90	10	46.4	34.8	21.0
75	25	53.2	25.1	23.5
50	50	41.8	35.3	11.7
0	100	53.6	25.1	6.96

work is in progress to both minimise the formation of non-crystalline phases and maximise the resolution between the supposed two homo-polymer relaxations, simultaneously.

Moreover, correlating T_g values to the EVOH content, a non-monotonic trend with positive deviations from the mixing rule for Ny6-based systems and negative deviations for systems containing an excess of EVOH copolymer, was obtained (Fig. 9).

Similar behavior, already reported by Kwei [26] for s-PMMA/Novolac blends, could be ascribed to the well established interactions occurring at the interphase of studied formulations. In detail, these interactions seem to be maximized in nylon rich blends where they may also be responsible of the occurrence of physical crosslinks within the amorphous phase. Vice versa, the reverse trend shown by EVOH based blends may simply be attributed to the expected modifications of the matrix morphology occurring when small amounts of a second semicrystalline phase is added. In general, blending is expected to modify the structural organization, e.g. crystallinity, of polymers mixed together and these effects could give rise to a higher flexibility

of the mixed amorphous phase producing new products with lower glass transition temperature.

Kwei [26] demonstrated that this behavior is analytically described by using a modified Gordon–Taylor equation:

$$T_g = \frac{W_1 T_{g_1} + k W_2 T_{g_2}}{W_1 + k W_2} + q W_1 W_2$$

where k is a parameter linked to the entity of mutual phase miscibility while the last quadratic term $q W_1 W_2$ is proportional to the number of specific interactions existing in the mixture and can be interpreted as the contribution of the hydrogen bonding.

The values of the constant parameter k and q in the Kwei equation are normally determined by standard least-square procedures to obtain a best fit with the experimental points. For the present work, the low amount of available data provided only a poor fitting of experimental results with the above equation as clearly seen from the dashed line reported in Fig. 9. From area values of the second peak it is evident that the entity of the third *para*-crystalline phase was magnified in blend systems for a content of EVOH close to 25%.

3.4. Thermogravimetric analysis

Plasticization effects on the glass transition temperature of the investigated system were quantified by the thermogravimetric analysis on film samples. Results showed for all wet films a water equilibrium up-take of about 2% by weight with the exception of Ny6 film, in which the weight gain at room conditions reached 2.6%.
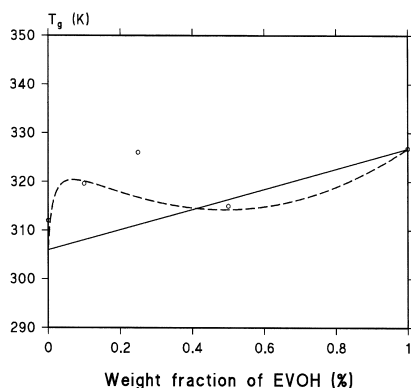

Fig. 9. Correlation between glass transition temperatures evaluated as loss modulus sub-peak temperatures and composition for blends investigated. The dashed line indicates the best-fitting of experimental results according to the Kwei equation. (o—experimental points).

4. Conclusion

Blown films from Ny6-based blends containing a high barrier polymer poly(ethylene-co-vinyl alcohol) as dispersed phase, were investigated in terms of thermal and mechanical properties comparing results from dried and environmentally aged samples.

Moisture sensibility of both polymers soon indicated a non-equilibrium performance of blend films as prepared. As expected, due to the intrinsic chemical structure of base polymers, responsible for specific hydrogen interactions at interface, positive deviations of modulus–composition relationships were emphasised on dried specimens. A reverse trend was, instead, manifested by humid samples maybe as a consequence of the achieved relative poor degree of crystallisation of both polymeric phases mixed together worsened by their relevant sensibility to moisture.

The presence of interactive sites was also considered to explain the particular T_g-composition trend. Work is in progress to detect general effects also in the molten state by rheological analysis of Ny6/EVOH blends.

The presence of a single T_g seemed to be verified. The closeness on neat polymer T_gs has made it difficult to retain, a priori, the occurrence of a single glass–rubber transition and a possible explanation has been found in the achievement of a fine dispersion between the matrix and the dispersed EVOH amorphous phases.

In conclusion, it is clear that a critical system formulation is Ny6/EVOH 75/25 by weight. In fact, at this composition, with respect to other ones, several observations have been made:

1. a better dispersion between amorphous phase (narrow relaxation loss signal);
2. a stronger interaction between phases (maximum positive deviation of tensile modulus for predried samples and minimum T_g of wet samples);
3. wider negative deviations from the mixing rule for humid tensile properties.

References

[1] Alger MM, Stanley TJ, Day J. Barrier polymers and structures. Am Chem Soc Ed, 1990. p. 203.
[2] Subramanian PM. Polym Eng Sci 1985;25:483.
[3] Subramanian PM, Mehra V. Polym Eng Sci 1987;27:663.
[4] Kirckpatrick DE, Ranck D, Finlayson KM, editors. Plastic film technology. Technomic publication, 1989. 1. p. 173.
[5] Lohfink GW, Kamal MR. Polym Engng Sci 1993;33:1404.
[6] Kit KM, Schultz JM, Gohil RM. Polym Engng Sci 1995;35:680.
[7] Lee SY, Kim SC. Polym Engng Sci 1997;37:463.
[8] Plochocki RP. Polym Engng Sci 1986;26:82.
[9] Wu S. Polym Engng Sci 1987;27:335.
[10] Kamal MR, Garmabi H, Hozhabr S, Arghyris L. Polym Engng Sci 1995;35:41.
[11] U.S. patent 4,427,825. 1984.
[12] U.S. patent 4,347,332. 1982.
[13] Ide F, Hasegawa A. J Appl Polym Sci 1974;18:963.
[14] Venkatesh GM, Gilbert YD, Fornes RE. J Mater Sci 1977;12:2310.
[15] Prevorsek DC, Kwon YD, Sharma RK. J Mater Sci 1977;12:2310.
[16] Khanna YP. J Appl Polym Sci 1990;40:569.
[17] Oswald HJ, Turi EA, Harget PJ, Khanna YP. J Macromol Sci 1977;B13:231.
[18] Nishio Y, Suzuki H, Morisaki K. Polym Int 1993;31:15.
[19] Murthy NS. Polym Comm 1991;32:301.
[20] Parker JP, Lindenmeyer PH. J Appl Polym Sci 1977;21:821.
[21] Murthy NS, Aharoni SM, Szollosi AB. J Appl Polym Sci 1985;23:2549.
[22] Holmes DR, Bunn CW, Smith DJ. J Polym Sci 1955;17:159.
[23] Arimoto H. J Polym Sci Part A 1964;2:2283.
[24] Arimoto H, Ishibashi M, Hirai M, Chatani Y. J Polym Sci Part A 1965;3:317.
[25] De Petris S, Laurienzo P, Malinconico M, Pracella M, Zendron M. J Appl Polym Sci 1996;68:637.
[26] Kwei TK. J Polym Sci Polym Lett Edn. 1984;22:307.