Effect of Poly(epichlorohydrin) on the Crystallization and Compatibility Behavior of Poly(ethylene oxide)/Polyphosphazene Blends

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ABSTRACT: In this research a study was conducted with the aim of gaining insight into the effect exerted by poly(epichlorohydrin) (PECH) on the compatibility and microstructure of the blend consisting of poly(ethylene oxide) (PEO) and a polyphosphazene (PPz). For the different PEO/PPz systems and varying amounts of PECH isothermal crystallization was analyzed, as well as non-isothermal crystallization, spherulite growth geometry, and the Flory–Huggins interaction parameter. The results obtained point towards a partially compatibilizing effect of PECH on PEO/PPz.

KEY WORDS Poly(ethylene oxide) / Polyphosphazene / Poly(epichlorohydrin) / Crystallization / Glass Transition Temperature / Spherulite Growth Rate / Compatibility /

According to our findings in previous work,¹ the blend between poly(ethylene oxide) (PEO) and poly(octafluoropentoxytrifluoroethoxy) phosphazene (PPz) proved to be incompatible over the whole range of compositions. In pursuance of our interest in the synthesis of polymeric electrolytes resulting from solvating the polymeric blend with lithium salts, one of the objective set for this research was to attempt a compatibilization of this polymer blend by means of incorporating another polymer which would act as a compatibilizer, with the effect that ion transfer through the resulting blend would no longer be hindered or interfered with by the presence of interphases.

In this sense poly(epichlorohydrin) (PECH) was chosen as a compatibilizing polymer to combine with the different compositions of the binary system PEO/PPz. The main interest of our work focused on gaining insight into the microstructure and compatibility of the system PEO/PPz. In the course of this study the crystallization kinetics was analyzed, glass transition temperature was measured, spherulite

growth kinetics was recorded and the Flory–Huggins interaction parameter was determined *via* PEO melting point depression.

EXPERIMENTAL

The following commercial polymers were used: Poly(ethylene oxide) (PEO) ($M_w = 5.0 \times 10^6$) was supplied by Aldrich; the poly(octafluoropentoxytrifluoroethoxy) phosphazene (PPz) PNF-200 was obtained from Firestone and the poly(epichlorohydrin) (PECH) ($M_w = 7.0 \times 10^5$) from Aldrich.

The blends were obtained by dissolving in acetonitrile and chloroform the already proportioned polymers, subsequently vaporizing the solvent and drying the samples under high vacuum conditions until constant sample weight was achieved.

Isothermal crystallization and melting were measured in a Perkin Elmer differential scanning calorimeter DSC 7. The samples were heated to 100°C, where they were held for five minutes in order to delete their thermal

antecedents and then quenched ($350^{\circ}\text{C min}^{-1}$) down to their crystallization temperature T_c . When they had completely crystallized, the samples were brought to melt at a rate of $10^{\circ}\text{C min}^{-1}$.

Non-isothermal crystallization was studied by recording the respective non-isothermal crystallization thermograms in a Mettler differential scanning calorimeter TA 4000 at rates of 20, 10, 5, 2, and $1^{\circ}\text{C min}^{-1}$.

The glass transition temperature T_g was measured in a Mettler differential scanning calorimeter TA 4000. The samples remained at 100°C for 5 minutes and were then quenched down to -100°C , their thermograms being subsequently recorded at a rate of $10^{\circ}\text{C min}^{-1}$.

Spherulite growth was monitored under a Jenaval microscope coupled to a Hot Stage Mettler FP82. The samples were heated to 100°C for 5 minutes and then quenched to their T_c , where the radii were measured. The tri-dimensional (3D) graphs were obtained with GOLDEN graphics software.

RESULTS AND DISCUSSION

Study of the Microstructure and Morphology of the PEO/PPz, PEO/PECH, and PEO/PPz/PECH Blends

The isothermal crystallization kinetics of all the experimental systems were analyzed applying Avrami's equation²

$$X_t = 1 - \exp(-K_t^n) \quad (1)$$

where X_t is the weight fraction of the crystallizable material at time t , K stands for the rate constant, and n is the Avrami exponent, which depends on the type of nucleation and the growth geometry of the crystals.

The values of K and n are obtained for each crystallization temperature from the Y-intercept and the slope, respectively, of the plot of $\log(-\ln(1 - X_t))$ vs. $\log t$.

In Tables I—III the results are compiled as obtained from the study of the crystallization kinetics of the systems PEO/PPz, PEO/PECH,

Table I. Isothermal crystallization of the PEO/PPz system

Blend composition PEO/PPz	T_c °C	n	$\log K$ min ⁻ⁿ	$t_{1/2}$ min
100/0	44	2.427	-0.433	1.298
	46	2.405	-0.730	1.727
	48	2.543	-2.515	8.439
80/20	44	1.945	-0.013	0.841
	46	1.949	-1.060	2.898
	48	2.110	-2.423	11.820
60/40	44	2.807	-0.103	0.955
	46	2.081	-0.369	1.262
	48	2.178	-1.176	2.967
40/60	44	2.256	-0.413	1.297
	46	2.328	-1.380	3.349
	48	2.259	-2.359	9.435
20/80	44	2.080	-0.560	1.556
	46	2.070	-1.390	3.942
	48	2.696	-3.240	13.940

Table II. Isothermal crystallization of the PEO/PECH system

Blend composition PEO/PECH	T_c °C	n	$\log K$ min ⁻ⁿ	$t_{1/2}$ min
100/0	44	2.427	-0.433	1.298
	46	2.405	-0.730	1.727
	48	2.543	-2.515	8.439
80/20	44	2.222	-1.491	1.659
	46	2.599	-2.969	2.722
	48	2.409	-4.103	4.716
60/40	40	2.359	-1.230	1.442
	46	2.462	-2.010	1.949
	44	2.618	-3.202	2.953
40/60	40	2.546	-4.136	4.393
	42	2.343	-5.246	6.403
	44	2.242	-5.354	9.252

as well as that of the ternary system PEO/PPz/PECH. Figure 1 shows the logarithm of the rate constant ($\log K$) plotted against blend composition at a crystallization temperature of 44°C for the binary systems PEO/PPz and PEO/PECH, whereas Figure 2 represents the response surface of the PEO rate constant at 44°C , when contained in ternary blends with PPz and PECH. As can be observed in Figure

Figure 1. Effect of the PPz or PECH contents on the isothermal overall kinetic rate constant $\log K$ crystallized at 44°C .

Table III. Isothermal crystallization of the PEO/PPz/PECH system

Blend composition PEO/PPz/PECH	T_c °C	n	$\log K$ min ⁻ⁿ	$t_{1/2}$ min
100/0/0	44	2.427	-0.433	1.298
	46	2.405	-0.730	1.727
	48	2.543	-2.515	8.439
60/20/20	44	1.947	-2.330	2.740
	46	1.766	-2.817	4.007
	48	1.817	-3.587	5.883
20/60/20	44	2.108	-1.457	1.689
	46	1.682	-1.612	2.096
	48	1.649	-2.207	3.053
20/20/60	44	2.077	-0.472	1.052
	46	1.801	-1.333	1.711
	48	1.603	-2.080	2.911
33.3/33.3/33.3	44	1.772	-1.626	2.036
	46	1.554	-2.194	3.243
	48	1.841	-3.221	4.715

Figure 2. Effect of the PECH on the isothermal overall kinetic rate constant K of the PEO/PPz blend crystallized at 44°C .

1A, the PEO crystallization rate constant remains practically the same for all PPz concentrations, as is characteristic of an incompatible system. In Figure 1B, however, which corresponds to the binary system PEO/PECH, the rate constant diminishes inversely proportionate to PECH concentration, which is indicative of the compatible nature of the system. In Figure 2 (ternary system), in contrast, two clearly differentiated effects are discernible for each PEO/PPz concentration;

there is an initial section, where with increasing PECH portion in the system the PEO rate constant diminishes. As of *ca.* 20% PECH concentration this behavior is reversed, and the PEO rate constant grows with all subsequent PECH increments in the blend. This behaviour is typical of binary or ternary systems in which one of the polymers, apart from acting as a dilutant vis-à-vis the other (in our case this role is played by PECH), exerts a highly prominent nucleating effect on the

crystallization of the crystalline polymer.

The PEO crystal growth geometry, as inferred from the Avrami exponent (n), is not affected by the presence of neither PPz nor PECH in the case of binary blends, considering that constancy of n suggests a growth geometry intermediate between bi- and tri-dimensional-ity. In the case of ternary composites, there coexist two distinct growth geometries, one monodimensional, and the other bidimensional, as can be inferred from the values of n in Table I—III, in clear contrast to the binary systems.

The PEO *non-isothermal crystallization kinetics* was analyzed applying Avrami's method extended to non-isothermal conditions,² as well as the Ozawa method.³

In the first case, Avrami's equation (eq 1)

was directly applied to the data obtained from the non-isothermal crystallization thermograms. The plot of $\log(-\ln(1-\alpha(t)))$ vs. $\log t$ for each crystallization rate yielded ever so many straight lines, from whose slopes the values of n were determined, whereas the values of K were taken from the respective Y-intercepts. In non-isothermal crystallization the values of n and K do not have the same meaning as in isothermal crystallization, due to the fact that under non-isothermal conditions the temperature changes constantly, and hence spherulite growth rate and nucleation are temperature-dependent.

The Ozawa method takes Avrami's equation as a starting point, yet modifies it conveniently by means of the temperature function,⁴ thus providing an equation capable of describing

Table IV. K and n parameters for non-isothermal crystallization of PEO/PPz

Blend composition PEO/PPz	Ozawa			Avrami		
	T_c	n	K	Rate	n	K
	$^{\circ}\text{C}$					
100/0	36	0.892	1.745	20	1.808	1.416
	38	1.022	1.653	10	1.882	1.399
	40	1.234	1.610	5	2.059	0.239
	42	1.430	1.446	2	2.053	0.052
	44	1.624	1.059	1	2.356	0.011
80/20	40	1.142	2.294	20	1.807	1.706
	42	1.175	1.824	10	1.870	0.778
	44	1.313	1.515	5	1.854	0.406
	46	1.413	0.909	2	2.082	0.086
60/40				1	2.664	0.008
	40	1.209	2.472	20	2.041	1.637
	42	1.037	2.010	10	2.046	0.731
	44	0.924	1.280	5	2.003	0.276
	46	1.400	1.398	2	2.332	0.064
40/60	48	1.813	1.055	1	2.107	0.035
	40	1.483	2.645	20	2.110	1.603
	42	1.734	2.437	10	2.257	0.668
	44	1.691	1.476	5	2.447	0.262
	46	1.542	0.638	2	2.382	0.058
20/80				1	2.546	0.014
	40	2.098	3.369	20	2.078	2.999
	42	2.198	2.893	10	2.100	1.172
	44	2.200	1.706	5	2.693	0.475
	46	3.028	0.789	2	3.486	0.038
				1	2.642	0.047

Table V. K and n parameters for non-isothermal crystallization of PEO/PECH.

Blend composition PEO/PECH	Ozawa			Avrami		
	T_c	n	K	Rate	n	K
	$^{\circ}\text{C}$		min^{-n}	$^{\circ}\text{C min}^{-1}$		min^{-n}
100/0	36	0.892	1.745	20	1.808	1.416
	38	1.022	1.653	10	1.882	1.399
	40	1.234	1.610	5	2.059	0.239
	42	1.430	1.446	2	2.053	0.052
	44	1.624	1.059	1	2.356	0.011
80/20	34	0.768	2.000	20	2.219	1.489
	36	0.913	1.951	10	2.403	0.616
	38	1.022	1.744	5	2.345	0.366
	40	1.263	1.609	2	2.944	0.036
	42	1.797	1.499	1	3.271	0.006
60/40	32	1.509	3.054	20	2.276	1.956
	34	2.937	1.681	10	2.492	0.823
	36	2.419	3.396	5	2.792	0.266
	38	2.690	1.897	2	3.167	0.031
				1	3.696	0.002
40/60	24	2.465	3.997	20	2.780	1.387
	26	2.965	4.137	10	3.423	0.326
	28	2.076	2.082	5	3.725	0.058
	30	2.602	1.819	2	3.734	0.005
	32	3.338	1.404	1	3.125	0.002

non-isothermal crystallization in a semi-crystalline polymer:

$$\ln(-\ln(1-\alpha(t))) = \ln X(T) - n \ln \beta \quad (2)$$

$$X(T) = nA \int_{T_0}^T \exp\left(\frac{E'}{T}\right) (T - T_0)^{n-1} dT \quad (3)$$

where $E' = E/R$ and β is the cooling rate.

Applying eq 2 the Avrami exponent is determined as a function of the cooling rate and the crystallized polymer fraction $\alpha(t)$.

Tables IV–VI compile the values of the Avrami exponent n and those of K , as obtained from applying the Avrami and the Ozawa methods both to binary to ternary systems, Figures 3 and 4 show Avrami rate constant K plotted against amorphous polymer concentration as obtained by applying both the Avrami and the Ozawa method to non-isothermal conditions. In Figure 3A it can be observed that K grows with increasing PECH concentra-

tion, as is typical for compatible systems, whereas in the case of the blend PEO/PPz (Figure 4A) the K value of PEO remains practically invariable when increasing the PPz portion in the blend, this latter effect becoming the more prominent the higher the crystallization rates. This behavior identifies an incompatible system, where the PEO crystals grow in their own melt and remain unaffected by the presence of another polymer. In Figures 3B and 4B the Ozawa K values are plotted against the PECH and PPz concentrations, respectively. K is shown to increase with increasing amorphous polymer portion. This effect, however, is stronger in the case of PECH, this confirming the compatibility existing in the case of PEO/PECH blends and the only partial compatibility in the case of PEO/PPz. Regarding the K of PEO in the ternary blends (Table VI, Figure 6), for each rate and blend composition, K is observed to diminish

Table VI. K and n parameters for non-isothermal crystallization of PEO/PPz/PECH

Blend composition PEO/PPz/PECH	Ozawa			Avrami		
	T_c	n	K	Rate	n	K
	$^{\circ}\text{C}$			$^{\circ}\text{C min}^{-1}$		
100/0/0	36	0.892	1.745	20	1.808	1.416
	38	1.022	1.653	10	1.882	1.399
	40	1.234	1.610	5	2.059	0.239
	42	1.430	1.446	2	2.053	0.052
	44	1.624	1.059	1	2.356	0.011
60/20/20	32	1.227	2.590	20	2.056	1.312
	34	1.347	2.478	10	2.150	0.469
	36	1.562	2.438	5	2.386	0.138
	38	1.686	3.170	2	2.337	0.034
	40	1.365	1.067	1	2.571	0.005
20/60/20	34	1.402	2.774	20	2.871	1.977
	36	1.518	2.341	10	3.305	0.456
	38	1.962	2.277	5	3.307	0.107
	40	2.480	2.050	2	3.863	0.003
				1	3.551	0.001
20/20/60	28	0.464	0.794	20	2.123	1.134
	30	0.573	0.771	10	2.072	0.314
	32	0.709	0.405	5	1.588	0.164
	34	0.911	0.308	2	1.726	0.026
	36	0.603	0.071	1	1.696	0.011
33.3/33.3/33.3	32	1.478	1.912	20	2.444	0.649
	34	1.557	1.419	10	2.633	0.173
	36	1.141	0.673	5	2.856	0.033
	38	1.675	0.827	2	2.429	0.013
				1	2.006	0.013

Figure 3. Effect of the PECH on the non-isothermal rate constant using A) Avrami method and B) Ozawa method.

inversely proportionate to PECH concentration, the decrease becoming the more prominent the greater the PECH portion in the blend, an

identical regularity having been observed for isothermal conditions. The same phenomenon became apparent, when K was analyzed in

Figure 4. Effect of the PPz on the non-isothermal rate constant using A) Avrami method and B) Ozawa method.

Figure 5. Effect of the PECH on the non-isothermal rate constant of the PEO/PPz blend using A) Avrami method and B) Ozawa method.

terms of the Ozawa method (Figure 5B), although the values obtained were, on the whole, slightly higher than those calculated with the Avrami approach. These findings allow for the interference that PECH exerts a diluting effect, both when in the presence of PEO or in combination with PEO/PPz. Yet full PEO/PPz compatibilization is not achieved by the presence of PECH.

Under non-isothermal conditions the values

of the Avrami exponent, as a general rule, are observed to be higher than those computed for isothermal conditions. Yet opposite is observed, when the n values are obtained *via* the Ozawa method; they are always lower than the Avrami values, both for isothermal and non-isothermal conditions (Tables IV—VI).

Spherulite Growth

PEO presents a spherulite structure when

crystallized from a melt.^{5,6} The plot of the spherulite growth rate vs. blend composition is reproduced in Figure 6, which shows that, when the system PEO/PPz crystallizes in the presence of PECH, the spherulite growth rate increases together with PPz increments (basically incompatible systems). In the presence of PECH, however, the growth rate diminishes, which is behavior to be expected of a compatible systems. As these behaviors are directly related to nucleation density and the nucleus formation energy, we determined these latter parameters in terms of general theory, in order to relate them to blend composition and

compatibility.

The nucleus formation energy relates to the nucleation factor K_g , which is obtained from the equation describing spherulite growth rate for crystalline polymers when containing a diluting polymer.⁷⁻⁹

The spherulite growth rate for dilutant polymer blends can be expressed through the following equation:

$$\alpha = \ln G - \ln v_2 + \frac{U^*}{R(T_c - T_g + C)} - \frac{0.2T_m \ln v_2}{\Delta T}$$

$$= \ln G_0 - \frac{K_g}{T_c \Delta T_f} \quad (4)$$

where G_0 is a constant (pre-exponential factor); $U^* = U_1^* + U_2^*$ is the sum of activation

Figure 6. Variation of the spherulite growth rate with the concentration at different PECH composition.

Table VII. K_g and nucleation density values of studied blends at 48°C

Blend composition PEO/PPz/PECH	$N \times 10^3$ nuclei cm ⁻³	$K_g \times 10^{-4}$ (K ²)	$\ln G_0$
100/0/0	0.04	6.928	28.184
80/20/0	0.02	5.123	26.955
60/40/0	3.66	3.196	25.168
40/60/0	—	3.066	27.173
80/0/20	2.33	7.146	29.382
60/20/20	22.90	8.331	32.232
20/60/20	882.70	11.138	38.141

Figure 7. Plots α vs. $1/T_c \Delta T_f$ for A) PEO/PPz blend, B) PEO/PECH blend and C) PEO/PPz/PECH blend.

Table VIII. Glass transition temperature values of studied blends

Blend composition		T_g^{POE}	T_g^{Blend}	T_g^{PECH}	T_g^{PPz}
PEO/PPz	PECH				
wt%	wt%	°C	°C	°C	°C
100/0	0	—	−52.9	—	—
80/0	20	—	−47.2	—	—
60/0	40	—	−30.3	—	—
40/0	60	—	−36.4	—	—
20/0	80	—	−30.8	—	—
100/0	0	−52.9	—	—	—
80/20	0	−54.6	—	—	−64.5
60/40	0	−51.8	—	—	−62.6
40/60	0	−51.6	—	—	−62.2
20/80	0	−50.5	—	—	−60.9
100/0	0	—	—	—	−60.7
0/0	100	—	—	−23.1	—
0/20	80	—	—	−23.8	—
0/40	60	—	—	−23.7	—
0/60	40	—	—	−23.8	−63.1
0/80	20	—	—	−22.6	−62.0
60/20	20	—	−36.03	—	−65.93
20/20	60	—	−32.90	—	−63.63
20/60	20	—	−30.83	—	−62.47
33.3/33.3	33.3	—	−35.53	—	−63.30

energies movement of the crystallizable and non-crystallizable molecules in the melt and has value 4120 for these systems. T_g is the glass transition temperature and T_m the melting temperature. C represents a constant, and f is a factor taking into account the dependence of ΔH_v on the crystallization temperature,¹⁰ equivalent to $f = 2T_c/(T_m^0 + T_c)$, where T_m^0 is the thermodynamic melting temperature, v_2 the volume fraction and K_g the nucleation factor.

Plotting α vs. $1/(T_c \Delta T_f)$ (Figure 7) straight lines are obtained whose slopes determine the values of K_g , and whose Y-intercepts yield the values of the pre-exponential factor G_0 , which in our case is $G_0 = 12 \times 10^{-5} \text{ cm s}^{-1}$, in reasonable agreement with the value described in the literature.¹¹ The values of K_g and N are listed in Table VIII. The nucleation density was determined applying the following expression, which assumes nucleation to be of a heterogeneous and morphology to be spherulitic nature:

$$K_n = \frac{4}{3} \pi N G^3 \frac{\rho_c}{\rho_a} \frac{1}{1 - X_t} \quad (5)$$

where G is the spherulite growth rate, K_n the crystallization growth rate constant (as obtained from the expression $K_n = \ln 2/(t_{1/2})^n$ (13) where n is the Avrami exponent and $t_{1/2}$ the crystallization half time, ρ_c and ρ_a are the densities of the crystalline and amorphous phases, respectively, and X_t stand for the maximum conversion. The results obtained suggest that the number of nuclei (N) grows with increasing PPz content in the blend, as a consequence of a greater presence of PPz content in the PEO phase. When crystallization takes place in the presence of PECH, N increases considerably, due to the nucleating influence of PECH. In the case of ternary blends, an enormous increase of N is noted for the blend PEO/PPz/PECH (20/60/20), owing to the fact that there coexist two nucleating actions, that of PECH and that of PPz.

Parallely a decrease in nucleating energy (K_g) is produced, as a function of PPz increase in the blend, *i.e.*, the opposite effect of the one observed in the PECH systems, where K_g increases.

COMPATIBILITY STUDY

With the aim of studying the compatibility of the binary systems PEO/PPz and PEO/PECH, as well as the compatibilizing effect of PECH when incorporated into the incompatible binary system PEO/PPz, both the glass transition temperature and the Flory–Huggins interaction parameters were determined following the crystalline polymer melting point depression method, when in the presence of a diluting polymer.

The results of T_g analysis, as obtained from the DSC thermograms of the systems under study are compiled in Table VIII. For the system PEO/PECH a single T_g is found, intermediate between those of the two polymers in isolation, which is indicative of total miscibility over the whole compositional range. The systems PEO/PPz and PPz/PECH each present two T_g values which remain practically constant independent of blend composition, as is characteristic of immiscible systems. Nevertheless, in the ternary system there appear two

transitions, the first of which can be attributed to the result of PEO/PECH compatibilization, and the second is the T_g of PPz, which suggest the idea of partial compatibilization.

The interaction parameter was determined via the depression undergone by the melting point of crystalline polymers, when in the presence of a polymeric dilutant, according to the Nishi–Wang equation^{18–20}:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_{2u}}{\Delta H_{2u}V_{1u}} X_{23}v_1^2 \quad (6)$$

where T_m is the melting temperature, X_{23} the Flory–Huggins interaction parameter, V_u represents the molar values and the subscripts 1 and 2 identify the amorphous and the crystalline polymers, respectively; v_1 is the volume fraction of the non-crystallizable component in the blend, and T_m^0 is the thermodynamic melting temperature obtained by applying the Hoffman–Weeks method¹⁷ (Figures 8 and 9). The values taken from the literature²⁰ were as follows: $V_{2u} = 39.2 \text{ cm}^3 \text{ mol}^{-1}$, $\Delta H_{2u} = 2100 \text{ cal mol}^{-1}$, $V_{\text{PECH}} = 47.43 \text{ cm}^3 \text{ mol}^{-1}$, $V_{\text{PPz}} = 220.59 \text{ cm}^3 \text{ mol}^{-1}$. From eq 6 the interaction parameters of the binary and ternary systems were computed as follows: $X_{23} = -0.172$ for the PEO/PECH blend, a typically negative value of a compatible system; $X_{23} = 0.032$ for PEO/PPz, positive and ap-

Figure 8. Hoffman–Weeks plots for A) PEO/PPz blend and B) PEO/PECH blend.

Figure 9. Hoffman-Weeks plots for PEO/PPz/PECH blend.

proaching zero, thus pointing toward the existence of incompatibility. Finally for the ternary blend PEO/PPz/PECH the value $X_{23} = -0.183$ was negative, identifying a compatible system.

By way conclusion and in the light of our data it is not unreasonable to consider that there exists sufficient evidence to confirm the remarkably (although not totally) compatibilizing effect exerted by PECH on the blend PEO/PPz, an effect which is enhanced by increasing the PECH portion in the blend.

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