Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 6010–6017
polymer
www.elsevier.com/locate/polymer

Miscibility of binary blends of ethylene/norbornene copolymers: Comparison to a lattice cluster theory

M. Blochowiak [a], T. Pakula [a,✠], H.-J. Butt [a], G. Floudas [b,*]

[a] *Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*
[b] *University of Ioannina, Department of Physics, 45110 Ioannina, Greece and Foundation for Research and Technology-Hellas (FORTH), Biomedical Research Institute (BRI), P.O. Box 1186, Greece*

Received 15 April 2007; received in revised form 1 August 2007; accepted 4 August 2007
Available online 9 August 2007

Abstract

The mutual miscibility of five binary ethylene/norbornene copolymers of the N_xE_{1-x}/N_yE_{1-y} type where x and y represent the norbornene content in the first and second copolymers, respectively (with x/y of 0.36/0.52, 0.36/0.56, 0.36/0.62, 0.46/0.60 and 0.46/0.66), in five different compositions was studied by rheology and differential scanning calorimetry. Most of the blends do not obey the principle of time–temperature superposition, i.e., they can be considered as thermorheologically complex, and hence immiscible. The experimental data from rheology were compared to a recent lattice cluster theory. The theoretical miscibility diagram correctly predicts the experimental cases for most blend compositions except for the very asymmetric compositions.

Keywords: Ethylene/norbornene copolymers; Miscibility; Blends

---

1. Introduction

In a recent study [1] we reported on the structural, thermal, thermodynamic, and rheological properties of a series of *pure* amorphous cycloolefin copolymers (COCs) of ethylene (E) and norbornene (NB) of the N_xE_{1-x} type. The NMR results revealed substantial structural heterogeneity along the backbone; in the copolymers with NB content $x > 0.50$ the structure consists of blocks of norbornene of varying lengths, together with some alternating norbornene/ethylene units. In contrast, in the copolymers with lower norbornene content ($x < 0.50$) the structure consists mainly of alternating norbornene/ethylene sequences and of some ethylene sequences comprising two or more units. This microstructural heterogeneity was found to have direct consequences on several dynamic properties. For example, results on the ratio of the activation energies at constant volume E_V^* and constant pressure H^* (enthalpy of activation), the pressure dependence of the glass temperature T_g, and the dynamic "fragility" m, all suggested increasing dynamic heterogeneity with increasing NB content. In addition, all copolymers with compositions in the range $0.36 \leq x \leq 0.62$ obeyed the principle of time–temperature superposition, i.e., they could be considered as thermorheologically simple.

Mixing cycloolefin copolymers is an easy way of producing new materials with desired properties, provided that the blends are miscible. An earlier theoretical study [2] on the mutual miscibility of COC blends of the N_xE_{1-x}/N_yE_{1-y} type, where x and y represent the norbornene content in the first and second copolymer, respectively, revealed large deviations from the extension of Flory–Huggins theory to random copolymers [3,4]. In particular, a lattice cluster theory (LCT) [2,5] applied to symmetric blend compositions demonstrated a dependence of miscibility on the actual copolymer chemical compositions x and y on top of the $|x-y|$ dependence. Within the LCT, three different theoretical models were considered in order to assess the relevance of chain stiffness of norbornene monomers as

---

[*] Corresponding author. Tel.: +30 2651098564; fax: +30 2651098693.
E-mail address: gfloudas@cc.uoi.gr (G. Floudas).
[✠] Deceased on June 7, 2005.

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.08.015

well as of the steric interactions between successive NB monomers on the mutual miscibility. It was found [2,5] that the miscibility of COC blends is mostly determined by the entropic portion of the interaction parameter χ_S, and that the presence of stiffness either in the NB side group or in the chain backbone enhances the miscibility.

In our previous study [1] we examined the viscoelastic properties of a series of pure cycloolefin copolymers. The norbornene content ranged from $0.36 \le x \le 0.62$ including all the commercially available copolymers (with codes 8007, 5013, 6013, 6015 and 6017) is listed in Table 1. In this work, we are extending the pure copolymer study to mixtures of $x = 0.66$ and report on the shear rheology of symmetric and asymmetric ethylene/norbornene copolymer blends. The aim is to (i) analyze the composition ranges that the different copolymers behave as thermorheologically simple and (ii) to examine the influence of increasing NB content on the mutual miscibility of the copolymer blends. For the latter purpose, five different N_xE_{1-x}/N_yE_{1-y} blends of different compositions and of various $|x-y|$ differences are studied by rheology and differential scanning calorimetry aiming at providing recipes in designing new COC copolymers with desired compositions and hence controlled material properties. Thermal analysis was employed to detect the miscibility/immiscibility, using as a criterion the presence of single/dual glass temperatures. We found that this is an inadequate criterion of miscibility. Rheology, on the other hand, provides a more stringent test of miscibility and was employed to test the range of validity of the time–temperature superposition principle, i.e., the thermorheological simplicity. The present investigation delineates the composition range of the COC blends that are thermorheologically simple/complex. We found that the vast majority of blends is thermorheologically complex and hence immiscible. The experimental results were compared to the LCT [2,5] and the reason for the miscibility/immiscibility is discussed. Furthermore, we provide experimental miscibility diagrams for asymmetric blend compositions that have not been investigated either theoretically or experimentally so far.

Table 1
Sample characteristics and thermal properties obtained from DSC (rate 10 K/min)

Sample	$M_w \times 10^3$ [g/mol]	$M_n \times 10^3$ [g/mol]	NB content x	T_g [K]	Δc_P [J/g/K]
8007[a]	104	59	0.36	352	0.39
1905[b]	89	50	0.46	392	0.28
5013[a]	92	45	0.50	408	0.37
6013[a]	101	56	0.52	415	0.31
6015[a]	109	53	0.56	434	0.35
1827[b]	177	61	0.60	448	0.33
6017[a]	106	51	0.62	454	0.30
1826[b]	149	60.5	0.66	473	0.22
PNB	–[c]	–[c]	1.0	647	0.30

[a] Commercially available copolymers.

[b] Copolymers specifically prepared for this study.

[c] The PNB molecular weights could not be determined because of solubility reasons.

2. Experiment

2.1. Samples

The blends studied were prepared from a series of statistical amorphous cycloolefin copolymers consisting of ethylene and norbornene comonomers. These copolymers were prepared according to the methods described elsewhere [6,7]. Briefly, the monomers were copolymerized using metallocene catalysts in a solution process. The amount of ethylene was varied by changing the ethylene pressure applied during the polymerization. The glass temperature T_g of the copolymers was adjusted within a broad range by varying the concentration of norbornene and pressure of ethylene. The molecular weight was adjusted by addition of hydrogen to the reactor vessel. The initial copolymers, from which the blends were prepared, had compositions ranging from $0.36 \le x \le 0.62$, molecular weights of about 0.9–1.8×10^5 g/mol and polydispersities of 1.8–2.0. The sample characteristics (molecular weights, compositions) and thermal properties (glass temperatures and associated step in specific heat, Δc_P) are given in Table 1. In this study five N_xE_{1-x}/N_yE_{1-y} ethylene/norbornene copolymer blends were investigated: 8007/6013 (with $x/y = 0.36/0.52$), 8007/6015 (0.36/0.56), 8007/6017 (0.36/0.62), 1905/1827 (0.46/0.60) and 1905/1826 (0.46/0.66). Here “0.36/0.52” denotes a blend of a copolymer with 0.36 norbornene and 0.64 ethylene subunits mixed with a copolymer made of 0.52 norbornene and 0.48 ethylene. Each blend was prepared by a solution process in five different compositions with weight fractions: 0.1, 0.3, 0.5, 0.7 and 0.9. The pure copolymers were dissolved in toluene, blended and precipitated in acetone. The thus obtained blends were dried in vacuum for several days.

2.2. Differential scanning calorimetry (DSC)

A Mettler 30 DSC was used to determine the glass temperatures and the associated step in specific heat. Experiments were conducted with cooling and heating rates of 10 K/min. The T_gs were determined from the second heating run at the inflection point. As an example the DSC traces and the derivatives of the heat flow curves for the 8007/6017 (0.36/0.62) blend are shown in Fig. 3.

2.3. Dynamic mechanical spectroscopy

Measurements were made by means of a Rheometrics Mechanical Spectrometer RMS 800 on samples (pellets of 6 mm diameter and around 1 mm thickness) placed between two parallel plates. Different experiments were made: (i) isothermal strain sweeps at different temperatures aiming at separating the linear from the non-linear viscoelastic regimes, and (ii) isothermal frequency sweeps at selected temperatures aiming at obtaining the complete viscoelastic response.

3. Results and discussion

Five blends (0.36/0.52, 0.36/0.56, 0.36/0.62, 0.46/0.60 and 0.46/0.66 NB content) in five compositions (10/90, 30/70, 50/

50, 70/30 and 90/10), as well as the pure copolymers were studied first by rheology and subsequently by differential scanning calorimetry. Notice that both the 0.36/0.56 and the 0.46/0.66 blends exhibit the same difference in NB content (0.20) between the blend components, whereas this difference in the blends 0.36/0.52 and 0.46/0.60 is 0.16 and 0.14, respectively. According to the principle of time–temperature superposition (tTs), the frequency (ω) dependence of the complex shear modulus G^* at any temperature can be obtained from a master curve at a reference temperature (T_r) according to the equation:

$$G^*(\omega;T) = b_T G^*(a_T\omega;T_\mathrm{r}) \tag{1}$$

when the tTs is valid, then at each temperature, a single frequency-scale shift factor a_T and a single modulus-scale shift factor b_T allow superposition of all viscoelastic data at temperature T. Our attempted superpositions involved independent estimation of the two shift factors by first shifting the loss tangent ($\tan\delta = G''/G'$) data on the frequency scale, thus obtaining a_T, and subsequently determining b_T by an independent modulus-scale shift of G^*. The G^* and $\tan\delta$ superpositions for the copolymer 1826 (i.e., the copolymer with the highest NB content, $x = 0.66$) are shown in Fig. 1. The high- and low-frequency dispersions in the G^* master curve correspond to the segmental and terminal relaxations, respectively. In the $\tan\delta$ superpositions there exist some distinct features that include the minimum in a region between the segmental and chain relaxations and the deviations from a perfect superposition in the frequency range from the $\tan\delta$ minimum to the segmental relaxation maximum. The latter has been discussed in a variety of homopolymers as reflecting the different shift factors for the segmental and chain relaxations on approaching T_g [8–10]. To quantify the efficacy of tTs in the copolymer we employ the temperature dependence of the local minimum in the loss tangent, $(\mathrm{d}\tan\delta_\mathrm{min})/\mathrm{d}T$ [11]. The values of the $(\mathrm{d}\tan\delta_\mathrm{min})/\mathrm{d}T$ for all pure copolymers are given in Table 2. Notice that, in comparison to all pure copolymers herein and previously examined [1], the 1826 copolymer violates the time–temperature superposition, and hence is considered as thermorheologically complex. This shows that in the copolymers with higher than $x = 0.66$ NB content the intrinsic mobility differences between the NB and the E sequences become strong and result in the breakdown of tTs.

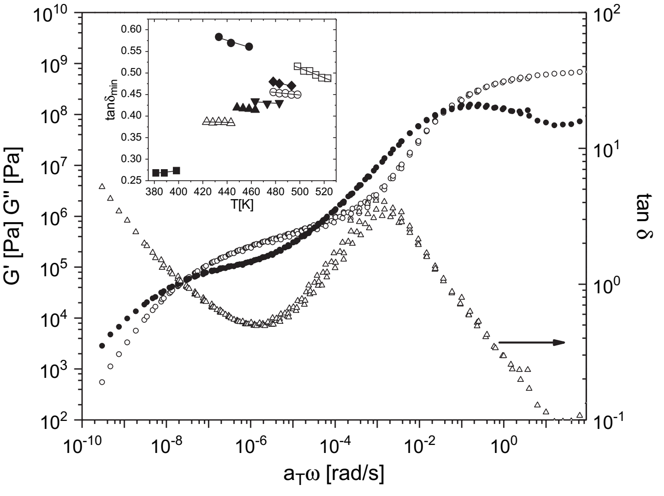

Fig. 1. Master curve for the storage modulus (G', open circles), the loss modulus (G'', filled circles) and the loss tangent ($\tan\delta$, triangles) for 1826 blend (0.66 NB content) using data in the T-range $473 < T < 543$ K. The reference temperature was at 473 K. The pure copolymer violates the tTs (see Table 2). Inset: temperature dependence of the loss tangent minimum for the different pure copolymers; filled symbols – (squares): 8007 with 0.36 NB content, (circles): 5013 with 0.50 NB, (up triangles): 6013 with 0.52 NB, (down triangles): 6015 with 0.56 NB and (rhombus): 6017 with 0.62 NB; open symbols – (triangles): 1905 with 0.46 NB, (circles): 1827 with 0.60 NB, (squares): 1826 with 0.66 NB content. The $(\mathrm{d}\tan\delta_\mathrm{min})/\mathrm{d}T$ values are summarized in Table 2.

An attempt to superimpose the moduli and the loss tangent for four of the symmetric blends (0.36/0.52, 0.36/0.56, 0.36/0.62 and 0.46/0.66 NB content) is shown in Fig. 2. To quantify the efficacy of tTs in the copolymer blends the same criterion as for the pure COCs is employed, namely, the $(\mathrm{d}\tan\delta_\mathrm{min})/\mathrm{d}T$ [11]. The values of the $(\mathrm{d}\tan\delta_\mathrm{min})/\mathrm{d}T$ for the different blends and compositions are given in Table 2. Notice that the magnitude for the majority of compositions is characteristic of blends that are acknowledged to violate tTs [11], i.e.,

$$\left|\frac{\mathrm{d}\tan\delta_\mathrm{min}}{\mathrm{d}T}\right| \geq 5\times10^{-4}\ \mathrm{K}^{-1} \tag{2}$$

The temperature dependence of $\tan\delta_\mathrm{min}$ is controlled by the difference in the temperature dependences of the terminal relaxations of the blend components. In the blends, the higher T_g component chains have a stronger T-dependence of terminal relaxation times than the lower T_g component chains, yielding $[(\mathrm{d}\tan\delta_\mathrm{min})/\mathrm{d}T] < 0$ [12]. It can be observed that while $\tan\delta_\mathrm{min}$ shows a weak T-dependence in the pure components, it is strongly T-dependent for the majority of blends. This dependence is the strongest for the symmetric blends and increases with the NB content of the blend components. Therefore, rheology predicts that the vast majority of blends are thermorheologically complex and thus immiscible.

The DSC traces and their derivatives for various compositions of the 0.36/0.62 blend and the pure components are shown in Fig. 3. Notice the dual glass temperatures and the broadening of the transitions at some intermediate compositions. The glass temperatures, and the corresponding widths of the transitions, ΔT_g, for all the blends and compositions are included in Table 3. It can be seen (Table 3) that the number and the width of glass temperatures increase with increasing NB content. For example, two T_gs are obtained in all symmetric blends except in the 0.36/0.52 where only a single, albeit broad transition is evident. In the blends with the higher NB content two glass temperatures are evident (also for some asymmetric compositions) despite the smaller $|x-y|$. In addition, ΔT_g increases and attains maximum values for the symmetric compositions. The broadening occurs for most blend compositions, and is associated with the different molecular mobilities of the blend components resulting from the structural heterogeneity along the backbone [1,13]. Nevertheless, based on the single/dual calorimetric T_g, for a large number

Table 2
Values of the local minimum in the loss tangent for the 0.36/0.52, 0.36/0.56, 0.36/0.62, 0.46/0.60 and 0.46/0.66 blends and the pure components used to quantify the efficacy of the tTs. With an asterisk (*) are indicated blend compositions that do not pass the stringent test of miscibility

N_xE_{1-x}/N_yE_{1-y} blend composition	$(d\tan\delta_{min})/dT$ [K^{-1}]				
	0.36/0.52	0.36/0.56	0.36/0.62	0.46/0.60	0.46/0.66
0/100	-3×10^{-4}	-2×10^{-4}	-6×10^{-4}	-3×10^{-4}	$-11 \times 10^{-4*}$
10/90	-2×10^{-4}	$-11 \times 10^{-4*}$	$-26 \times 10^{-4*}$	$-7 \times 10^{-4*}$	$-18 \times 10^{-4*}$
30/70	$-14 \times 10^{-4*}$	$-24 \times 10^{-4*}$	$-19 \times 10^{-4*}$	$-12 \times 10^{-4*}$	$-45 \times 10^{-4*}$
50/50	$-14 \times 10^{-4*}$	$-81 \times 10^{-4*}$	$-30 \times 10^{-3*}$	$-19 \times 10^{-4*}$	$-12 \times 10^{-3*}$
70/30	$-17 \times 10^{-4*}$	$-7 \times 10^{-4*}$	$-7 \times 10^{-4*}$	$-17 \times 10^{-4*}$	$74 \times 10^{-4*}$
90/10	$-14 \times 10^{-4*}$	$-9 \times 10^{-4*}$	-2×10^{-4}	$-8 \times 10^{-4*}$	$-10 \times 10^{-4*}$
100/0	3×10^{-4}	3×10^{-4}	3×10^{-4}	-7×10^{-5}	-7×10^{-5}

of blends, one might draw the erroneous conclusion that the blends are thermorheologically simple/complex and thus miscible/immiscible. This deficiency of normal DSC (i.e., at a scan rate of 10 K/min) can be resolved using modulated DSC with a low scanning rate (1 K/min). It is known that given enough time for phase separation to proceed (i.e., during physical aging) results in large domains of different compositions. Such domains manifest in clearly separated enthalpy recovery peaks even in cases of materials with closely matched T_gs [14,15]. Nevertheless, the presence of a single/dual T_g does not necessarily warranty miscibility/immiscibility [16,17].

Rheology is very sensitive to thermorheological complexity and thus to immiscibility in the COC blends. For example, the single calorimetric T_g criterion (under the DSC conditions of 10 K/min) would suggest that 16 out of the 25 blends are miscible whereas the stringent test of Eq. (2) applied to the same blends reveals that only two blends are actually miscible.

A theoretical model for the analysis of the mutual miscibility of the cycloolefin copolymers was recently proposed [2,5]. It was designed to determine how the size and stiffness disparity the ethylene and norbornene comonomers, and the microstructure (monomer sequence distribution) affects the miscibility patterns. The simplest model for describing binary random

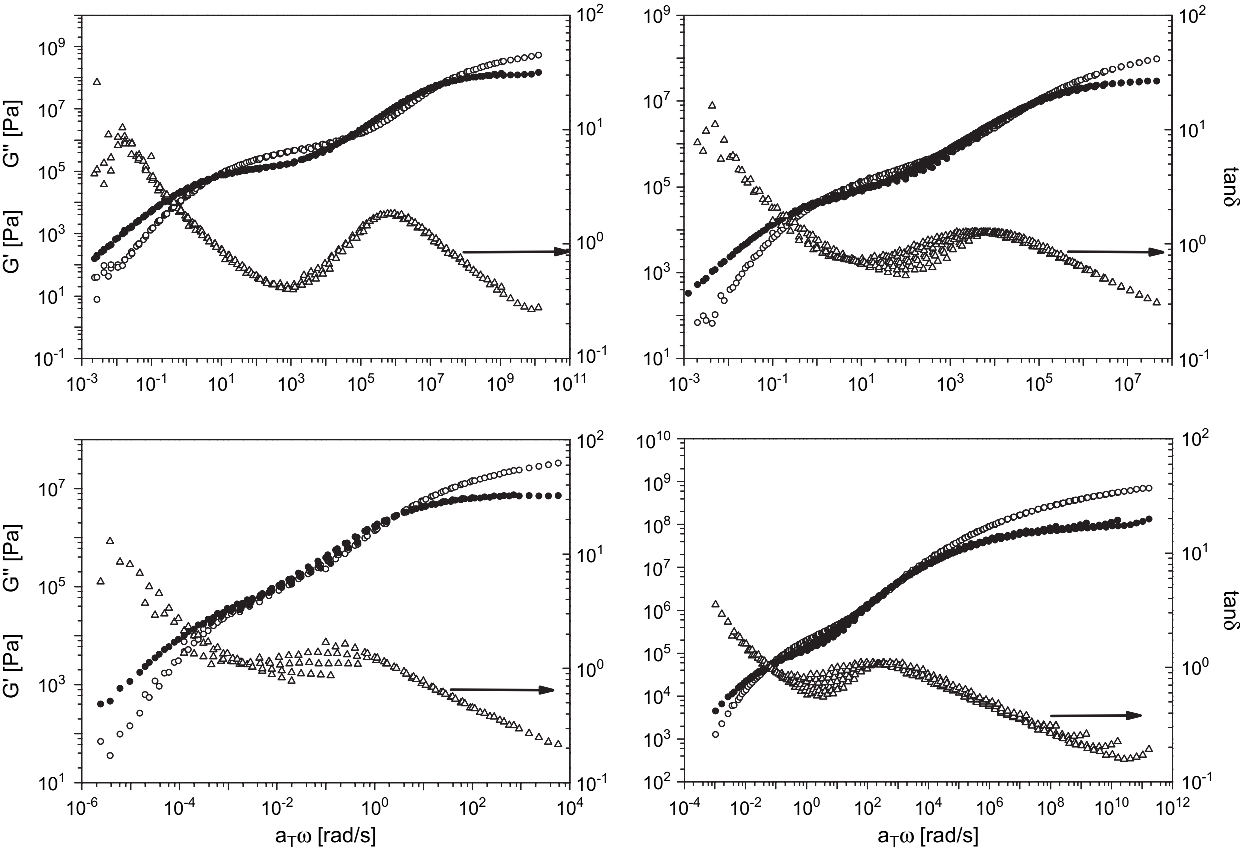

Fig. 2. Master curves for the storage modulus (G', open circles), the loss modulus (G'', filled circles) and the loss tangent (tan δ, triangles) for the 50/50 composition of the 0.36/0.52 (top left), 0.36/0.56 (top right), 0.36/0.62 (bottom left) and 0.46/0.66 (bottom right) blends. The reference temperatures were at 453 K for the first two blends, 433 K for the third blend, and 473 K for the 0.46/0.66 blend. Note the failure of tTs in all cases.

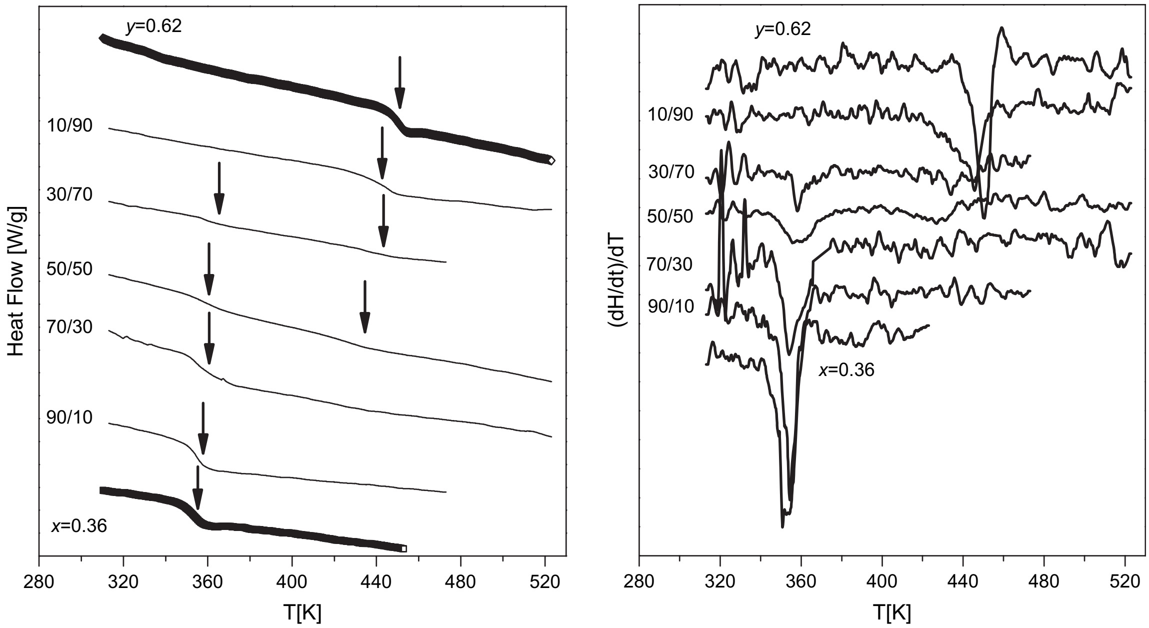

Fig. 3. Left: DSC traces of the binary N_xE_{1-x}/N_yE_{1-y} blends with (x, y) NB content 0.36/0.62 (8007/6017) for various compositions (10/90, 30/70, 50/50, 70/30, 90/10) and the pure components obtained during the second heating run (rate 10 K/min). Notice the dual transition for some compositions (30/70 and 50/50). The traces have been shifted vertically for clarity. Right: derivatives of the heat flow curves of the same 0.36/0.52 NB blends and the pure components. Notice the broadening of the transition at intermediate compositions.

copolymers is an extension [3,4] of the Flory–Huggins (FH) theory to random copolymers. For a blend of two copolymers of the same nature but different compositions (x, y), the FH theory predicts that the miscibility region exists for

$$|x-y|\langle|x-y|_c \tag{3}$$

which is independent of the copolymer composition (the subscript c denotes a critical value) [18]. Thus, the miscibility region is independent of the copolymer composition [3]. This contrasts with our results as well as previously published data [2]. To explain differences with respect to the random copolymer FH theory, a theory based on the so-called "united atom model" was applied to ethylene/norbornene copolymers. The theory is an extension of the lattice cluster theory (LCT) [19–21]; LCT includes contributions from local correlations and specifies structures for individual monomers. Three variations of the model for cycloolefin copolymers have been proposed, ranging from fully flexible chains to models that include chain stiffness arising within each norbornene unit or from the steric interactions between neighboring norbornene monomers (semiflexible backbones). The interaction parameter, $\chi(x)$, exhibits a highly asymmetric shape that is independent of the particular model. This suggests that N_xE_{1-x}/N_yE_{1-y} binary blends are more miscible for the blend components with higher NB content; thus for the same $|x-y|$ the result on blend miscibility may be very different depending on the actual values of x and y. As expected, the region of miscibility is not governed solely by $|x-y|$.

One surprising finding, is that the presence of stiffness either in the NB side group or in the chain backbone is expected to enhance the miscibility. Indeed, the model with the rigid NB side groups shows the lowest χ, and hence, the highest ability of mixing. Our thermal and rheological studies, however, provide evidence that the miscibility decreases with the increase in chain rigidity (or NB content). For further analysis we employ the model with the rigid NB side group due to its outermost phase boundaries. We should mention, however, that the phase boundaries obtained from the different model variations lie relatively close to each other. The stability condition (i.e., spinodal line, used to construct the miscibility region in Figs. 4 and 5) for a blend of two random copolymers is provided by

$$S \equiv \frac{1}{M_1\varphi_1}+\frac{1}{M_2\varphi_2}-2\chi=0 \tag{4}$$

where φ_i are the volume fractions ($\varphi_1+\varphi_2=1$). The latter are obtained from the weight fractions of the two components [2]. M_1 and M_2 are the site occupancy indices for the single N_xE_{1-x} and N_yE_{1-y} chains, respectively. They are defined as

$$M_1 = s_N n_1^{(N)} + s_E n_1^{(E)} \tag{5}$$

$$M_2 = s_N n_2^{(N)} + s_E n_2^{(E)} \tag{6}$$

where $n_i^{(N)}$ and $n_i^{(E)}$ are the average numbers of norbornene and ethylene monomers in copolymers of species i. They satisfy

$$\frac{n_1^{(N)}}{n_1^{(N)}+n_1^{(E)}}=x \text{ and } \frac{n_2^{(N)}}{n_2^{(N)}+n_2^{(E)}}=y, \tag{7}$$

Table 3
Thermal properties of the binary N_xE_{1-x}/N_yE_{1-y} ethylene/norbornene blends obtained from DSC

Blend composition	NB content x	T_{g1} [K]	ΔT_{g1} [K]	T_{g2} [K]	ΔT_{g2} [K]
8007/6013 (0.36/0.52)					
	0.52	415	20	–	–
10/90	0.50	407	28	–	–
30/70	0.47	388	38	–	–
50/50	0.44	381	47	–	–
70/30	0.41	365	35	–	–
90/10	0.38	356	26	–	–
	0.36	352	28	–	–
8007/6015 (0.36/0.56)					
	0.56	434	24	–	–
10/90	0.54	423	35	–	–
30/70	0.50	413	47	–	–
50/50	0.46	361	25	401	31
70/30	0.42	362	34	–	–
90/10	0.38	356	30	–	–
8007/6017 (0.36/0.62)					
	0.62	454	20	–	–
10/90	0.59	443	35	–	–
30/70	0.54	436	93	361	10
50/50	0.49	431	32	361	29
70/30	0.44	359	26	–	–
90/10	0.39	355	28	–	–
1905/1827 (0.46/0.60)					
	0.60	448	19	–	–
10/90	0.59	443	25	–	–
30/70	0.56	428	35	394	7
50/50	0.53	413	25	394	7
70/30	0.50	408	17	395	11
90/10	0.47	394	20	–	–
	0.46	392	22	–	–
1905/1826 (0.46/0.66)					
	0.66	473	20	–	–
10/90	0.64	462	32	–	–
30/70	0.60	394	7	446	52
50/50	0.56	395	13	408	51
70/30	0.52	405	17	396	7
90/10	0.48	394	24	–	–

where $N_1 = n_1^{(N)} + n_1^{(E)}$ and $N_2 = n_2^{(N)} + n_2^{(E)}$ are the polymerization indices of the blend components and s_N and s_E are the lattice sites of norbornene and ethylene, respectively. Within the united atom model the norbornene monomer contains seven united atom groups and therefore occupies seven lattice sites ($s_N = 7$), while the ethylene molecule is a two-bead dimer composed of two CH_2 ($s_E = 2$).

The interaction parameter χ consists of enthalpic and entropic parts. The former is obtained by extending the FH random mixing counting methods to random copolymers composed of monomers with united atom groups as [2,5]

$$\chi_h = \left[\frac{s_N s_E (x-y)}{s_1 s_2}\right]^2 \frac{z\varepsilon}{2kT} \tag{8}$$

where s_1 and s_2 are defined as

$$s_1 = s_N x + s_E(1-x) \tag{9}$$

$$s_2 = s_N y + s_E(1-y) \tag{10}$$

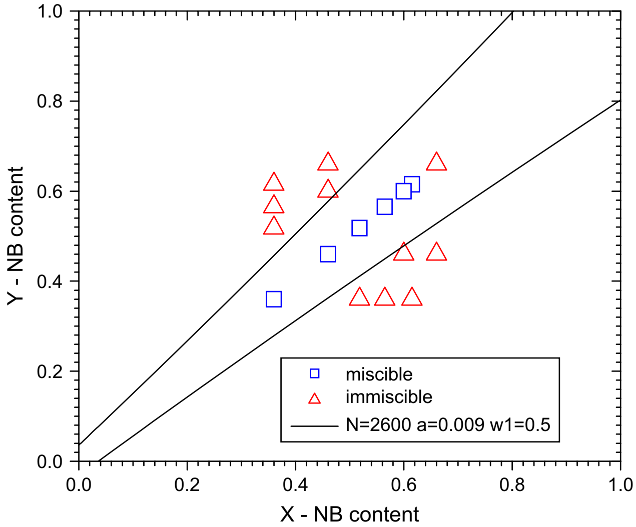

Fig. 4. Phase diagram of the symmetric (50/50) binary N_xE_{1-x}/N_yE_{1-y} blends obtained from rheology. Squares and triangles denote the compositions (x, y) for which the system is miscible and immiscible, respectively. The black lines refer to the phase boundaries as obtained from the LCT model with rigid norbornene side groups. The dimensionless exchange energy is taken as $\varepsilon/kT = 0.009$, and for the polymerization indices $N_1 = N_2 = 2600$. Notice the failure of the tTs for the pure copolymer with 0.66 norbornene content.

and designate as the average numbers of united atom groups in the monomers of components 1 and 2, respectively [22]. z is the lattice coordination number and is taken as $z = 6$, k is Boltzmann's constant, T is the absolute temperature, and $\varepsilon = \varepsilon_{NN} + \varepsilon_{EE} - 2\varepsilon_{EN}$ is the exchange energy with ε_{NN}, and ε_{EE} denoting the attractive van der Waals energies between united atom groups of the respective monomer pairs. The entropic contribution χ_S of the interaction parameter χ can be expressed as

$$\chi_S = \frac{1}{z^2}\left[\frac{(x-y)}{s_1 s_2}\right]^2 \left[s_E\left(s_N^{tri} - 2\right)\right]^2 \tag{11}$$

where s_N^{tri} denotes trifunctional united atom groups in norbornene monomers (the monomer structure has 3 of the united atom groups that are trifunctional, i.e., $s_N^{tri} = 3$).

As we mention earlier, the calorimetric method is not sensitive enough to draw conclusions about the thermorheological simplicity/complexity of the blends. Comparison between the data obtained from DSC and rheology shows many discrepancies due to the low sensitivity of the former technique. For that reason only the rheological data are compared with the theory in testing its validity for the different COC compositions. Thus the miscibility diagrams in Figs. 4 and 5 for the symmetric and asymmetric blends, respectively, are constructed using the validity criterion of the time–temperature superposition (Eq. (2)). It can be observed (Table 2) that, except for two very asymmetric compositions (10/90 in 0.36/0.52 and 90/10 in 0.36/0.62), all blends are thermorheologically complex and thus immiscible. Notice, however, that the "degree" of immiscibility, given by the values of (dtan δ_{min})/dT (Table 2), differs for the various blend compositions.

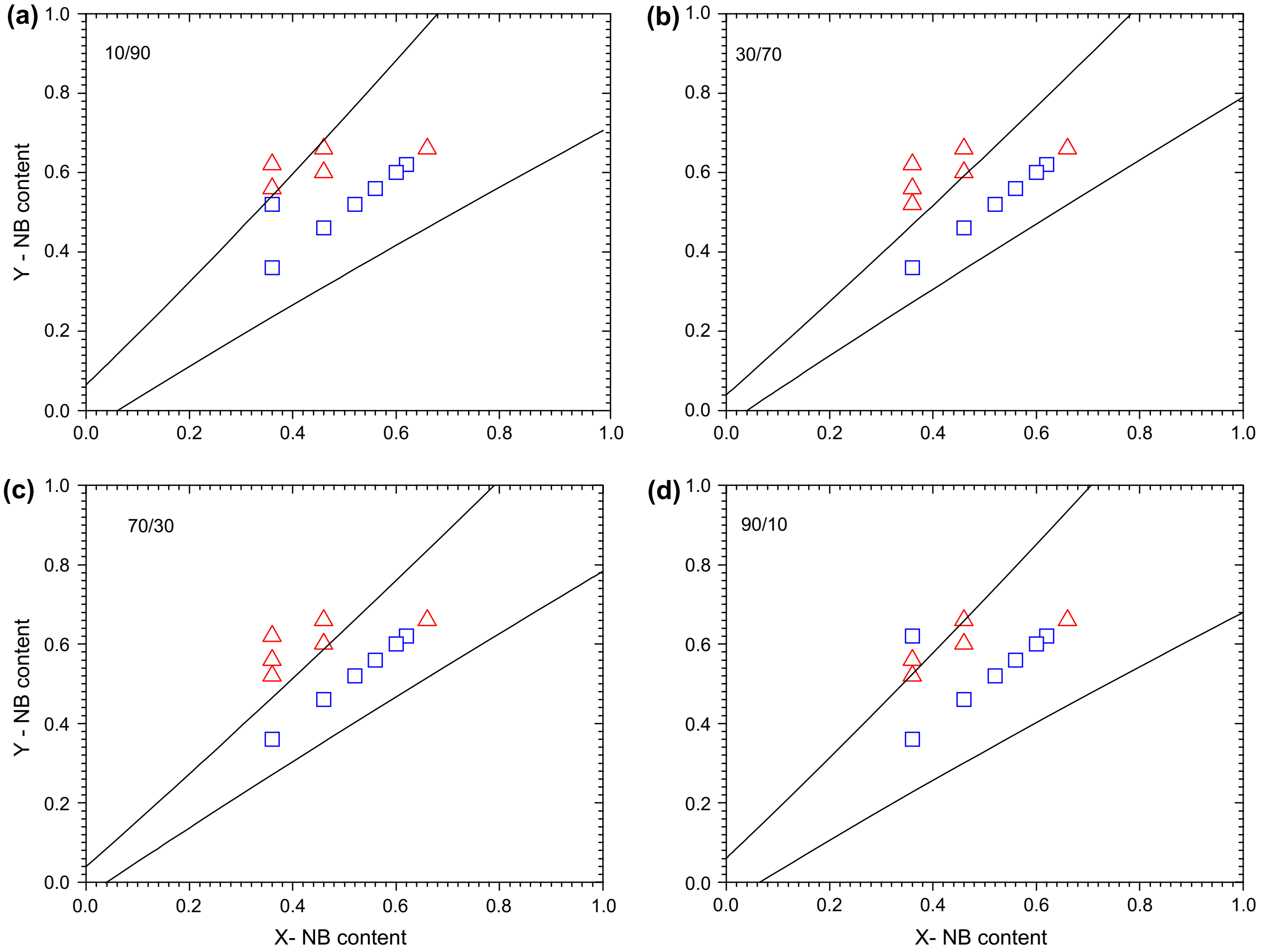

Fig. 5. Miscibility diagram of the asymmetric binary blends obtained from rheology: (a) 10/90, (b) 30/70, (c) 70/30, (d) 90/10. The exchange energy and the polymerization indices are the same as in Fig. 4. Notice the similarities of the diagrams for the 30/70 and 70/30 compositions with the symmetric case. The theory correctly predicts the most compositions except for the very asymmetric (10/90 and 90/10) blends.

Testing the theoretical predictions against experimental data requires some control of the parameters involved in the model, namely the degree of polymerization (N), the exchange (ε) and, in general, the bending energies (E_b) of NB backbone bonds connecting adjacent norbornene units associated with the chain backbone stiffness. The degree of polymerization was found to exhibit a large influence on the phase boundaries; increasing N reduces the miscibility window, which is consistent with the experimental findings. For the present copolymers the range of N values is: $2150 \leq N_1 \leq 2660$ and $2000 \leq N_2 \leq 3650$. However, for such N values the change in the phase boundaries is very small. In order to facilitate the comparison for the different copolymers we employ $N_1 = N_2 = 2600$ for all blend components which is a good approximation. The phase boundaries are also very sensitive to the exchange energy reflecting the attractive van der Waals energies between united atom groups of the respective monomer pairs. Decreasing the exchange energy makes a wider miscibility region due to the smaller interaction between monomers. The minimal value of the dimensionless exchange energy, ε/kT, being still in agreement with the experimental data for all the symmetric blends, was found to be 0.009 (Fig. 4). On the other hand, the miscibility window is not sensitive to the bending energy (E_b). Moreover, this parameter does not enter in the model variation employed herein.

We employ the above mentioned values for the degree of polymerization and exchange energy from the symmetric blends (Fig. 4), and critically test the model predictions for all *asymmetric* blend compositions (Fig. 5). As a result, the model correctly predicts the immiscibility for all the 30/70 and 70/30 compositions, as well as for some of the 10/90 and 90/10 compositions. From the comparison it can be concluded that the theoretical model works best for the "middle" (70/30–30/70) compositions, and partially fails for the extreme ones. Such success of the LCT theory with the experimental results is appreciated by taking into account the number of approximations involved, such as blend incompressibility, the oversimplified structure of norbornene monomer, as well as experimental uncertainties originating from the polydispersity, and the value of the criterion set for tTs violation (Eq. (2)). Given the above, the agreement between theory and experiment is considered as reasonable.

4. Conclusions

The mutual miscibility in a series of cycloolefin copolymers of ethylene and norbornene was investigated by rheology and differential scanning calorimetry by following, respectively, the T-dependence of the $\tan \delta_{\min}$ and the presence of a single glass temperature. The latter technique, under high heating/cooling rates, can lead to erroneous conclusions with respect to the state of miscibility in the blends. The more stringent test employed in rheology leads to several conclusions:

(i) Copolymers with NB content in the range $0.36 \leq x \leq 0.62$ are thermorheologically simple but increasing NB content to 0.66 enhances the intrinsic mobility differences of the NB and E sequences and results in the breakdown of time–temperature superposition and thus leading to immiscibility.
(ii) Most of the blends are thermorheologically complex; the temperature dependence of $\tan \delta_{\min}$ is the strongest for the symmetric blends and increases with the NB content of the blend components.
(iii) The theoretical model based on a lattice cluster theory correctly predicts the miscibility of all the "middle" (70/30–30/70) blend compositions, and partially fails for the very asymmetric compositions.

Overall our experimental results together with the theoretical predictions can be employed as recipes in designing new COC copolymers with desired compositions and hence controlled material properties.

Acknowledgment

We are indebted to Dr. U. Stehling (Ticona GmbH) for the synthesis of some of the new copolymers investigated herein. Support by the GRST (PENED2003/856) is acknowledged.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2007.08.015.

References

[1] Blochowiak M, Pakula T, Butt H-J, Bruch M, Floudas G. J Chem Phys 2006;124:134903.
[2] Delfolie C, Dickinson LC, Freed KF, Dudowicz J, MacKnight WJ. Macromolecules 1999;32:7781.
[3] Paul DR, Barlow JW. Polymer 1984;25:487.
[4] ten Brinke G, Karasz FE, MacKnight WJ. Macromolecules 1983;16:1827.
[5] Dudowicz J, Freed KF. Macromolecules 2000;33:3467.
[6] Brekner M-J, Rohrmann J, Spaleck W, Antberg M. U.S. Patent 5,087,677; 1992.
[7] Weller T, Osan F, Kuber F, Aulbach M. U.S. Patent 5,698,645; 1997.
[8] Plazek DJ, Schlosser E, Schönhals A, Ngai KL. J Chem Phys 1993;98:6488.
[9] Nicolai T, Floudas G. Macromolecules 1998;31:2578.
[10] Floudas G, Reisinger T. J Chem Phys 1999;111:5201.
[11] Pathak JA, Colby RH, Kamath SY, Kumar SK, Stadler R. Macromolecules 1998;31:8988.
[12] Pathak JA, Colby RH, Kumar SK, Krishnamootri R, Floudas G, in preparation.
[13] Rische T, Waddon AJ, Dickinson LC, MacKnight WJ. Macromolecules 1998;31:1871.
[14] Grooten R, ten Brinke G. Macromolecules 1989;22:1761.
[15] Borma M, ten Brinke G, Ellis TS. Macromolecules 1988;21:1465.
[16] Lodge TP, Wood ER, Haley JC. J Polym Sci Polym Phys 2006;44:756.
[17] Lodge TP, McLeish TCB. Macromolecules 2000;33:5278.
[18] Scott RL. J Polym Sci 1952;9:423.
[19] Freed KF, Dudowicz J. Trends Polym Sci 1995;3:248.
[20] Dudowicz J, Freed KF. Macromolecules 1991;24:5076.
[21] Nemirovsky AM, Bawendi MG, Freed KF. J Chem Phys 1987;87:7272.
[22] Dudowicz J, Freed KF. Macromolecules 1998;31:5094.