Analysis of the Density and the Enthalpy of Poly(ε-caprolactone)–Polycarbonate Blends: Amorphous Phase Compatibility and the Effect of Secondary Crystallization

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ABSTRACT: The dependency of the density of poly(ε-caprolactone)–polycarbonate (PCL–PC) blends on composition has been studied. PCL/PC blends are typical of miscible blends containing crystallizable components, and miscibility is therefore considered with respect to the amorphous phase. In literature, a single glass transition temperature is reported for the PCL–PC system; however, the exact dependency on amorphous phase composition is not clear. For quenched amorphous blends, we found the Fox equation to be appropriate in order to describe the glass transition temperature as a function of composition. For amorphous samples containing low amounts of PCL ($\leqq$40 wt %), an increase in the density of the blend over that of a linear average of the densities of amorphous PC and PCL was observed experimentally. This is indicative of significant interactions in the blend. For samples containing $\geqq$ 50 wt % PCL, crystallization of PCL has to be accounted for in the analysis of the density. It is shown that the experimental density data can only be described satisfactorily by assuming that secondary crystallization of PCL does not lead to an increase of the overall blend density. This is attributed to the rigid and volume filling primary crystalline structure at room temperature, i.e., below the melting point of PCL. Excess density is present in the amorphous phase of the PCL/PC blend over the whole range of composition; therefore, specific interactions exist in the amorphous phase of the blend over the whole range of composition. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 921–927, 1997

INTRODUCTION

Blending of polymers is considered to be an efficient and cost-effective way towards obtaining materials with new or modified properties.[1] From this point of view, poly(ε-caprolactone) (PCL) comprising blends have been given considerable attention.[2–7] Especially, the blend of poly(ε-caprolactone) with polycarbonate (PC) appears to have a complex phase behavior.[8] The low glass transition temperature of PCL enables PC to crystallize in blends containing high amounts of PCL. In pure PC, this is seen only after extended annealing at high temperatures.[9] In these blends, both PCL and PC are therefore semicrystalline. For low PCL contents, on the other hand, both PCL and PC are amorphous. Depending on composition, the morphology in PCL–PC blends can therefore range from semicrystalline to semicrystalline to amorphous to amorphous.

The amorphous phase compatibility of PCL and PC is judged from a single, composition-dependent glass transition temperature. The exact de-

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pendency of the glass transition temperature on composition is not clear, however, and both continuous[3,10] and discontinuous[8] dependencies have been reported. Recently, it has been noted[11] that the density of PCL–PC blends increases over that of a linear average upon the addition of small amounts of PCL ($\leq$20 wt %) to PC. Such an increase is indicative of significant interactions in the blend compared to the homopolymers[12,13] and would be in agreement with the glass transition analysis. However, due to PCL and PC crystallinity, the amorphous phase density is only accessible experimentally for low PCL contents. In order to establish the amorphous phase density over the whole range of composition, PCL and PC crystallinity have to be accounted for, which will be addressed in this article.

EXPERIMENTAL

Poly(ε-caprolactone) was obtained from Union Carbide, USA (Tone polymer P-787) and dried at room temperature for 40 hours under vacuum before use. Bisphenol-A polycarbonate was obtained from Teijin Chemical, Japan (Panlite, grade L1250) and dried for 16 hours at 120°C. Blend sheets were produced using a twin screw extruder (Labo Plastomill, Toyo Seiki) operated at 12 rpm with a die temperature of 250°C. After extrusion, samples were pressed on a hot press at 200°C. All samples were subsequently annealed at 25°C for several weeks.

Differential scanning calorimetry (DSC) experiments were performed on a Seiko DSC-120 at 5°C/min and on a Perkin-Elmer DSC-7 at 20°C/min. The glass transition temperature was taken at half the height of the ΔC_p jump. Quenched samples were obtained in the Perkin-Elmer DSC-7 by quenching to -100°C at 200°C/min after 5 min at 250°C.

A water/NaCl–solution density gradient column was used at 25°C. As the maximum density for such a column is approximately 1.20 g/cm^3, a water/NaBr-solution–isopropyl-alcohol column was used for higher densities.[14] With this column, it was found that for samples containing crystalline PCL ($\geq$50 wt % PCL), the density decreased slowly over time. Since this was in contrast to the water–NaCl column, it is attributed to an uptake of isopropyl–alcohol by crystalline PCL, making this column unsuitable for these samples. For the density of amorphous PCL, 1.081 g/cm^3 is used[15] and 1.195 g/cm^3 for 100% crystalline PCL.[16]
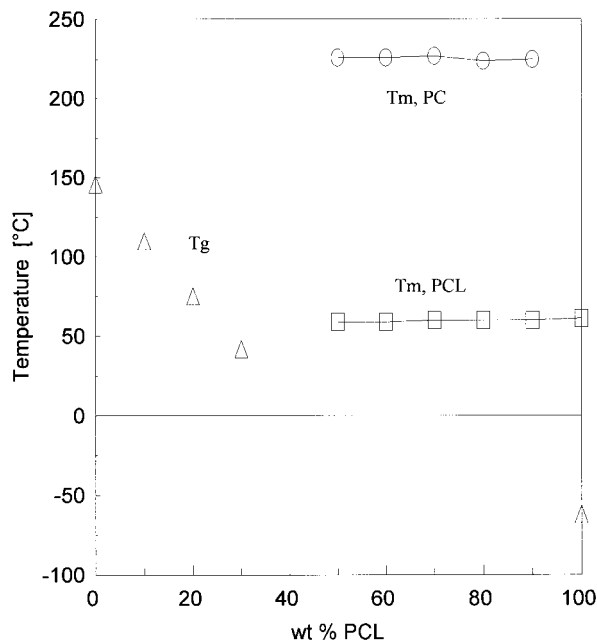

Figure 1 Glass transition temperature and melting temperatures as a function of composition of the PCL–PC blend annealed at 25°C for several weeks. Heating rate: 5°C/min; ($\triangle$, glass transition temperature; $\square$, melting temperature of PCL; $\bigcirc$, melting temperature of PC).

The values for PC are 1.196 and 1.315 g/cm^3, respectively.[17] Based on our density and DSC data for pure PCL (1.1408 $\pm$ 0.004 g/cm^3 and 75.1 $\pm$ 0.5 J/g, respectively) and assuming 1.081 g/cm^3 for the density of amorphous PCL, a value of 137 J/g can be derived for the heat of fusion of 100% crystalline PCL. This is within the experimental range reported.[15] For the heat of fusion of crystalline PC, 148 J/g is used.[17]

RESULTS AND DISCUSSION

Glass Transition Temperature

The glass transition temperature of the amorphous phase of the PCL–PC blend, as well as the melting temperature of crystalline PCL and PC, are shown for the annealed samples in Figure 1. The corresponding melting enthalpies of PCL and PC are shown in Figure 2. Since the glass transition temperature of PCL is much lower than the one for PC, the glass transition temperature of the blend decreases upon the addition of PCL to PC. No detectable glass transition was observed for blend compositions containing more than 40 wt % PCL.
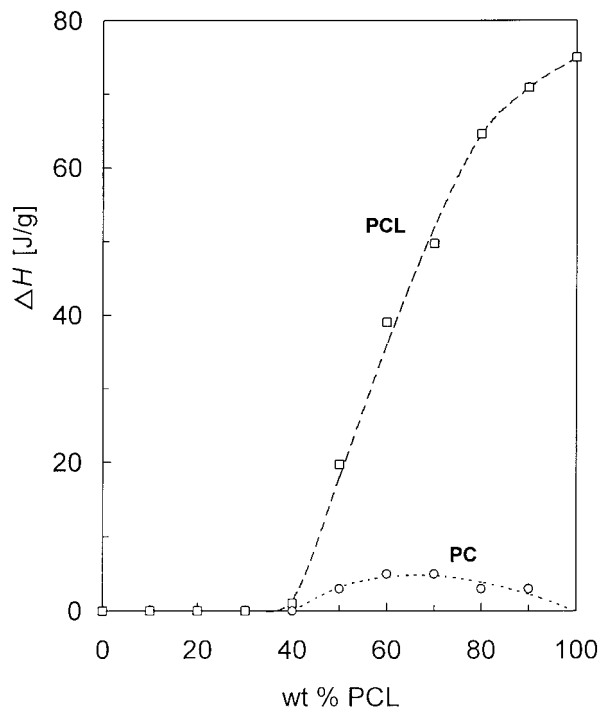
Figure 2 Melting enthalpies of PCL and PC of the samples in Figure 1. Heating rate: 20°C/min: (□, PCL; ○, PC).

For systems containing crystalline PCL, this is considered[18] to be a result of the broadening of the glass transition zone due to crystallinity.

The decrease of T_g upon the addition of PCL causes PC to crystallize for compositions containing more than 40 wt % PCL; however, polycarbonate crystallinity is only limited (Fig. 2). PCL crystallinity is rather high for pure PCL (55%), in accordance to observations in literature.[3,4] The melting enthalpy of PCL decreases with decreasing PCL content in the blend, and blends containing $\leq$ 40 wt % PCL are completely amorphous. The fact that both the PCL and PC melting temperatures are independent of composition indicates that the blend constituents crystallize in two separate crystal structures, as was confirmed by small-angle X-ray scattering (SAXS) measurements.[19]

In order to relate T_g to the amorphous phase composition, quenched samples were produced and analyzed in the DSC with as low a crystallinity as possible. All samples were completely amorphous, except for those containing 100, 90, and 80 wt % PCL, with the melting enthalpy being 75, 56, and 26 J/g, respectively. In all cases, a single glass transition was observed (Fig. 3). From Figure 3, it is clear that the Fox equation is appropriate to describe the dependency of the glass transition temperature for a completely amorphous phase. Note that this is in disagreement with previously published results for this system,[8] in which a discontinuous dependency was reported. In that work, considerable crystallinity was present in the sample which, as discussed earlier, makes the interpretation of the glass transition very difficult.

In Figure 4, the width of the glass transition zone is reported as a function of overall blend composition for the quenched blends. There is a considerable increase in the width of the transition zone of the blend compared to the pure constituents. It is commonly believed that this is a result of inhomogeneities in the blend, indicating borderline miscibility.[1,20,21] This increase in the width of the glass transition zone makes it very difficult to determine accurately the glass transition temperature in the blend, especially when PCL crystallinity (and hence a melting endotherm) is present. This is most likely the cause of the ambiguity related to the compositional variation of the glass transition temperature reported in literature.[3,8,10] Note that in quenched samples (Fig. 4), the broadening is not a result of PCL crystallinity.

Density of PCL–PC Blends

The density of the PCL–PC blend as a function of composition is given for the samples annealed
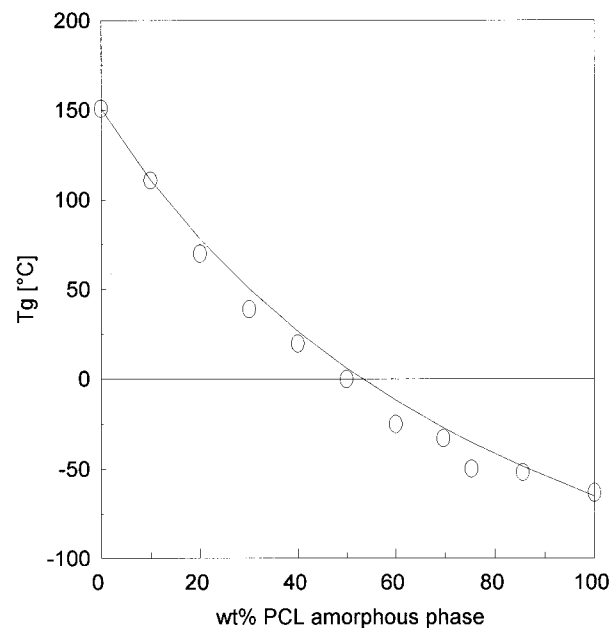

Figure 3 Glass transition temperature as a function of amorphous phase composition for quenched PCL–PC blends. The line represents the Fox equation.
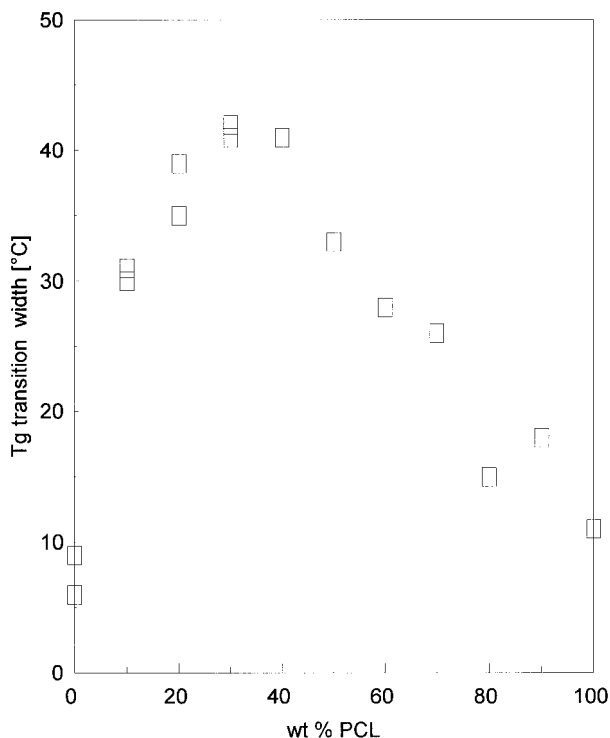
Figure 4 Width of the glass transition zone as a function of overall blend composition for the quenched blends.

at room temperature in Figure 5. The density of the samples containing 10 and 20 wt % PCL increases over the density of pure PC, even though the density of amorphous PCL is much lower than for PC. Note that for samples containing up to 40 wt % PCL, crystallinity is negligible and therefore cannot account for this effect. The increase in density with a corresponding decrease in glass transition temperature is the cause of so called antiplasticization for this blend system.[11]

In order to describe the compositional variation of the density for miscible systems, an excess density parameter g is defined as follows:[12]

$$g = \frac{V_E/V}{\phi_1\phi_2} \qquad (1)$$

in which V_E is the specific excess volume, V is the total specific volume, and ϕ_1 and ϕ_2 are the volume fraction of the low T_g and high T_g constituents, respectively. The excess volume V_E is defined as $V = V_1 + V_2 - V_E$. Therefore, V_E and g are both positive if the average interactions in the blend are stronger than in the homopolymers.[12] This is apparently the case for the PCL–PC sys-

tem, and a value of 0.12 for g is able to describe the experimental density up to 40 wt % PCL. For compositions containing $\geq$ 50 wt % PCL, crystallinity has to be accounted for, which will be addressed further on.

Since the density data suggest favorable interactions in the blend, at least for compositions up to 40 wt % PCL, it is interesting to compare this to literature. Favorable interactions for the PCL–PC blend were reported,[22] based on the exothermic heat of mixing of small molecules similar to PCL and PC. Both favorable[23] and unfavorable[10] interactions are reported, based on melting point depression, the ambiguity being a result of the influence of effects of morphological nature that interfere with this type of analysis.[24] Unfavorable interactions were reported based on a fit of the Braun–Kovacs theory[13] to the compositional variation of the glass transition temperature.[8] However, an excess density parameter ($g = -0.023$) not in agreement with our density data was derived from the fit, making the analysis questionable.
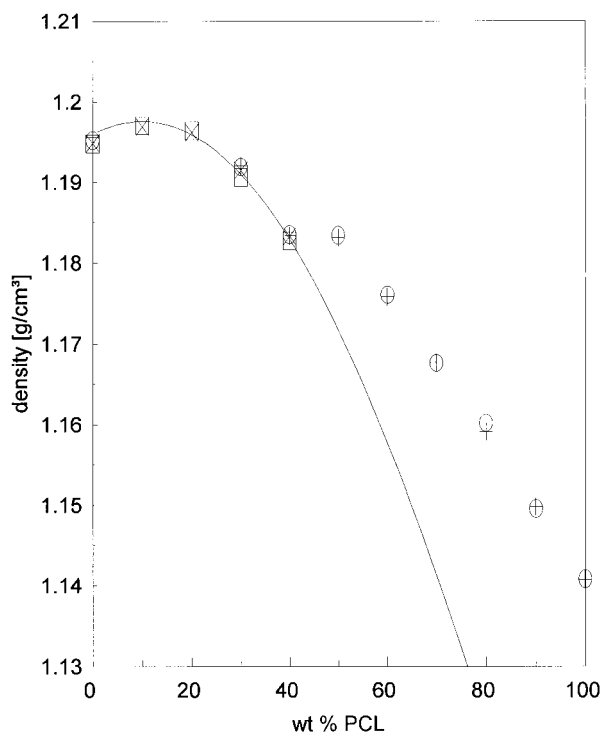
As was mentioned previously, the deviation

Figure 5 Density at 25°C of annealed PCL–PC blends. Data derived with either water–NaCl ($\bigcirc$, $+$) or water–NaBr/isopropyl alcohol ($\square$, $\times$). The line represents the amorphous density according to eq. (1) with $g = 0.12$.
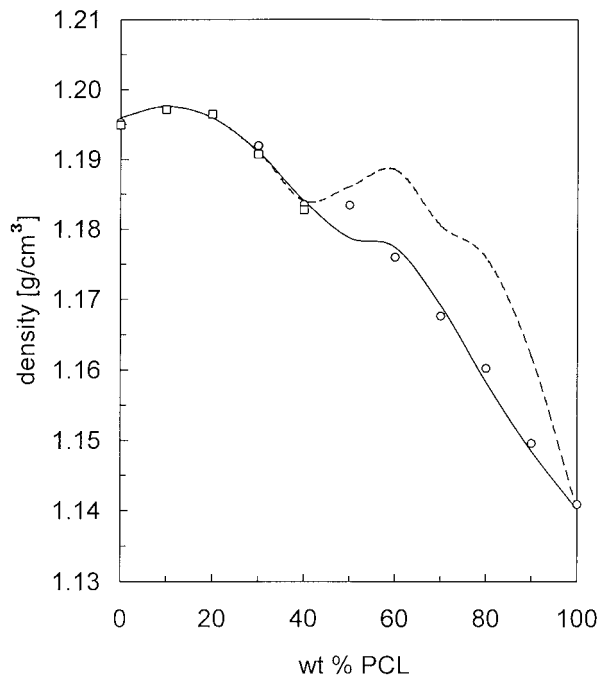
Figure 6 Density of annealed PCL–PC blends as a function of overall blend composition. Data from Figure 5: (– – – – , calculated using total blend crystallinity); (——, calculated using the PC crystallinity and the crystallinity from the primary crystallization of PCL only).

from the experimental values of the calculated density according to eq. (1) with $g = 0.12$ is a result of PCL and, to a lesser extent, PC crystallinity. Since the value for g is derived from amorphous samples only ($\leqq 40$ wt % PCL), it would be interesting to see if it is possible to describe the data over the whole composition range using a single value for g by including the effect of crystallinity and thus conclude that favorable interactions exist in the blend and over the whole range of composition.

Using the literature values for the material properties of PCL and PC, the density was calculated over the whole composition range. The melting enthalpies of Figure 2 are used, and the composition of the amorphous phase is calculated accordingly. It is assumed that the amorphous phase density is accurately described by eq. (1) and $g = 0.12$ over the whole range of composition. The results are given in Figure 6.

From Figure 6 (dashed line), it is clear that the density calculated with the melting enthalpy of PCL and PC deviates considerably from the experimental data for blends containing 50 wt % PCL or more. This seems to imply that the under-

lying assumption that the amorphous phase density can be described using eq. (1) and a single value for g over the whole composition is incorrect. However, quite a considerable deviation from the line $g = 0.12$ would be required in the amorphous phase density in order to describe the experimental results; furthermore, it would occur quite abruptly once PCL crystallinity is present (>50 wt % PCL). For these reasons, it is believed that the deviation in Figure 6 between experimental and calculated density is related to PCL crystallinity itself. In order to explain this, a closer look at the crystallization process of PCL in the blend is necessary (see Fig. 7).

As is shown in Figure 7, all PCL–PC blends have, apart from a melting peak with a melting temperature close to that of pure PCL, an additional melting peak at lower temperatures. The nature of this low-temperature peak for PCL comprising blends has been extensively discussed in the literature [15,25,26] and should be attributed to secondary crystallization. Upon cooling from the melt, due to the high crystallization rate of PCL, a primary crystal structure is readily formed. In the amorphous phase of this structure, however, crystallizable PCL is still present. Due to the trapped nature of this PCL and the increase of PC content in the amorphous phase (and, hence, T_g and viscosity) as a result of exclusion from the
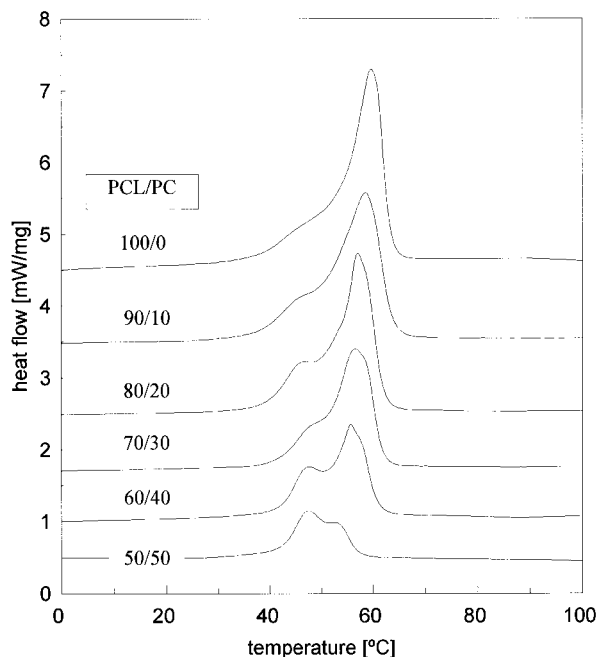

Figure 7 Melting endotherms of annealed PCL–PC blends at 20°C/min.

Table I   Melting Enthalpies of Samples Annealed at Room Temperature with Subdivision in Primary and Secondary Crystallization Peaks

Wt % PCL (Overall)	Density at 25°C (g/cm^3)	Melting Enthalpy PC* (J/g)	Melting Enthalpy PCL (J/g)		
			Total for PCL	Primary Crystal Structure	Secondary Crystal Structure
100	1.1408	—	75		
90	1.1498	3	73	56	17
80	1.1591	3	67	44	23
70	1.1677	5	51	35	16
60	1.1760	5	42	25	17
50	1.1831	3	22	9	13
40	1.1833	—	—	—	—
30	1.1921	—	—	—	—
20	1.1964	—	—	—	—
10	1.1971	—	—	—	—
0	1.1956	—	—	—	—

* Obtained from peak area at 220°C.

PCL lamellae, the subsequent secondary crystallization of PCL occurs only in due time.

This type of two-stage crystallization process is believed to have a consequence for the density of the blend. Primary crystallization of PCL at high PCL contents produces a volume-filling crystalline structure.[26,27] Since room temperature is below the melting temperature of PCL and the primary structure is volume-filling, it is reasonable to believe that the primary crystalline structure is fixed at this temperature once primary crystallization is completed. Therefore, the total volume of this structure is fixed; and since, obviously, the total mass is constant, the density of the sample is fixed too. In other words, secondary crystallization within the amorphous phase of the primary structure will not lead to a change of the overall density but will only lead to a local variation of the density within the primary structure. Application of this idea in describing the density data gives the solid line in Figure 6. As can be seen from this figure, the experimental data is described very well.

To obtain the solid line in Figure 6, the melting endotherms of the blends were, in a first approximation, separated into two separate Gaussian peaks. The total melting enthalpy was then divided according to the areas under each peak. The results are shown in Table I. The density of the samples can now be calculated by considering the enthalpy of the high temperature peak only (primary crystallization) and assuming that the sec-

ondary crystallization process has not yet occurred. In this way, the fact that secondary crystallization does not lead to a change in overall density is accounted for. The results are included in Figure 6 (solid line). The deviation for the 50 wt % PCL samples is probably a result of the fact that there is no volume-filling crystal structure due to the low amount of crystalline PCL.[27]

From the good fit in Figure 6, it follows that the amorphous phase density can indeed be described accurately over the whole composition range using eq. (1) and a single value for the excess density parameter $g = 0.12$. This implies that favorable interactions persist in the amorphous phase of the blend over the whole range of composition.

CONCLUSIONS

It has been shown that a single glass transition is present over the whole range of composition for quenched poly(ε-caprolactone)–polycarbonate blends. In contrast to previously published results, the compositional variation of this glass transition temperature could accurately be described by the Fox equation.

The excess density observed for this system is indicative of favorable interactions in the blend compared to the homopolymers. It has been shown that a single excess density parameter is able to describe the amorphous phase density as a function of composition over the whole range of

composition. In addition to this, it was shown that secondary crystallization does not lead to a change in the density of this blend as a result of the volume-filling nature of the primary crystalline structure.

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