

Development of partial miscibility in polycarbonate/polypropylene blends via annealing

Jenkins, Michael; Kukureka, Stephen; Samsudin, Sani Amril

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**Partial miscibility in polycarbonate/polypropylene blends
through annealing process**

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|-------------------------------|--|
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3 Dear Prof. Ana Vera Machado
4 Associate Editor, Journal of Polymer Engineering
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7 **Manuscript ID: POLYENG.2016.0254**

8
9 **Title: "Partial miscibility in polycarbonate/polypropylene blends through annealing**
10 **process"**
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15
16 We thank the reviewers for their comments on our manuscript and we are pleased that
17 reviewer one has decided that the work should be published without modification. In terms of
18 the comments made by reviewer two, we have integrated our response to point 1 and 2 as we
19 believe that they are closely related.
20
21

22
23
24 *1. Mechanical properties are important for polymer blend, but the authors did not provide*
25 *any solid evidence for the difference of PC/PP blend before and after annealing.*

26
27
28 *2. In the manuscript, the authors indicated that blend would appear miscibility due to that the*
29 *annealing process gave rise to the degradation of PP. In that cases, whether the mechanical*
30 *properties would decrease and what is the significance of research?*
31
32

33
34 ***Answer:***
35

36 We agree that mechanical properties of polymer blends are important, but that was not the
37 focus of this manuscript. Instead, this is a work that is focused on thermal analysis and the
38 interaction between the polymer components that is a consequence of thermal degradation in
39 the PP. We did not undertake any mechanical testing so this cannot be included at this stage.
40 Furthermore, mechanical properties of this blend system have been extensively reported
41 elsewhere, but not the development of partial miscibility and its characterization.
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50 *3. The scale of x and y axis shown in Figure 3 did not conform to the criteria.*
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52 ***Answer:***
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54 Despite careful consideration of this comment, we simply do not understand what is being
55 asked of us (the comment does not make sense!)
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4. *Figure 4a and b show the SEM images of the blend before and after annealing, but there is no distinct difference between the two images.*

Answer:

This is not the case. In the text the reader is directed to the regions in which there is localized adhesion between the droplets of PC and the PP matrix.

We hope that our responses above are sufficient to allow publication of this work and look forward to your decision in due course.

Yours sincerely,

Dr S.A. Samsudin

Correspondent

Partial miscibility in polycarbonate/polypropylene blends through annealing process

Sani A. Samsudin^{1,2*}, Catherine A. Kelly¹, Stephen N. Kukureka¹, Mike J. Jenkins¹

¹ College of Engineering and Physical Science, School of Metallurgy and Materials, The University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom.

² Department of Bioprocess and Polymer Engineering, Faculty of Chemical and Energy Engineering (FCEE), Universiti Teknologi Malaysia, 81310 UTM Johor Bharu, Malaysia.

* Corresponding author; Sani A. Samsudin, (T) +44 121 414 2841 (F) +44 121 414 7468

E-mail: saniamril@cheme.utm.my

ABSTRACT: The morphology, dynamic mechanical properties and infra-red spectra of polycarbonate/polypropylene blends were investigated. As expected, polycarbonate and polypropylene were immiscible when blended together; however partial miscibility was developed following annealing. The miscibility of one polymer in the other was examined using the modified Fox equation and the values of the Flory-Huggins polymer-polymer interaction parameter (χ_{12}) were also calculated following the Kim and Burns approach. Moreover, the possible causes for partial miscibility in the annealed polycarbonate/polypropylene blends were explored by infra-red spectroscopy. It was concluded that annealing caused degradation of polypropylene leading to the formation of polar groups which were then able to interact with polycarbonate generating regions of partial miscibility.

Keywords: Polycarbonate; polypropylene; blend; annealing; partial miscibility; Flory-Huggins

1. Introduction

Polypropylene (PP) is a semi-crystalline thermoplastic. It is of prime commercial importance as it offers a combination of a relatively low price and ease of processing [1]. However, PP can display brittle characteristics and is commonly blended with other materials to improve its properties.

Blends of polycarbonate (PC) and PP have been of interest for many years [1-10] PC/PP blends are known to be immiscible [10] and many researchers have shown that the size and shape of PC particles dispersed in a PP matrix depend significantly on the processing conditions as well as the presence of any compatibilisers [2-5, 11]. In addition Xu *et al.* has shown that the tensile strength of PC deteriorates with increasing PP content due to poor compatibility between the two polymers [9]. However, the mechanical properties were greatly improved on the addition of compatibilisers. The rheological properties [4-6] and crystallisation behaviour of PC/PP blends [7, 9, 12-14] have also been investigated, but the dynamic mechanical properties and the effects of annealing, have not been explored in any detail and are therefore the subject of this paper.

The main focus of this work is to investigate the influence of annealing on the morphology and dynamic mechanical properties of PC/PP blends. More specifically, the potential for the development of partial miscibility during annealing will be investigated and values for the Flory-Huggins polymer-polymer interaction parameter (χ_{12}) will be calculated in order to quantify any such blending. The existence of possible interactions between the two polymer blend components during annealing will be examined by infra-red spectroscopy.

2.0 Experimental

2.1 Materials

Polycarbonate (Calibre 303-15) was supplied by the Dow Chemical Company (Midland, Michigan, USA) in the form of moulding pellets. The density and melt flow index are specified by the manufacturer as 1.2 g/cm³ and 15 g/10 min at 300 °C and 1.2 kg, respectively. Polypropylene (Sabic PP 575P) was obtained from Sabic EuroPetrochemicals (Teesside, UK) in pellet form and has a density of 0.905 g/cm³ and a melt flow index of 11 g/10min at 230°C and 2.16 kg as specified by the manufacturer. To minimise hydrolytic degradation during processing, both PP and PC were first dried under vacuum at 90 °C for 17 hours.

2.2 Sample preparation

An APV model MP2000 twin-screw extruder (Saginaw, Michigan US) was used to melt-blend PP and PC at 250°C with a screw speed of 100-150 rpm. The extrudate was subsequently pelletised and plaques (10 x 10 x 0.1 cm) were produced *via* compression moulding using a Moore E1127 hydraulic hot press (George E. Moore & Sons Ltd, Birmingham, UK) at 250 °C with a pressure of 10 tonnes. Annealing was accomplished via prolonged storage within the hot-press at 250 °C for 90 mins followed by quenching to room temperature in a water bath.

2.3 Morphology studies

The fracture surfaces of the blends were examined using a JEOL 6000 scanning electron microscope (SEM) (JEOL, Welwyn Garden City, UK). Samples were prepared by mounting onto aluminium stubs with a conductive carbon disc. The surface of the stubs together with the fracture surfaces were coated in gold, prior to analysis, using a sputter coater.

2.4 Dynamic mechanical thermal analysis

Dynamic-mechanical testing was performed using a dynamic mechanical thermal analyser (DMTA) (Polymer Labs, Church Stretton, UK). Measurements were performed in which the loss tangent and storage modulus were recorded as a function of temperature on heating from -40 and 170 °C at a rate of 2 °C/min and a frequency of 1 Hz. The glass transition temperature (T_g) was determined as the temperature at which a peak in the loss tangent, corresponding to the α relaxation, was observed.

2.5 Fourier transform infrared (FTIR) spectrometer

A Nicolet Magna-IR 856 Fourier transform infrared (FTIR) spectrometer (ThermoScientific, Hemel Hempstead, UK) coupled to a Specac Golden Gate ATR supercritical fluid analyser (Specac, Slough, UK) was used to record the spectra of the homopolymers and blends prior to and following annealing. Spectra were recorded at room temperature with a resolution of 4 cm^{-1} . To achieve an acceptable signal to noise ratio 100 scans were recorded. Spectra were also collected over time using a heated ATR top-plate (Specac supercritical fluid heated top-plate) in conjunction with the FTIR in order to detect possible degradation of the samples. The samples were monitored at 250 °C for 90 minutes with a 2 cm^{-1} resolution.

3.0 Results and Discussion

3.1 Dynamic mechanical properties of unannealed PP/PC blends

The DMTA spectra of the loss tangent against temperature for the unannealed PC/PP blends showed several distinct relaxations (Figure 1). Pure PC displayed a maximum in $\tan \delta$ between 140 and 160 °C which is indicative of an α relaxation and therefore the glass transition of PC [13, 15]. The two peaks detected at lower temperatures (11 °C and 83 °C) can

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3 be attributed to the β relaxation and α relaxation of the PP component, respectively [13]. The
4
5 β relaxation at 10.7°C is associated with the glass transition of the amorphous phase [16-17]
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7 whereas the small α relaxation peak appears as a shoulder and corresponds to a lamellar-slip
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9 mechanism and rotation in the crystalline phase [17-18]. As expected the intensities of each
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11 of these three peaks were seen to diminish as the polymer concentration within the blend
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13 reduced.
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19 The composition dependence of the maximum intensity of the loss tangent α relaxation
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21 peak in PC was analysed (Figure 2). As expected the intensity of the peak was found to
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23 decrease with a reduction in PC content. This is a dilution effect created by the increasing
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25 presence of PP [19]. Moreover, it is apparent that there is a pronounced negative deviation
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27 from the line that represents linear additivity suggesting partial dissolution of PC into the PP
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29 phase.
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35 The point at which each maximum occurs corresponds to the α and β relaxation
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37 temperatures for PC, PP and the blends as shown in Table 1. No systematic variation in the α
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39 and β relaxation temperatures with blend composition was found. As these transitions
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41 correspond to the T_g of the materials, this lack of shift, together with the observation of two
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43 distinct relaxations, suggests that the blend systems are immiscible [19,20]. It was not
44
45 possible to resolve the peak temperatures for the α and β relaxations in the PP blend
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47 component at 90/10 (PC/PP) because the associated peaks were extremely broad. However,
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49 in the remaining blends, the temperatures associated with the α relaxation of PP were found
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51 to rise slightly with increasing PC content. Although this suggests some degree of partial
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53 dissolution of PC into the PP rich phase [19] it is more probable that there is constraint of the
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3 PP chains by the PC region, thereby resulting in an increase in the temperature at which the α
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5 relaxation occurs.
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10 The frequency dependence of the α relaxation in the PC component was probed using an
11 Arrhenius approach [21]. Plots of the natural logarithm of the applied frequency against the
12 reciprocal of the measured relaxation temperature were constructed and found to be linear.
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14 Activation energies between 600 and 1000 kJ mol⁻¹ were obtained by multiplying the
15
16 gradient of these plots by the gas constant. The variation in the calculated activation energy
17
18 with composition can be seen in Figure 3. It is apparent that the activation energy of the α
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20 relaxation in PC rises with increasing content. Furthermore, this trend reflects that shown in
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22 Figure 2, in that a negative deviation from the trend line is observed at low PC contents
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24 suggesting some degree of miscibility.
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32 **3.2 Development of miscibility in annealed PP/PC blends**

33 **3.2.1 Effect of annealing on morphology of blends**

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36 SEM micrographs of the blend containing 7.5% PC both prior to, and following,
37
38 annealing are shown in Figure 4. It can be seen that the boundaries between the polymer
39
40 phases are very well defined prior to annealing, whereas there is evidence of localised
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42 adhesion post-annealing. This suggests that the PC particles may undergo some chain
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44 entanglement with the PP chains in the matrix. Accordingly, it can be inferred that partial
45
46 miscibility has developed during the annealing of the 7.5% PC blend. Similar images were
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48 also obtained for the blends containing other compositions.
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54 The glass transition temperatures of both the PP and PC components of the annealed
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56 blends were determined by DMTA and plotted against composition (Figure 5). After
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annealing, two glass transitions were again visible, however in contrast to the unannealed blends (Table 1), the temperatures at which these transitions occurred was found to vary with composition. This observation is in accordance with the development of adhesion between the phases (Figure 4), and therefore constitutes further evidence of the development of partial miscibility in this blend system following annealing. In general, the change in T_g for both PP and PC follows a linear trend; however a deviation seen at low PC concentrations suggests a region of increased miscibility [10, 22].

3.2.2 Measurement of miscibility in annealed PC/PP blends

The interaction between the components of a polymer blend can be determined from the composition dependence of the glass transition temperature. If two polymers are completely miscible only one T_g occurs with its position determined by the composition of the blend. However, when two partially compatible polymers are blended, the glass transition temperatures of each component shift towards each other with the degree of movement dependent on both the concentration of the blend and the degree of miscibility [23]. DMTA analysis gave values for the T_g of the PC/PP blends after annealing (Figure 5). When the content of the PC component was more than 50 %, it was difficult to determine the glass transition temperature of PP due to the broad shape of $\tan\delta$. Thus this section focusses on the annealed blends with PC concentrations up to 50 %.

Theoretically, when two polymers are completely miscible, the T_g of the blend can be estimated by the Fox [24] equation, as follows;

$$\frac{1}{T_g^b} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (1)$$

where W_1 and W_2 are the weight percentages of polymers 1 and 2; T_{g1} , T_{g2} and T_g^b are the glass transition temperatures of each composition in isolation and the blend, respectively.

The Fox equation is commonly only applied to miscible polymers; however this theory can also be expanded to partially miscible blends. If two polymers are partially miscible, two phases will exist following processing: a polymer-1 rich phase and a polymer-2 rich phase. If no further phase separation occurs, each of these phases may be considered as totally miscible systems. Therefore the Fox equation (1) will be applicable to each phase and the weight fraction of component 1 in the polymer-1 rich phase can be calculated as [25];

$$W_{11} = \left[\frac{T_{g1}(T_{g1}^b - T_{g2})}{T_{g1}^b(T_{g1} - T_{g2})} \right] \quad (2)$$

where subscript 1 and 2 represent the polymer 1-rich phase and polymer 2-rich phase, respectively; W_{11} is the apparent weight fraction of polymer 1 in the polymer 1-rich phase and T_{g1}^b is the observed T_g of the polymer 1-rich phase in the blend.

Similarly, the weight fraction of polymer 1 in the polymer-2 rich phase can be determined as:

$$W_{12} = \left[\frac{T_{g1}(T_{g2}^b - T_{g2})}{T_{g2}^b(T_{g1} - T_{g2})} \right] \quad (3)$$

where W_{12} is the apparent weight fraction of polymer 1 in the polymer 2-rich phase and T_{g2}^b is the observed T_g of the polymer 2-rich phase in the blend. Comparison of the T_g s of PC and PP in the annealed blends allows the apparent weight fractions of the PC and PP components dissolved in each phase to be estimated. By applying Equation 3, the apparent weight fraction of PC in the PP-rich phase (W_{12}) and PP in the PC-rich phase (W_{21}) were calculated (Table 2).

Following this, the apparent volume fraction (ϕ) of each polymer in each phase could then be calculated (Equation 5 and 6):

$$\phi_{12} = [(W_{12} / \rho_1) / (W_{12} / \rho_1 + W_{22} / \rho_2)] \quad (4)$$

$$\phi_{21} = [(W_{21} / \rho_2) / (W_{21} / \rho_2 + W_{11} / \rho_1)] \quad (5)$$

where ϕ_{12} is the apparent volume fraction of PC dissolved in the PP-rich phase, ϕ_{21} is the apparent volume fraction of PP dissolved in the PC-rich phase and ρ is the density of the respective polymers.

The miscibility of PC and PP after annealing can be examined by plotting the volume fraction of each polymer in the other phase as a function of PC concentration, (Figure 6). The volume fractions of PC within the PP-rich phase are considerably greater than the reverse, although the latter are not zero, as expected for totally incompatible blends. In the composition range studied, it is PC which shows the greater capacity to be incorporated and diluted within the PP-rich phase of the annealed blends with very little dissolution of PP occurring in PC. A linear decrease in the volume fraction is to be expected as the concentration of the minor component is reduced, however the large drop observed with 7.5 % PC suggests a region of greater miscibility as discussed previously.

3.2.3 Polymer-polymer interaction parameter of annealed PC/PP blends

From the discussion above, partial miscibility has been deduced in the annealed PC/PP blends. In such cases the approach developed by Kim and Burns [25-27] can be used to calculate the Flory-Huggins polymer-polymer interaction parameter (χ_{12}) (Equation 6). The theory of Kim and Burns is applicable to partially miscible systems in the absence of solvents and assumes that the equilibrium state has been accomplished.

$$\chi_{12} = \frac{\{(\phi_{11}^2 - \phi_{12}^2)[m_2 \ln(\phi_{12} / \phi_{11}) + (m_1 - m_2)(\phi_{21} - \phi_{22})] + (\phi_{21}^2 - \phi_{22}^2)[m_1 \ln(\phi_{22} / \phi_{21}) + (m_2 - m_1)(\phi_{11} - \phi_{12})]\}}{2m_1 m_2 (\phi_{11}^2 - \phi_{12}^2)(\phi_{21}^2 - \phi_{22}^2)} \quad (6)$$

where ϕ_{11} and ϕ_{22} are the apparent volume fractions of PC dissolved in the PC-rich phase and that of PP dissolved in the PP-rich phase; $\phi_{11} = 1 - \phi_{21}$; $\phi_{22} = 1 - \phi_{12}$; m_1 and m_2 are the number-average degrees of polymerisation of pure PC and PP, respectively.

The values of m_1 and m_2 can be obtained from the following relationships: $m_1 = V_1 / V_0$ and $m_2 = V_2 / V_0$, where V_1 and V_2 are the molar volume of PC and PP respectively. V_0 is a fictitious molar volume of one submolecule of polymer. The repeat unit of PP has been chosen as a lattice-site volume. The values of $m_1 = 4.19 \times 10^2$ and $m_2 = 1.18 \times 10^3$ were calculated for the PC and PP components, respectively.

Calculation of the interaction parameters of the annealed PP-PC blends showed very low, positive values for each composition (Table 2). In general, a large negative χ_{12} is associated with strong specific interactions, i.e. polymer miscibility; while a large positive value indicates immiscibility. Relatively low positive values, as seen here, indicates a degree of interaction and therefore partial miscibility between PC and PP. The interaction parameter was found to rise as the PC concentration within the blend increased indicative of the blends becoming less miscible. This is consistent with the sharp reduction in both the T_g and soluble weight fraction of PC at low PC concentrations.

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3 A more accurate method to determine the miscibility of a polymer blend is to compare
4 the interaction parameter with the critical interaction parameter as defined by Scott [28]. The
5 critical value of χ_{12} , $(\chi_{12})_{critical}$ is calculated as:
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$$(\chi_{12})_{critical} = \frac{1}{2} (m_1^{-1/2} + m_2^{-1/2})^2 \quad (8)$$

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12 The condition $(\chi_{12})_{critical} / \chi_{12} = 1$ corresponds to the transition of a polymer system from a
13 stable to a metastable state. Therefore, $\chi_{12} < (\chi_{12})_{critical}$ is a condition for the miscibility of
14 components in a blend. It has been suggested that if $\chi_{12} < (\chi_{12})_{critical}$ the polymers will be
15 miscible and no phase separation will occur. The larger the difference between the two values,
16 the wider the composition dependent miscibility window. If $\chi_{12} > (\chi_{12})_{critical}$ the polymers
17 will be immiscible and results in the occurrence of two distinct phases [29].
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30 The critical interaction parameter of the annealed PC/PP blends was calculated to be
31 3.05×10^{-3} . Each of the annealed blends studied possessed interaction parameters greater than
32 this value (Table 2) which is indicative of partially miscible or immiscible blends. These
33 results are consistent with the experimental data predicting a partially miscible blend.
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42 3.3 Time-resolved FTIR spectroscopy of the annealing process in PC/PP blends

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44 FTIR spectroscopy was used to monitor any chemical changes in the blends during the
45 annealing process. Initial experiments were conducted on the homopolymers, PC and PP. The
46 infra-red spectrum obtained from PC remained the same during the annealing process
47 indicating no significant chemical change in the polymer (data not shown). This is consistent
48 with the idea that PC is a thermally stable material. In contrast, the infra-red spectrum for PP
49 was found to change considerably during annealing (Figure 7). It is clear that a series of new
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4 bands appear in the region 1600 to 1800 cm^{-1} after 60 minutes annealing. This observation
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6 has been reported previously and attributed to the oxidation of PP, initiated from the surface
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8 of the material [30]. The by-products of the degradation process have been shown to be
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10 composed of many carbonyl containing species such as α,β -unsaturated ketones (1690 cm^{-1}),
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12 carboxylic acids (1710 cm^{-1}), methyl ketones (1720 cm^{-1}), aldehydes (1725 cm^{-1}), esters (1745
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14 cm^{-1}), and lactones (1780 cm^{-1}) [31].
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21 The FTIR spectra of the 7.5% PC blend before and after annealing are shown in Figure 8.
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23 It is again apparent that the PP component in the blend is sensitive to degradation, i.e.
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25 numerous bands appear following annealing. Particularly prominent is the development of the
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27 carbonyl band at 1774 cm^{-1} . To enable comparison of the effects of annealing on each blend
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29 the ratio of this carbonyl peak to a reference peak was calculated. The carbon-carbon
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31 vibrational band centred at 841 cm^{-1} was used as a reference as it remained unaffected by the
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33 annealing process [32]. The ratio of the intensity of these bands was found to increase from
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35 0.196 to 0.457 for the 7.5% PC blend after annealing, and from 0.573 to 0.757 for 30% PC.
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37 This highlights that the degradation process is more pronounced in the 7.5% blend than in the
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39 30% blend.
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46 Prior to annealing, the blend has been shown to be immiscible. However, the annealing
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48 process causes the PP component to degrade, which is accompanied by the formation of a
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50 range of functional groups, many of which are polar. The polar nature of these new groups
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52 offers regions for the PP component to interact with PC. The degradation of PP may also
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54 result in the formation of esters [33]. The presence of such functional groups within the PP
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56 component offers the possibility of transesterification between the degraded PP and the PC
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3 components. Given the fact that the blend was found to immiscible prior to annealing, such
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5 reactions would be limited to the interface between the phases. The result would be the
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7 formation of regions of adhesion between the phases as observed in Figure 4b.
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10 11 12 **4.0 Conclusions**

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14 The blending of polypropylene and polycarbonate has been evaluated. The glass
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16 transition temperatures of PP and PC, as analysed by DMTA, were unaffected by blending
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18 suggesting immiscibility. Following annealing at 250 °C for 90 minutes, sites of adhesion
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20 between the phases were observed. The glass transition temperatures were also found to
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22 converge following annealing pointing to the development of partial miscibility. These shifts
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24 in glass transition temperature were analysed in terms of the Flory-Huggins and Kim-Burns
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26 theories and the calculated interaction parameter was positive which supported the
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28 interpretation of partial miscibility. A study of the annealing process using time-resolved
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30 FTIR spectroscopy provided an explanation of why the blend components were able to
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32 participate in some degree of blending. The annealing process was found to cause PP to
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34 degrade. The degradation pathway involved the formation of polar groups which were able to
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36 participate in 'favourable interactions' with PC and thereby create regions of partial
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38 miscibility in a blend system that had previously been described as completely immiscible.
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45 46 **5.0 Acknowledgements**

47
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52 technical support and assistance.
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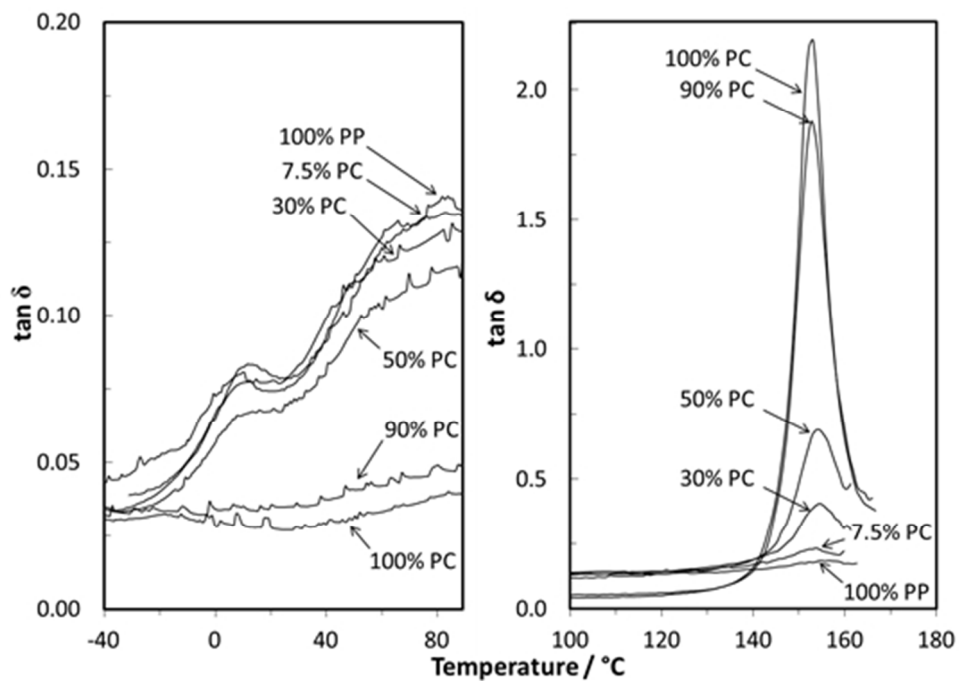


Figure 1. Variation of $\tan \delta$ with temperature for unannealed PC/PP blends of different compositions.

Figure 1

147x107mm (96 x 96 DPI)

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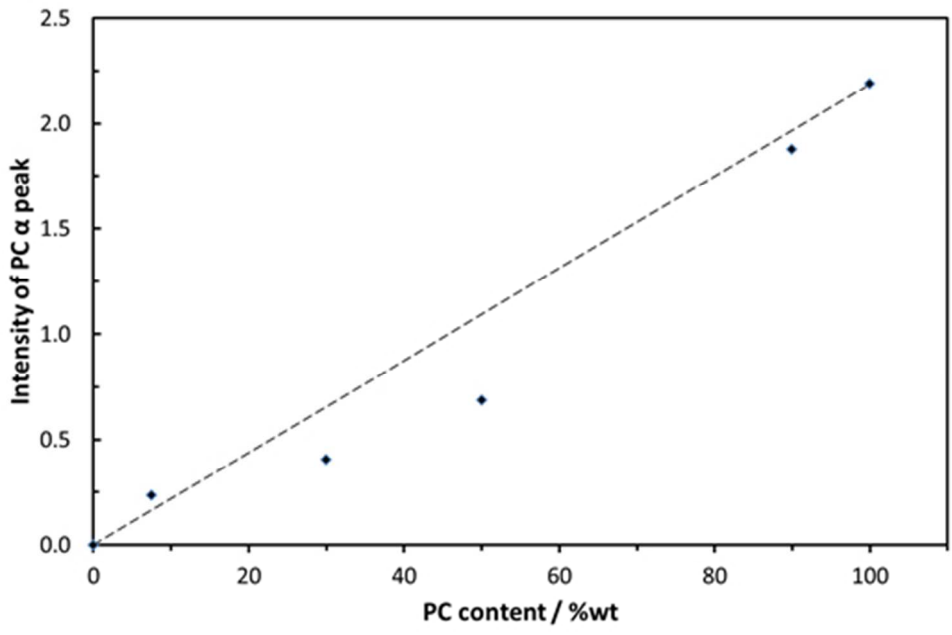


Figure 2. Maximum intensity of the PC α peak temperature as a function of PC composition in the unannealed PC/PP blends.

Figure 2
143x94mm (96 x 96 DPI)

www Only

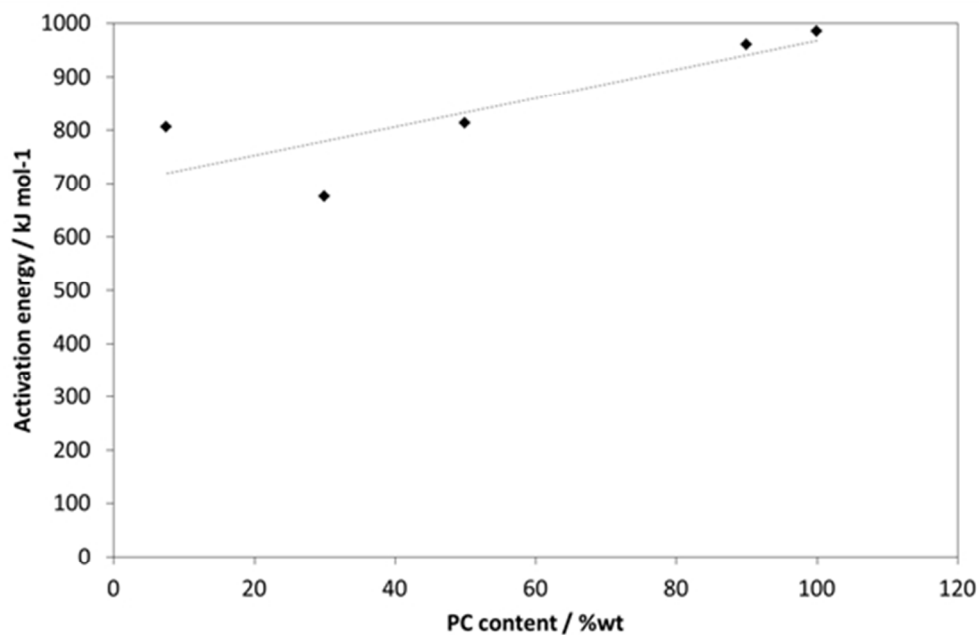


Figure 3. Variation in the activation energy of the α relaxation of PC with PC content for unannealed PC/PP blends.

Figure 3
149x97mm (96 x 96 DPI)

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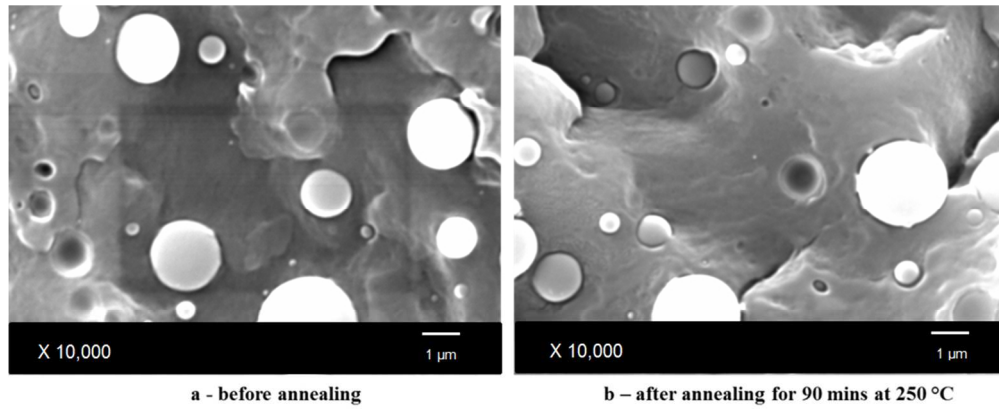


Figure 4. SEM micrographs of a PP blend containing 7.5% PC before and after annealing.
Figure 4
289x117mm (96 x 96 DPI)

Review Only

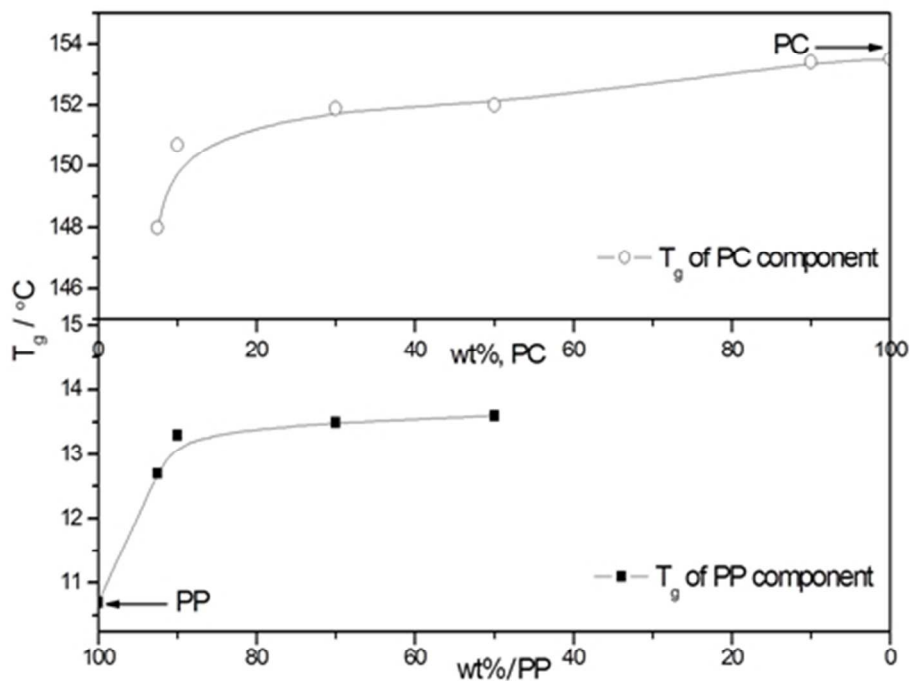


Figure 5. Variation of the glass transition temperatures with composition in annealed PC/PP blends.

Figure 5

135x107mm (96 x 96 DPI)

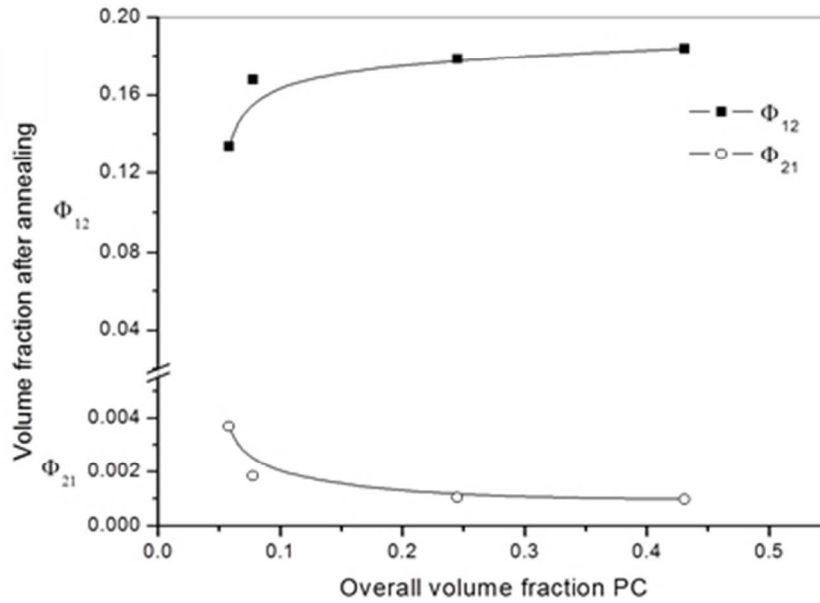


Figure 6. Volume fractions of each polymer in the opposite rich-phase as a function of PC content in the annealed PC/PP blends.

Figure 6
127x93mm (96 x 96 DPI)

Only

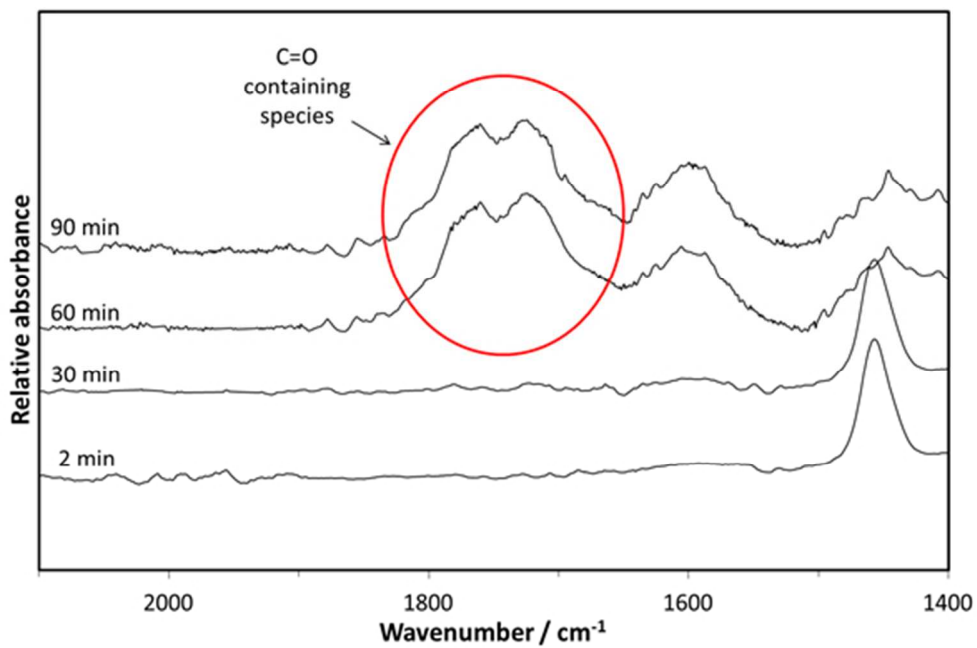


Figure 7. Selected time-resolved spectra of pure PP during annealing at 250 °C.

Figure 7

159x103mm (96 x 96 DPI)

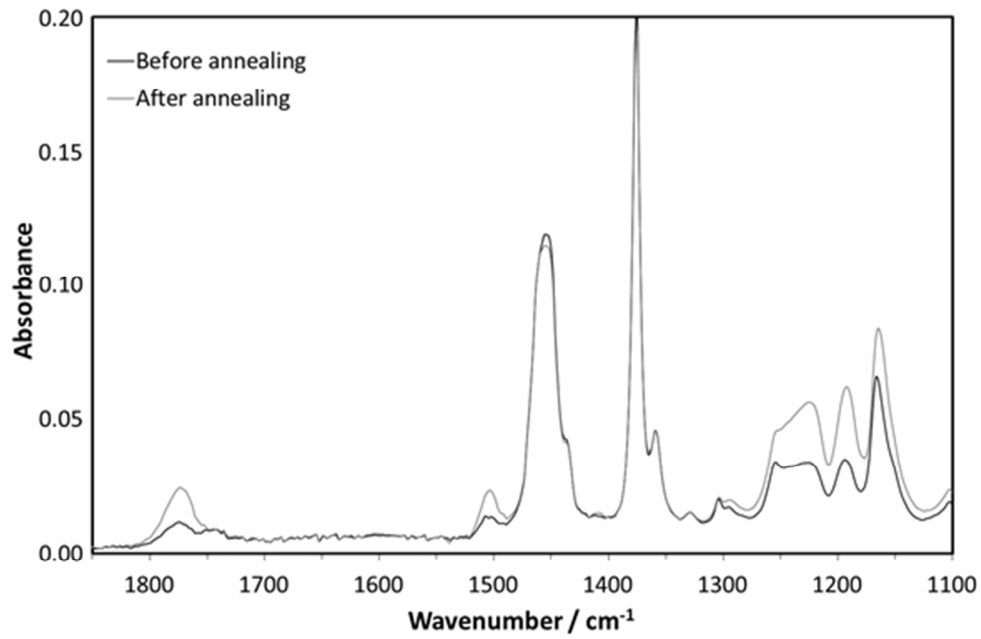


Figure 8. IR spectra of a PP blend containing 7.5% PC before and after annealing.

Figure 8

159x105mm (96 x 96 DPI)

Table 1 Variation in $\tan \delta$ peak temperature with composition for unannealed PC/PP blends.

| PC content / wt % | Relaxation Temperature / ± 0.1 °C | | |
|----------------------|---------------------------------------|---------------------------|---------------------------|
| | PP β relaxation | PP α relaxation | PC α relaxation |
| 0 | 10.7 | 82.8 | - |
| 7.5 | 12.5 | 83.7 | 153.6 |
| 30 | 11.6 | 85.2 | 154.6 |
| 50 | 13.2 | 87.3 | 154.4 |
| 90 | - | - | 153.1 |
| 100 | - | - | 153.5 |

Table 2 Glass transition temperatures, apparent weight and volume fractions of each component in the PC-rich and PP-rich phases and the polymer-polymer interaction parameter (χ_{12}) of the annealed PC/PP blends

| PC content / wt % | T_{g1}^b /°C | T_{g2}^b /°C | w_{12} | w_{21} | ϕ_{12} | ϕ_{21} | $\chi_{12} \pm 0.01$ (10^{-3}) |
|-------------------|-------------------|-------------------|----------|----------|-------------|-------------|---------------------------------------|
| 7.5 % | 148.0 | 12.7 | 0.169 | 0.0028 | 0.134 | 0.0037 | 5.38 |
| 10 % | 150.7 | 13.3 | 0.210 | 0.0014 | 0.168 | 0.0024 | 5.50 |
| 30 % | 151.9 | 13.5 | 0.223 | 0.0008 | 0.178 | 0.0011 | 5.70 |
| 50 % | 152.0 | 13.6 | 0.229 | 0.0007 | 0.184 | 0.0010 | 5.71 |