

MISCIBILITY STUDIES OF PC/PMMA BLENDS IN TETRAHYDROFURAN BY VISCOMETRY, FTIR AND SEM ANALYSIS

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The coefficients of viscosity for polycarbonate/poly(methyl methacrylate) (PC/PMMA) blends in tetrahydrofuran at 303.15 K and 313.15 K have been measured. The measured parameters were used to estimate other related physical quantities, like Huggins constants and the interaction parameters μ and α , proposed by Chee and Sun et al. to identify the molecular interaction arising in solutions of the mentioned polymer blends. The peculiar deviation confirmed the structural changes in the solutions of the blends. FTIR and SEM studies confirm the formation of physical blends.

Keywords: Viscosity, polymer blends, Polycarbonate (PC), Poly(methyl methacrylate) (PMMA), molecular interaction, FTIR, SEM.

1. Introduction

In continuation of our work [1] on the miscibility study of poly(vinyl chloride)-poly(methyl methacrylate) PVC/PMMA blends by viscometry and other analytical methods, we have now studied the miscibility of PC/PMMA blends in THF by viscometry, FTIR and SEM analysis. Polymer blending is one of the most important contemporary methods for the development of new polymeric materials. Schurer et al. [2] studied the addition of monomeric and polymeric methyl methacrylate to improve the thermal and mechanical properties of poly(vinyl chloride) (PVC), who concluded that PVC was partially miscible with atactic and syndiotactic PMMA, but almost completely immiscible with isotactic PMMA. Polymers play an important role in all branches of industry today. The miscibility characteristics of methylcellulose (MC) and poly(vinyl alcohol) (PVA) have been investigated by viscometry, ultrasonic velocity, density and refractometric techniques at 30 °C and 40 °C. Methylcellulose/ poly(vinyl alcohol) blend films were prepared by the solution casting method and studied by scanning electron microscopy (SEM) [3]. PVC/ PMMA polymer blends were characterized at the molecular level by FTIR-ATR spectroscopy, providing important insight into the molecular interactions responsible for the enhancement of its mechanical properties. The changes in mechanical properties are reflected by the changes in the FTIR-ATR spectrum. The mechanical properties of such polymer blends revealed a substantial increase in the Young's modulus and ultimate tensile strength after an initial drop at 10% PMMA. A comparative study of the mechanical properties of PVC/ PMMA polymer blends with different weight percentages was carried out and their results were correlated with FTIR – ATR spectral studies, allowing important conclusions to be drawn about the possible molecular interactions between the constituent polymers [4]. The manifestation of superior properties depended upon the miscibility of the homo-polymers at the molecular scale. The miscibility resulted in different blend morphologies, ranging from a single phase system to a two- or multiphase systems. Polymer nanocomposites prepared by melt compounding using a

Twin screw extruder [5] exhibited superior mechanical, electrical, thermal, and morphological properties, as shown by DSC, TGA, FTIR and SEM analyses. The basis of polymer-polymer miscibility may arise from several different interactions, such as hydrogen bonding, dipole-dipole forces, and charge transfer complexes for homo-polymer mixtures. In the present case, FTIR study showed that PC/PMMA blends are physical blends, because there is no obvious interactions between the components. SEM studies supported the formation of physical blends of PC and PMMA.

2. Experimental

Viscometry:– PC (From Chennai Cipet India) and PMMA (grade LG 2 Sumitomo chemical Singapore), tetrahydrofuran from Fisher Scientific was used after purification by fractional distillation. A dilute polymer solution of 1% w/v was prepared for viscometric studies. Stock solutions of polymers and the blends of PC/PMMA of different compositions, 0/100, 20/80, 40/60, 60/40, 80/20 and 100/0 were prepared in tetrahydrofuran. Viscosity measurements at 303.15 K and 313.15 K were carried out using an Ostwald viscometer. The total weight of the two components in the solution was always maintained at 1 g/dL. Different temperatures were maintained in a thermostat-regulated bath, with a thermal stability of ± 0.05 K.

FTIR and SEM analysis:– The remaining stock solutions for viscometric experiments were mixed at room temperature and stirred for several hours. The solutions were then placed in a glass petri-dish separately and THF was slowly evaporated under ambient conditions. The resulting polymer and polymer blends were dried in a hot air oven for 24 hours. The film of component polymers and their blends were stored properly for FTIR scanning and SEM analysis. FTIR experiments were performed on thin films using an FTIR spectrophotometer (FTIR spectrometer spectrum Perkin elmer 400) from Punjab University Chandigarh (India). SEM experiments were carried out using thin films of polymers (PC and PMMA) and their blends (PC/PMMA) of different compositions by a scanning electron microscope (ZEOL JSM6610 LV) from IIT Roper (India).

3. Results and discussion

Viscometry is a simple and effective technique for monitoring the interactions in polymer blend solutions. From viscometric measurements, the relative and reduced viscosities of pure polymers and their blends were obtained. Figures 1 and 2 shows the Huggins plots for the PC/PMMA at 303.15 K and 313.15 K for different weight fractions of polymer 1 and polymer 2 ($W_1 : W_2$), respectively. The K_H values were determined by extrapolation to infinite dilution of the Huggin's plots and the values of b are the slopes of the plots. This has been compared to the calculated results obtained from Huggins equation. The figure indicates a considerably higher slope variation for PC/PMMA blend compositions. This may be attributed to the mutual attraction of macromolecules in solution, because of the increase of hydrodynamic and thermodynamic interaction. Hence, the PC/PMMA blend was found to be miscible. Below this critical concentration, a sharp decrease in the slope was observed in the Huggin's plot because of phase separation. To quantify the miscibility of the polymer blends Chee (1990) [6] suggested that the general expression for the interaction parameter when polymers are mixed in weight fractions, W_1 and W_2 is as follows:

$$\Delta B = \frac{b - \bar{b}}{2W_1W_2},$$

where $\bar{b} = W_1b_{11} + W_2b_{22}$ in which, b_{11} and b_{22} are the slopes of the viscosity curves for the pure components. The coefficient b is related to the Huggins's coefficient K_H as follows:

$$b = K_H[\eta]^2,$$

and for the ternary system, the coefficient b is also given by:

$$b = W_1^2 b_{11} + W_2^2 b_{22} + 2W_1 W_2 b_{12},$$

where b_{12} is the slope for the blend solution. Using these values, Chee (1990) defined a more effective parameter as follows:

$$\mu = \frac{\Delta B}{\{[\eta]_2 - [\eta]_1\}^2},$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The blend is miscible when $\mu \geq 0$ and immiscible when $\mu < 0$.

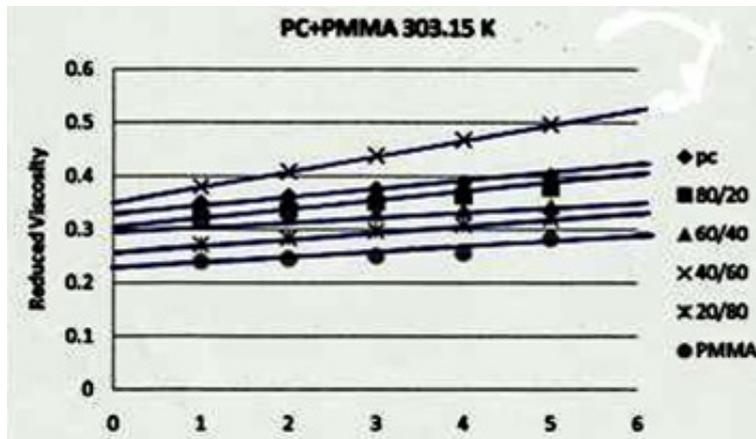


FIG. 1. Plot of η_{sp}/C vs. concentration for PC/PMMA/THF ternary systems at 303.15 K

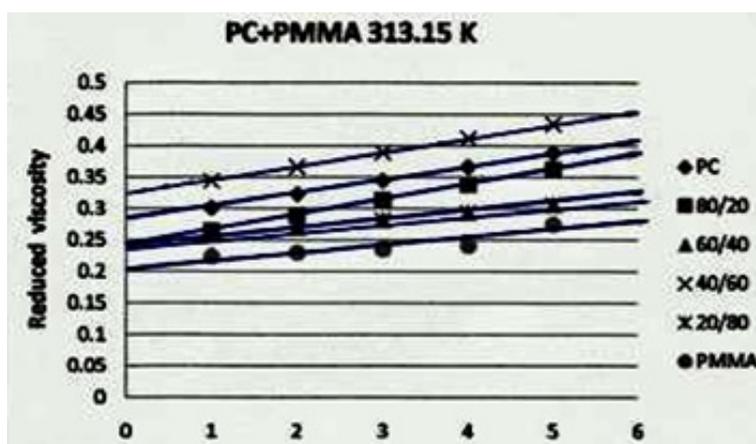


FIG. 2. Plot of η_{sp}/C vs. concentration for PC/PMMA/THF ternary systems at 313.15 K

The reduced viscosity data for PC/PMMA blends at different compositions at 303.15 K and 313.15 K have been recorded in Tables 1 and 2 respectively. Recently, Sun et al. (1992) have suggested a new formula for the determination of polymer miscibility as follows:

TABLE 1. The reduced viscosity data for PC/PMMA and their blends in tetrahydrofuran at 303.15 K at different concentrations

Concentration (g/dl)	PC/PMMA Composition of blends 303.15 K					
	100/0(PC)	80/20	60/40	40/60	20/80	0/100(PMMA)
0.2	0.34980	0.32361	0.31808	0.38129	0.27266	0.24045
0.4	0.36270	0.33702	0.32466	0.41059	0.28470	0.24592
0.6	0.37560	0.35044	0.33125	0.43988	0.29811	0.25133
0.8	0.38850	0.36385	0.33783	0.46918	0.30910	0.25681
1.0	0.40130	0.37727	0.34442	0.498481	0.32177	0.28308

TABLE 2. The reduced viscosity data for PC/PMMA and their blends in tetrahydrofuran at 313.15 K at different concentrations

Concentration (g/dl)	PC/PMMA Composition of blends 313.15 K					
	100/0(PC)	80/20	60/40	40/60	20/80	0/100 (PMMA)
0.2	0.30174	0.26455834	0.258320529	0.344648392	0.258359487	0.22441
0.4	0.32354	0.28913833	0.270324026	0.367186064	0.270326697	0.23009
0.6	0.34533	0.31371831	0.282327523	0.389723736	0.282293899	0.23577
0.8	0.36713	0.33829830	0.29433102	0.412261408	0.294261108	0.24145
1.0	0.38893	0.36287829	0.306334518	0.434799081	0.306228314	0.27543

$$\alpha = k_m - \frac{k_1[\eta]_1^2 W_1^2 + k_2[\eta]_2^2 W_2^2 + 2\sqrt{k_1 k_2}[\eta]_1[\eta]_2 W_1 W_2}{\{[\eta]_1 W_1 + [\eta]_2 W_2\}^2},$$

where k_1 , k_2 and k_m are the Huggins's constants for individual components 1, 2 and the blend respectively. Long-range hydrodynamic interactions were considered while deriving this equation. Sun et al. (1992) have suggested that a blend will be miscible when $\alpha \geq 0$ and immiscible when $\alpha < 0$.

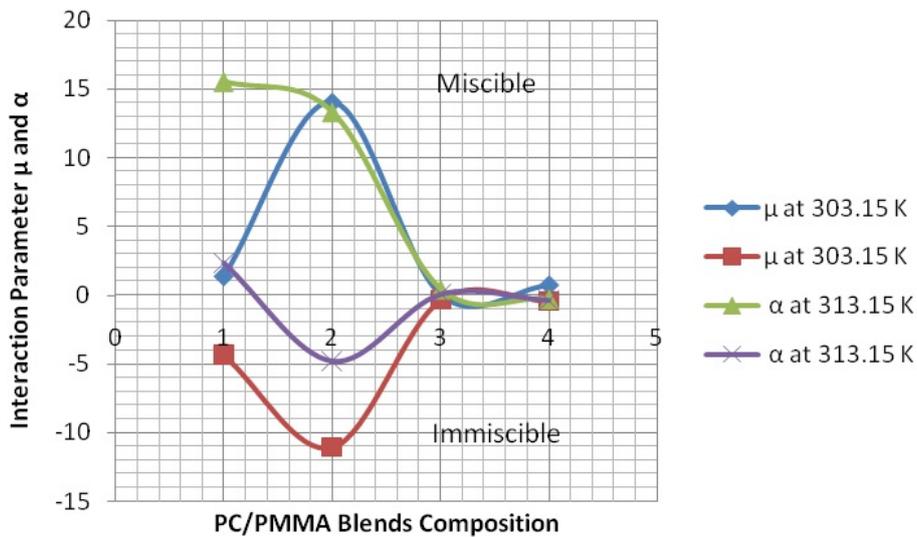
FTIR analysis:– The FTIR spectra of PC and PMMA are shown in Fig. 4 and 9. The IR spectrum of PMMA showed absorption bands at 2951 and 1736 cm^{-1} due to $-\text{CH}_3$ asymmetric stretching and C=O stretching respectively. The IR bands at 1481 and 1449 cm^{-1} were due to CH_2 scissoring and CH_3 asymmetric stretching. The characteristic peak at 1386 cm^{-1} appeared due to O- CH_3 deformation. C-O stretching resulted in the peak at 1271 cm^{-1} . O- CH_3 stretching resulted in a peak at 1148 cm^{-1} , while the peak at 752 cm^{-1} was due to the CH_2 rocking mode of vibration. Spectrum 1, was comparable to that of earlier reports [5,6]. The IR spectrum of PC showed absorption bands at 2968 cm^{-1} attributed to $-\text{CH}_3$ stretching vibration. Characteristic C=O stretching band was at 1773 cm^{-1} . The ring (C-C) vibrational mode appeared at 1507 cm^{-1} . Peaks at 1082 and 1013 cm^{-1} were attributed to C-C-C (bending)

TABLE 3. Interaction parameters and Huggins's constants of PC/PMMA blends at 303.15 K

PC/PMMA 303.15 K	$[\eta]$	K_H	μ	α
100/0(PC)	0.33668	0.57181	–	–
80/20	0.31019	0.69711	1.38991	0.075999
60/40	0.311492	0.33934	-4.35556	-0.34108
40/60	0.35199	1.182301	15.55101	0.42952
20/80	0.26047	0.90384	2.35459	0.061105
0/100(PMMA)	0.22615	0.95694	–	–

TABLE 4. Interaction parameters and Huggins's constants of PC/PMMA Blends at 313.15 K

PC/PMMA 313.15 K	$[\eta]$	K_H	μ	α
100/0(PC)	0.27995	1.39054	–	–
80/20	0.23997	2.13406	14.06064	0.74914
60/40	0.24631	0.989210	-11.07531	-0.38944
40/60	0.32211	1.08609	13.34568	-0.28553
20/80	0.24639	0.985617	-4.81296	-0.378072
0/100(PMMA)	0.206702	1.35465	–	–

FIG. 3. Effect of temperature on the interaction parameter μ and α of PC/PMMA blend in at 303.15 K and 313.15 K

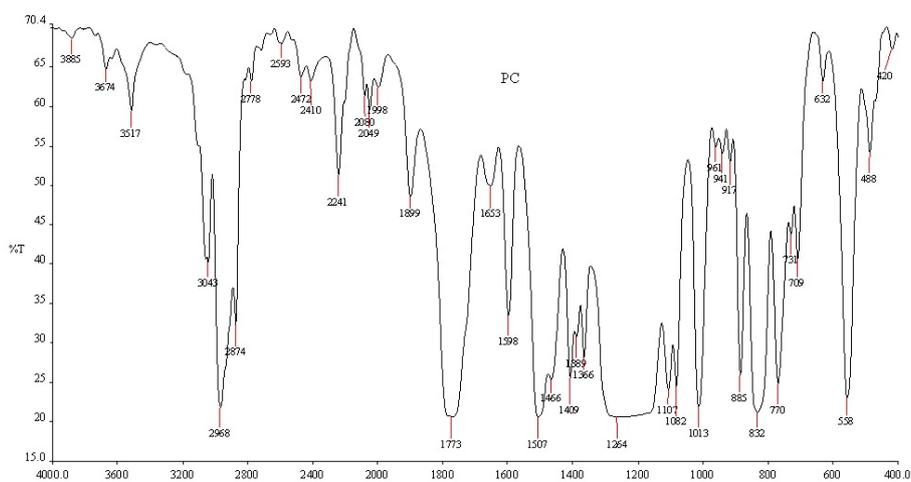


FIG. 4. PC

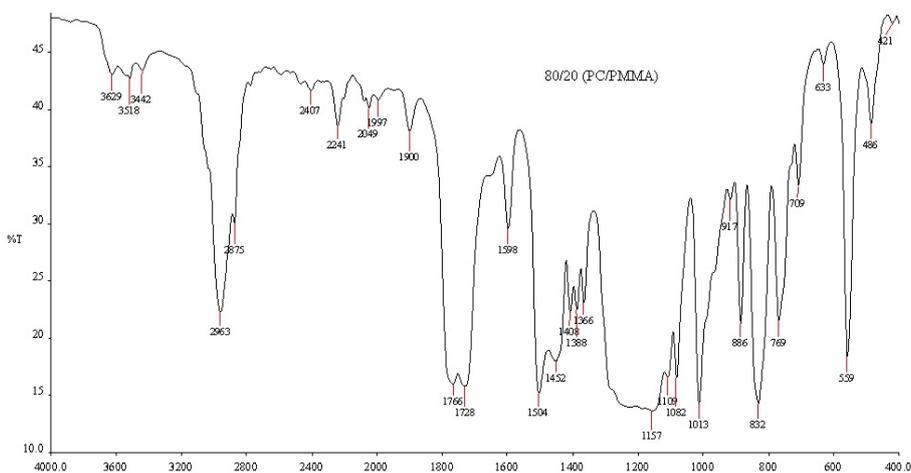


FIG. 5. PC/PMMA(80/20)

O–C–O stretching vibrational modes. These results were comparable to those given by Silverstein and Bassler [9] and Schnell [10]. Figures 5, 6, 7, 8 show the FTIR spectra of PC/PMMA blends with (80/20, 60/40, 40/60, and 20/80 %w/w) compositions respectively. These data showed that the blends did not indicate the existence of any chemical interaction between the components. A thorough analysis of the IR spectra for these blends showed a decrease in the transmittance of the carbonyl and methoxyl stretching of PMMA with an increase in the PMMA content and an increase in the transmittance of these peaks with an increase in the PC content. These data clearly indicate the formation of polymer blends, as there are no shifts in the peaks of any of these functional group in the PC/PMMA blend spectra, it may be concluded that there is no such chemical interaction between component polymers. Thus, these are certainly physical blends.

SEM analysis:– The scanning electron microscope (SEM) images the surface of a sample by scanning it with a high energy beam of electrons in a raster scan pattern. These electrons interact with surface atoms of sample, producing signals which reveal information about the surface topography of sample.

Figures 10 and 15 show the SEM images of PC and PMMA respectively. Fig. 11, 12, 13, and 14 exhibit SEM images of blends PC/PMMA of 80/20, 60/40, 40/60, and

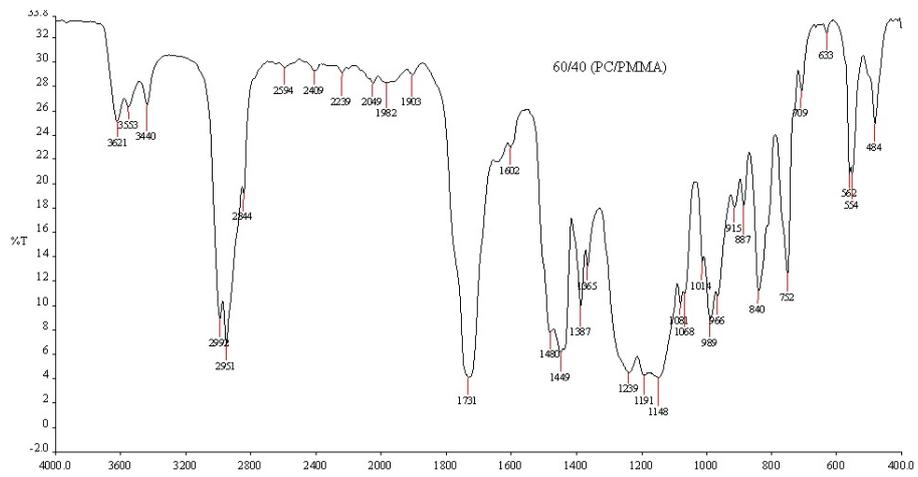


FIG. 6. PC/PMMA(60/40)

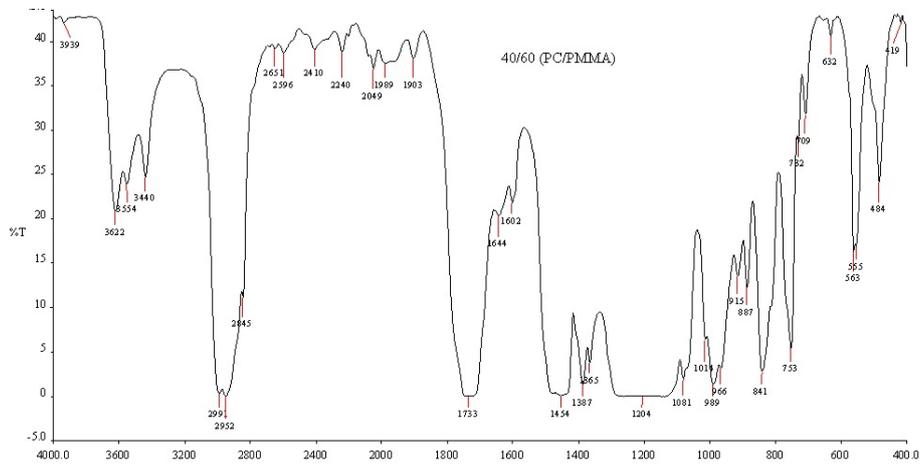


FIG. 7. PC/PMMA(40/60)

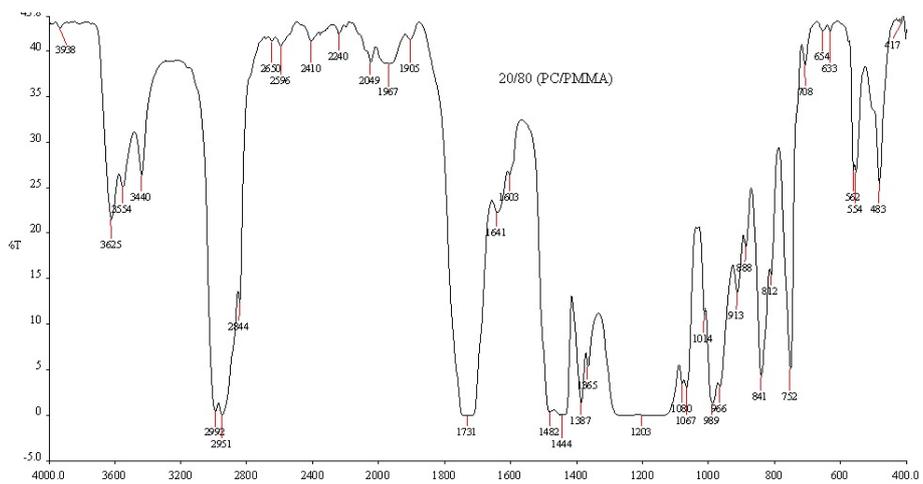


FIG. 8. PC/PMMA(20/80)

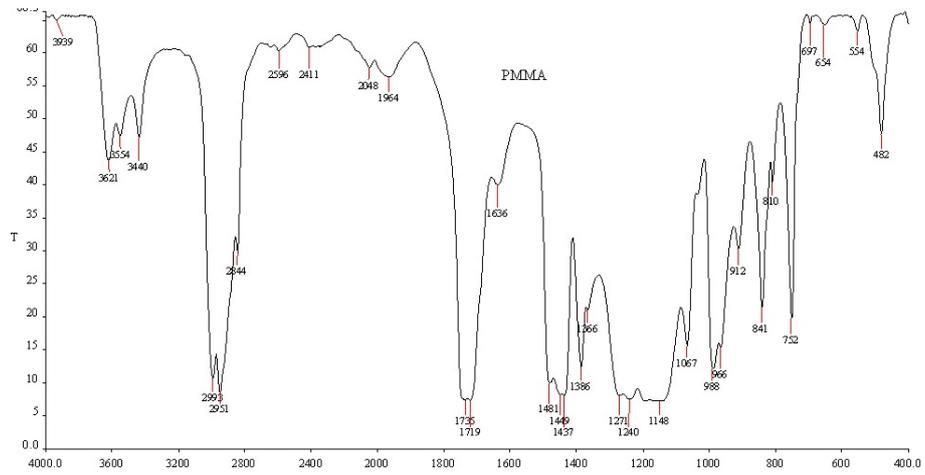


FIG. 9. PMMA

20/80 w/w % compositions respectively. The SEM images of each have been shown in three different magnifications. As can be seen from the images of blends, they show uniform morphological features without any phase separation. This shows the miscibility of blends to a large extent [9].

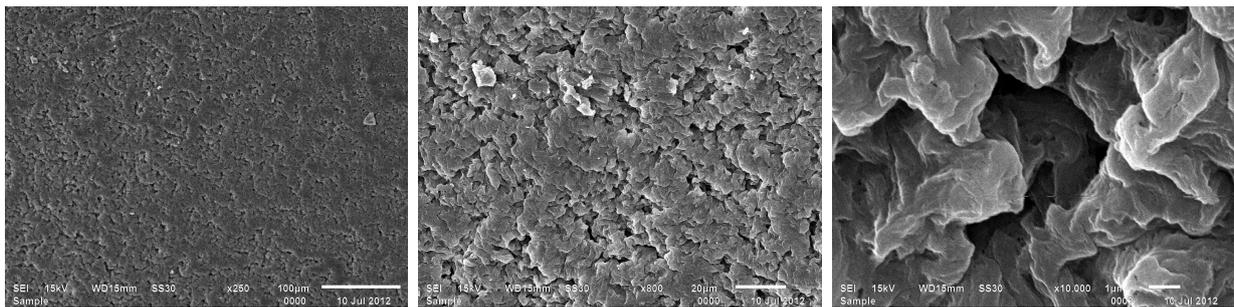


FIG. 10. PC

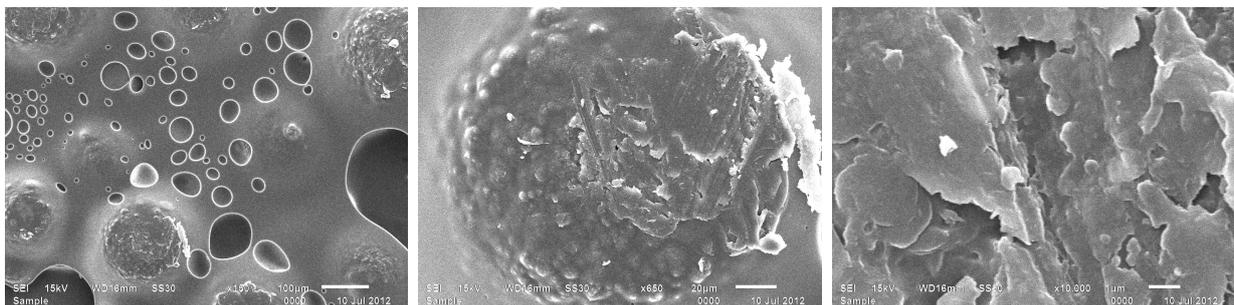


FIG. 11. 80/20(PMMA/PC)

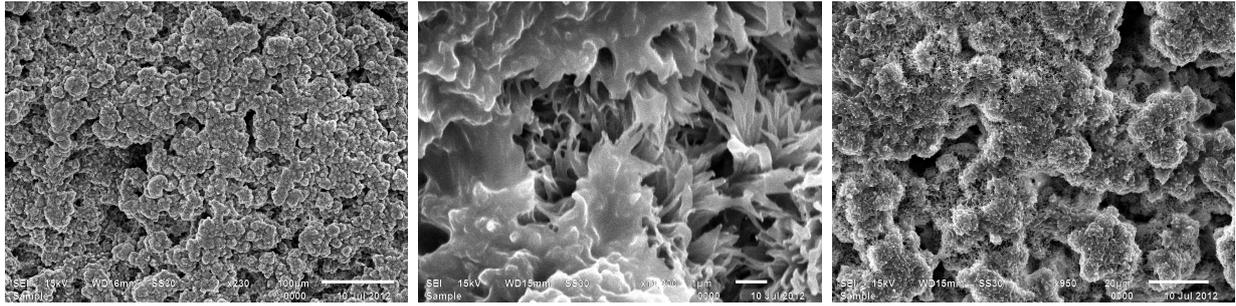


FIG. 12. 60/40(PMMA/PC)

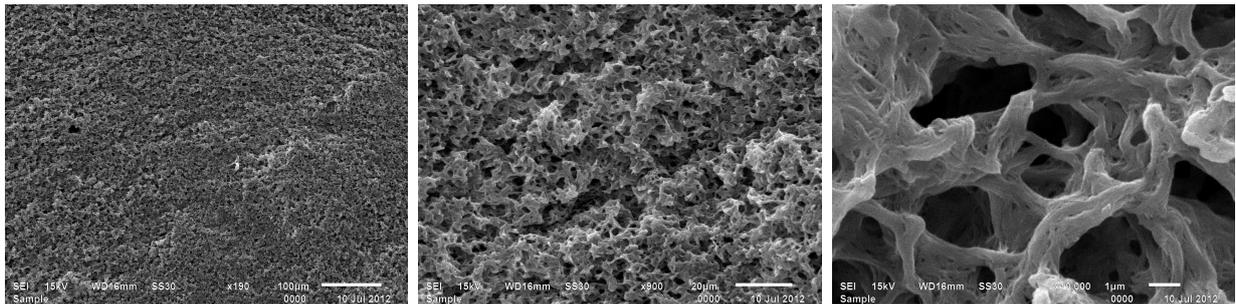


FIG. 13. 40/60(PMMA/PC)

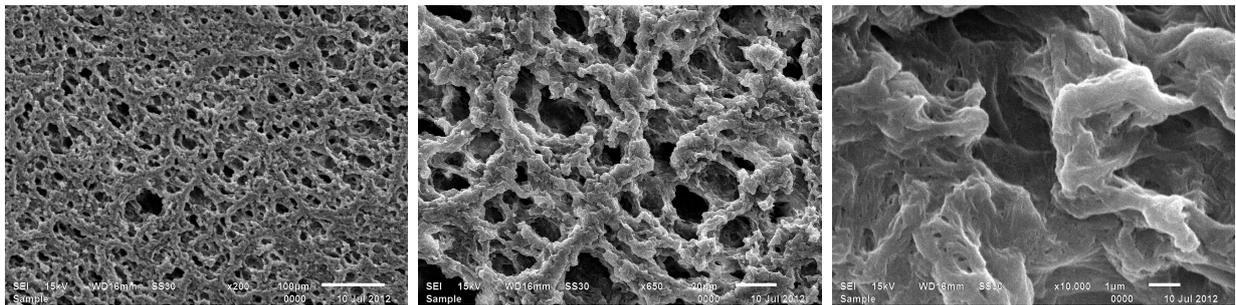


FIG. 14. 20/80(PMMA/PC)

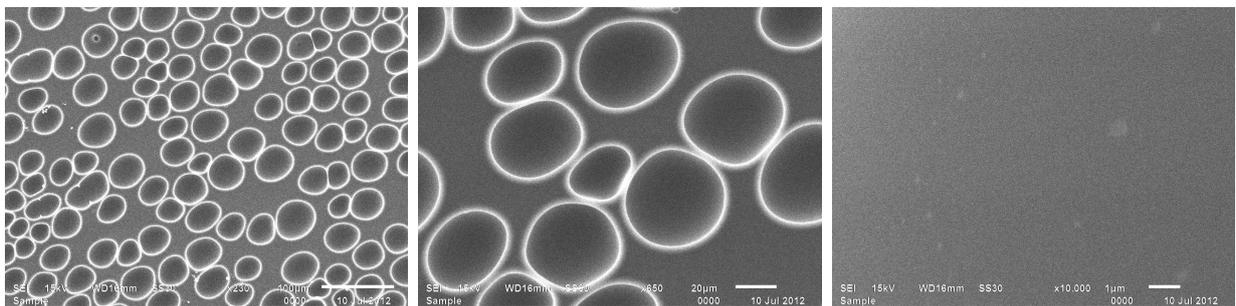


FIG. 15. PMMA

4. Conclusion

Viscometric studies showed that most PC/PMMA blends displayed miscibility at both temperatures. However, at the higher temperature, the small negative values for the interaction parameters, not in a consistent manner for some compositions, indicated some degree of immiscibility. However, FTIR and SEM analyses showed the blends of PC/PMMA to be miscible in all compositions tested at ambient temperature. FTIR scanning of the blends showed no change in the wavenumbers of the functional groups, which support the formation of PC/PMMA physical blends.

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