A comparative thermal, optical, morphological and mechanical properties studies of pristine and C15A nanoclay-modified PC/PMMA blends: A critical evaluation of the role of nanoclay particles as compatibilizers

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Characterization

DSC (Mettler-Toledo, 823) thermograms were used to measure the glass transition temperature (T_g) of the PC/PMMA blends. As it is well known in literature [19-20], reproducible results free from prior thermal history effects are obtained only after quenching the sample from a temperature well above T_g and then recording the thermograms. Accordingly, the second run DSC thermogram was recorded to measure the T_g. For measuring this, first we heated the pristine blend from 30 to 300 °C at a heating rate of 20 °C/min under nitrogen atmosphere, and then cooled the sample with the maximum possible cooling rate of 45 °C/min. (available with the DSC) which constituted the first DSC run. After this, we reheated the sample from 30 to 300 °C at a heating rate of 20 °C/min for recording the DSC data in the second run. Before using the DSC machine, it was calibrated with indium and zinc.

Thermal degradation behaviour of the pristine and compatibilized blends was studied using TGA (Mettler-Toledo, TGA/DSC-1) at a heating rate of 20 °C/ min under nitrogen and air atmosphere. The degradation temperature was measured corresponding to 5% weight loss of the sample.

The nanostructure of C15A nanoclay modified PC/PMMA blends were studied by Bruker AXS D8 Advance wide-angle X-ray diffractometer with Cu Kα radiation and a graphite monochromator (wavelength, λ = 0.154 nm). The generator was operated at 40 kV and 40 mA. The film samples (except for C15A nanoclay which was placed in powder form) were placed on a quartz sample holder at room temperature and were scanned at diffraction angle 2θ from 1° to 40° at the scanning rate of 1°/ min.

FT-IR measurements were conducted in transmission mode in a Thermo Scientific FTIR spectrometer (model: NICOLET 6700) from 650 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. Each spectrum was the average of thirty two scans.

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer (Avance 400) at ambient temperature in $CDCl_3$ solvent. The chemical shifts are reported in ppm relative to tetramethylsilane.

UV/Vis spectrophotometer (Lambda 25, Perkin Elmer, Germany) was used to measure the optical transmittance of PC/PMMA blends, in the range of 400-950 nm. The sample thickness was 2 mm.

Stress-strain behaviour was measured on the injection-molded tensile specimens using an Instron 3369 tensile tester at a strain rate of 2 mm/min at room temperature. Several samples were tested to obtain better error estimation.

Surface morphology was examined under field emission gun based SEM (ZEISS, model: SEM-Supra 40) operating at an accelerating voltage of 10 kV. The samples were sputter coated with gold before SEM examination to avoid charging.

The dispersion of C15A nanoclay within the blend matrix was examined by TEM using a Tecnai G2 20, FEI Corporation apparatus operating at an accelerating voltage of 200 kV. A thin layer of specimens were prepared by ultramicrotoming the blends with a diamond knife.

Thermal degradation behaviour of different organically modified nanoclays

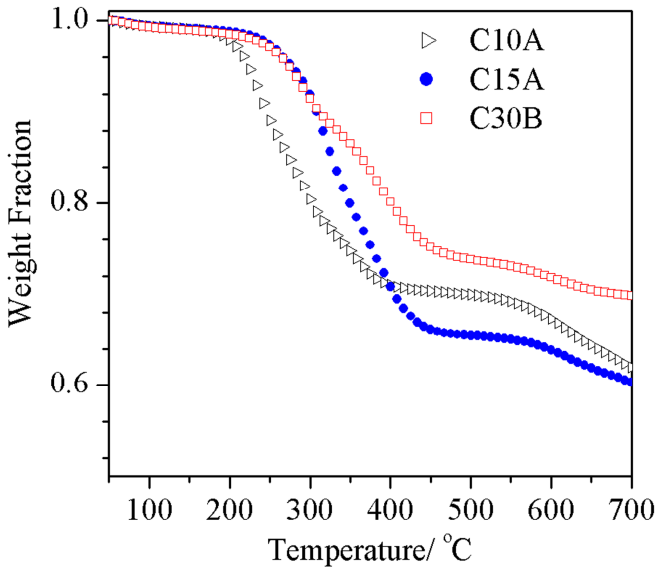

Figure S1 TGA thermograms of C30B, C10A and C15A nanoclays taken in N_2 atmosphere.

Optimization of C15A nanoclay content for getting homogeneous PC/PMMA blends

In order to optimize the content of C15A nanoclay for getting homogeneous PC/PMMA blends, we prepared PC/20PMMA blends with different nanoclay contents (2, 3 and 4%). Fig S2 shows second run DSC thermograms of these blends.

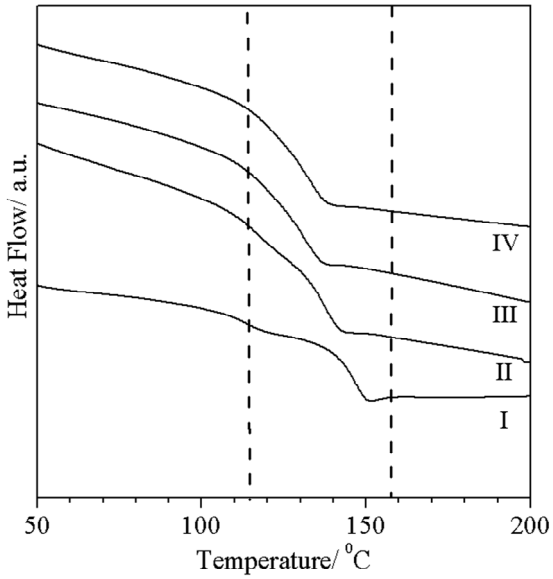

Figure S2 Second run DSC thermograms of (I) PC/20PMMA, (II) PC/20PMMA + 2% C15A, (III) PC/20PMMA + 3% C15A, and (IV) PC/20PMMA + 4% C15A. Vertical dotted lines are corresponding to the glass transition temperature of pure PMMA and PC, respectively.

Similar to the pristine PC/20PMMA blend, DSC thermogram of PC/20PMMA blend containing 2% of C15A nanoclay also shows two distinguishable T_gs corresponding to PMMA and PC-rich phases with slightly more shift suggesting better compatibility in PC/20PMMA + 2% C15A blend. On increasing the nanoclay content from 2 to 3%, we observed much larger shift in the T_g of PC. However, the shift in T_g of PMMA is comparable to that in PC/20PMMA blend prepared using 2% C15A. Unlike the PC/20PMMA blend prepared using 2% C15A here the glass transition is quite diffuse. On

further increasing the C15A content from 3 to 4% we did not observe any significant change in glass transition temperature, which suggests that 3% of C15A nanoclay is optimum for getting the compatibilized and homogeneous PC/PMMA blends. So, we prepared compatibilized PC/PMMA blends in whole composition range using 3% of C15A nanoclay.

First derivative of second run DSC thermograms of pristine PC/PMMA blends

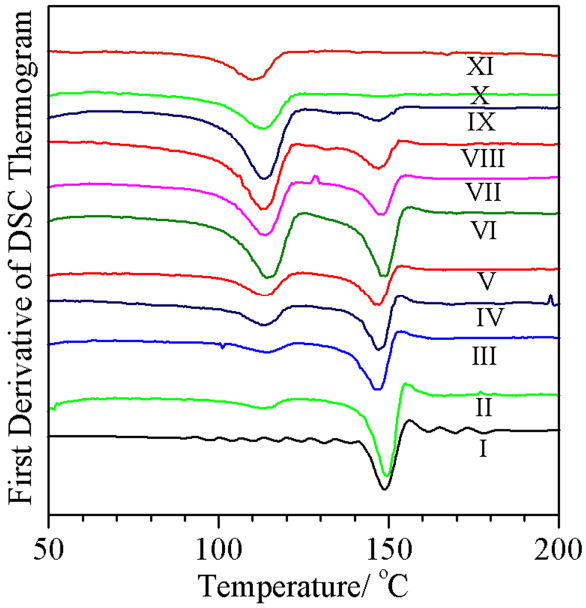

Figure S3 First derivative of second run DSC thermograms of PC/PMMA blend prepared using melt extrusion technique: (I) PC, (II) PC/10PMMA, (III) PC/20PMMA, (IV) PC/30PMMA, (V) PC/40PMMA, (VI) PC/50PMMA, (VII) PC/60PMMA, (VIII) PC/70PMMA, (IX) PC/80PMMA, (X) PC/90PMMA, and (XI) PMMA.

Optical transparency of Pristine and C15A nanoclay modified PC/PMMA blends

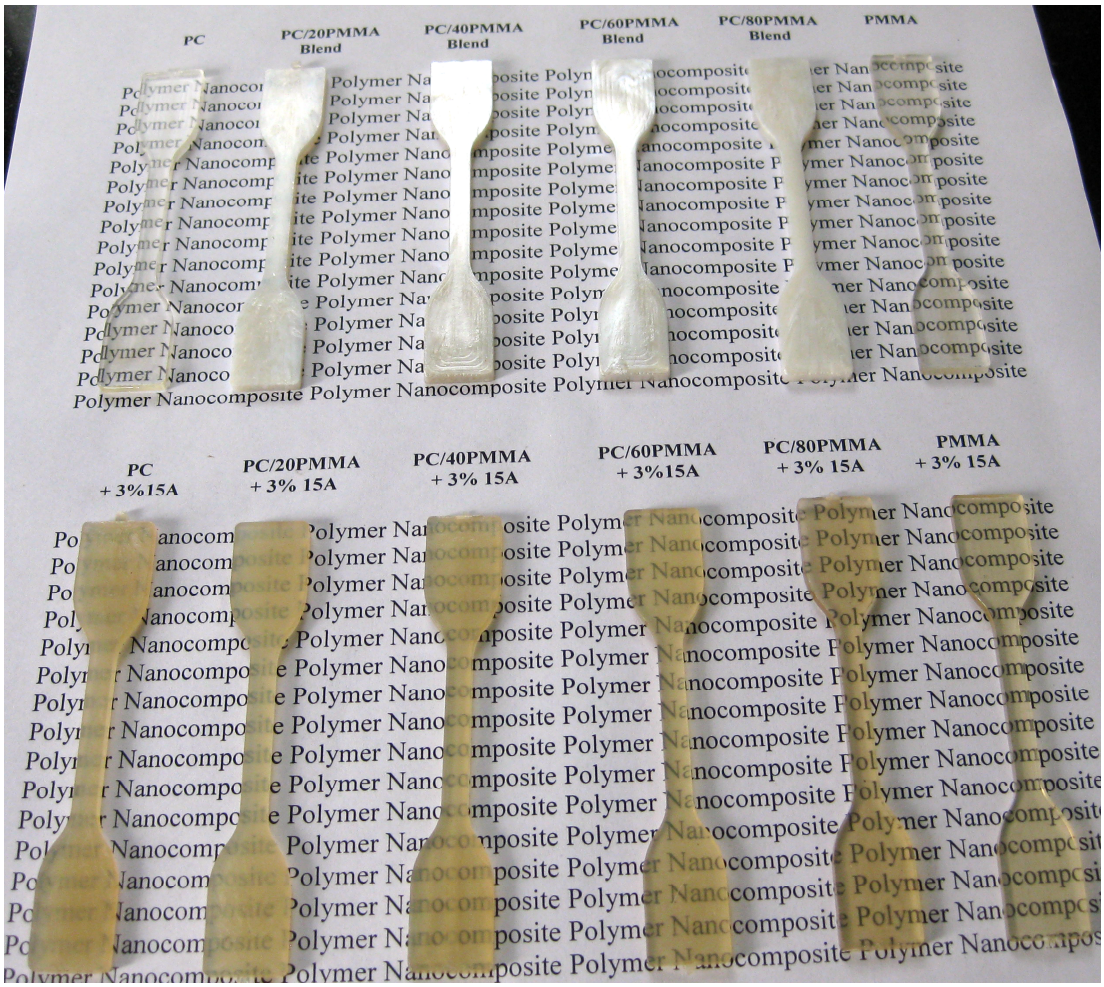

Figure S4: Digital photograph of tensile test specimens of pristine and C15A nanoclay modified PC/PMMA blends, showing optical transparency.

FTIR evidence for interaction between PC and PMMA phases in the compatibilized blends

FTIR spectra of pristine and C15A nanoclay modified PC, PMMA and PC/PMMA blends, in the wave number range 1000-2000 cm^{-1}, are shown in Figs. S5 (a) and (b), respectively. The stretching vibration peak of carbonyl group is a singlet and is known to occur at 1775 cm^{-1} and 1731 cm^{-1} in pure PC and PMMA, respectively [21]. In the case of nanoclay modified PC and PMMA nanocomposites, these peaks occur at 1776 and 1733 cm^{-1}, respectively. The peak corresponding to aromatic stretching of PC and the deformation of CH_3 of O-CH_3 group of PMMA, which are known to occur at 1503 and 1442 cm^{-1} in pure PC and PMMA, respectively, are observed at 1505 and 1445 cm^{-1} in nanoclay modified PC and PMMA, respectively. The blue shift in carbonyl group of PC and PMMA, aromatic stretching of PC and the deformation of CH_3 of O-CH_3 group of PMMA is although very little, it changes rather systematically in the C15A nanoclay modified PC/PMMA blends as a function of blend composition. This is shown in Fig. S5(c) for the carbonyl peak. It is interesting to note that the positions of the carbonyl peaks of PC and PMMA do not shift in the pristine PC/PMMA blends, whereas there is a perceptible blue shift in the carbonyl peak of PC with increasing PMMA content in the C15A nanoclay modified PC/PMMA blends, as can be seen from Fig.S5 (c). This suggests better interactions between the PC and PMMA phases in the blends prepared in the presence of C15A nanoclay.

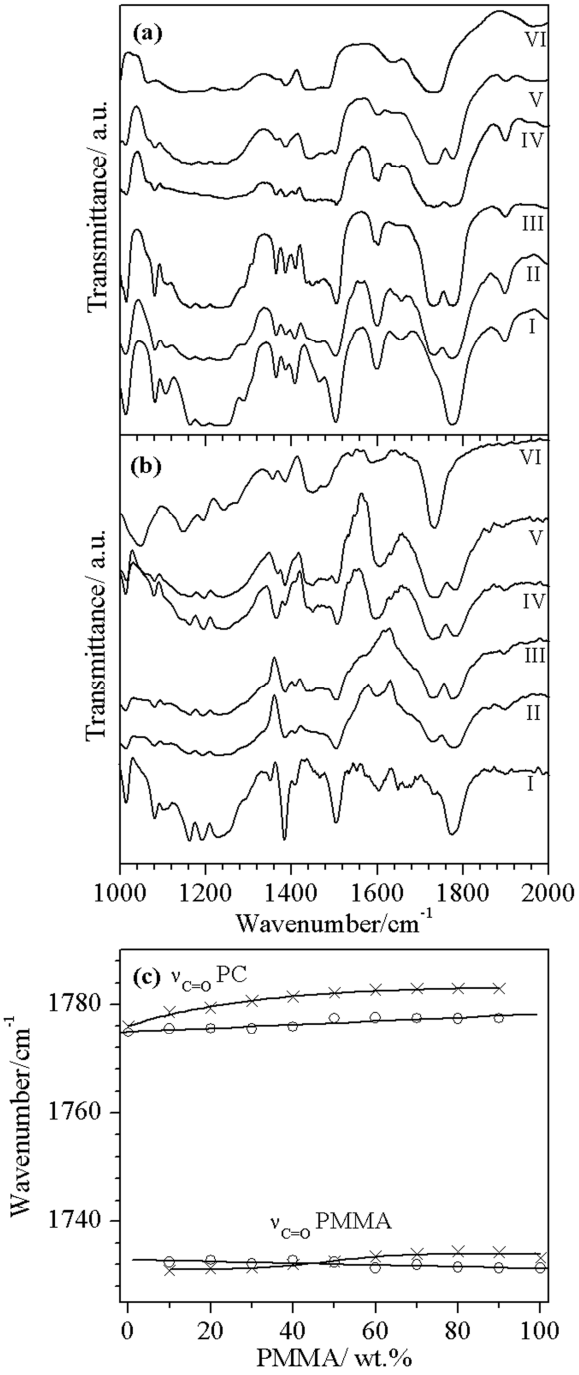

Figure S5 FTIR spectra of (a) pristine and (b) 3% C15A nanoclay modified PC, PMMA and PC/PMMA blends prepared using melt extrusion technique: (I) PC, (II) PC/20PMMA, (III) PC/40PMMA, (IV) PC/60PMMA, (V) PC/80PMMA and (VI) PMMA. (c) Variation of carbonyl peak position of stretching vibration ($\nu_{C=O}$) of PC and PMMA in PC/PMMA blends with C15A nanoclay (crosses) and without nanoclay (open circle) as a function of PMMA content.

Mechanical properties data

Table.S1 Mechanical properties of pristine and compatibilized PC/PMMA blends

Sample	Young's Modulus (GPa)	UTS (MPa)	Tensile Strain (%)	Toughness MJ/m^3
PC	1.14	61.6	67.5	33.5
PC/10PMMA	1.15	62	57.9	28.1
PC/20PMMA	1.18	65.4	47	26.6
PC/30PMMA	1.22	66.5	43.9	25.2
PC/40PMMA	1.24	66	36	20.5
PC/50PMMA	1.30	69.5	32.4	19.6
PC/60PMMA	1.33	67.4	28.3	17.2
PC/70PMMA	1.34	68.4	25	15.7
PC/80PMMA	1.40	72.6	16.9	11.7
PC/90PMMA	1.49	74.3	10.0	7.78
PMMA	1.49	74.5	11	6.5
PC + 3% C15A	1.39	66.8	8.5	5.3
PC/10PMMA + 3% C15A	1.42	37.9	3.0	0.6
PC/20PMMA + 3% C15A	1.50	51.8	4.2	1.2
PC/30PMMA + 3% C15A	1.55	56.2	4.6	1.5
PC/40PMMA + 3% C15A	1.60	38.9	2.7	0.6
PC/50PMMA + 3% C15A	1.66	37.1	2.5	0.5
PC/60PMMA + 3% C15A	1.68	33.9	2.2	0.4
PC/70PMMA + 3% C15A	1.69	57.8	4.4	1.4
PC/80PMMA + 3% C15A	1.70	59.5	4.9	1.7
PC/90PMMA + 3% C15A	1.75	62.9	4.6	1.7
PMMA + 3% C15A	1.77	58.6	4.2	1.4

^{1}H NMR data

Table S2 ^{1}H NMR peak positions of PC and PMMA in pure and C15A nanoclay modified PC, PMMA and PC/PMMA blends

Sample	**^{1}H NMR peak position of PC**					**^{1}H NMR peak position of PMMA**		
	Benzene Ring				Methyl Group	Methyl Ester	CH_2	CH_3
PC	7.261	7.239	7.175	7.153	1.677			
PMMA						3.599	1.815	0.853
PC + 3%C15A		7.241	7.167		1.674			
PC/60PMMA	7.252	7.231	7.165	7.144	1.670	3.602	1.822	0.856
PC/60PMMA + 3%C15A		7.231	7.155		1.665	3.588	1.807	0.836
PMMA + 3%C15A						3.600	1.817	0.852