Supporting information

Thermal evolution of polymer-nanoparticle binary mixture

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Materials and Methods

Materials used and preparation of the binary mixture

We use a model binary mixture in which the polymer is Hydroxyl terminated 1, 4-polybutadiene (molecular weight=2694 g/mol (Orion chemicals), functionality=2.4, glass transition temperature = -75° C) and the NP is clay nanoplatelets (Montmorillonite (Cloisite 10A, BYK Additives), The solubility parameters for both polymer and the organic surface modifier of NP are $\delta_{polymer}$=8.1 cal$^{1/2}$cm$^{-3/2}$ and $\delta_{modifier\ of\ NP}$=8.0 cal$^{1/2}cm^{-3/2}$,″ respectively. We select a well-established procedure for exfoliation and dispersion of clay nanoplatelets in the polymer [1-3].

Clay and HTPB were initially thoroughly dried by keeping them in a vacuum oven at 70° C for one day. Dried clay was slowly added to toluene and kept on a magnetic stirrer for 5 hours. An air-tight glass bottle was used to avoid the evaporation of toluene during dispersion. The stock suspension of clay in toluene was poured into the desired amount of polymer and then was placed under vigorous stirring conditions, using a mechanical stirrer (speed：3000 rpm, Remi Motors) for three to four hours at room temperature. Toluene was then evaporated by initially keeping it in an open beaker with magnetic stirring for 6 hours, followed by keeping the mixture in a vacuum oven for two hours at room temperature. This also removed the bubbles entrapped. By starting with a fixed weight of polymer (10 g) and varying the NP mass fraction, binary mixtures of clay and HTPB were prepared. The resulting mixtures were labeled as ϕ = X, where X stands for the initial weight fraction of clay in the mixture.

Structure and interface

Small-angle *X*-ray scattering was carried out at specific temperatures within the same temperature range used for rheological experiments. Scattering was conducted using a SAXS

system (SAXSess MC^2, Anton Paar, Austria), operated in line-collimation technique with Cu K$_\alpha$ X-ray source of wavelength, λ=0.154 nm and a sample-to-detector distance of 309 ($\pm$10) mm. This gave an effective scattering vector range of 0.15-6 nm^{-1}. The voltage and current of the X-ray generator were set at 40 kV and 50 mA, respectively. Mixtures were then placed between two polycarbonate sheets and the sample holder was tightly screwed, to make it leak-proof. The experiments were performed at eleven different constant temperatures between 25° C to 125° C with an interval of 10° C. The scattering patterns were recorded for 600 s (60 frames × 10 s exposure times for each frame) at each temperature. The scattering profiles were subtracted from that of the polycarbonate sheets, followed by desmearing. The temperature was controlled using a computer-controlled Peltier heating system. The small angle X-ray scattering data is analysed using a dedicated scattering software SASfit tools [4,5].

Relaxation

Polymer relaxation in the binary mixtures was examined by dielectric relaxation spectroscopy. Small volumes of binary mixtures were placed between two parallel electrodes of 20 mm diameter with 100-micron silica fibers as spacers. The measurements were conducted between frequencies 0.1 Hz to 5 MHz, at different temperatures, ranging from 25°C to 125°C, beyond which the generated spectra contained significant noise. This was conducted using a Novo control broadband dielectric spectrometer. This spectrometer comprises an Alpha-A analyzer, interfaced with the sample cell (BDS1200) and Quatro liquid nitrogen gas heating /cooling system. The temperature was controlled within +/- 0.3° C. The RMS voltage applied was 0.5 V.
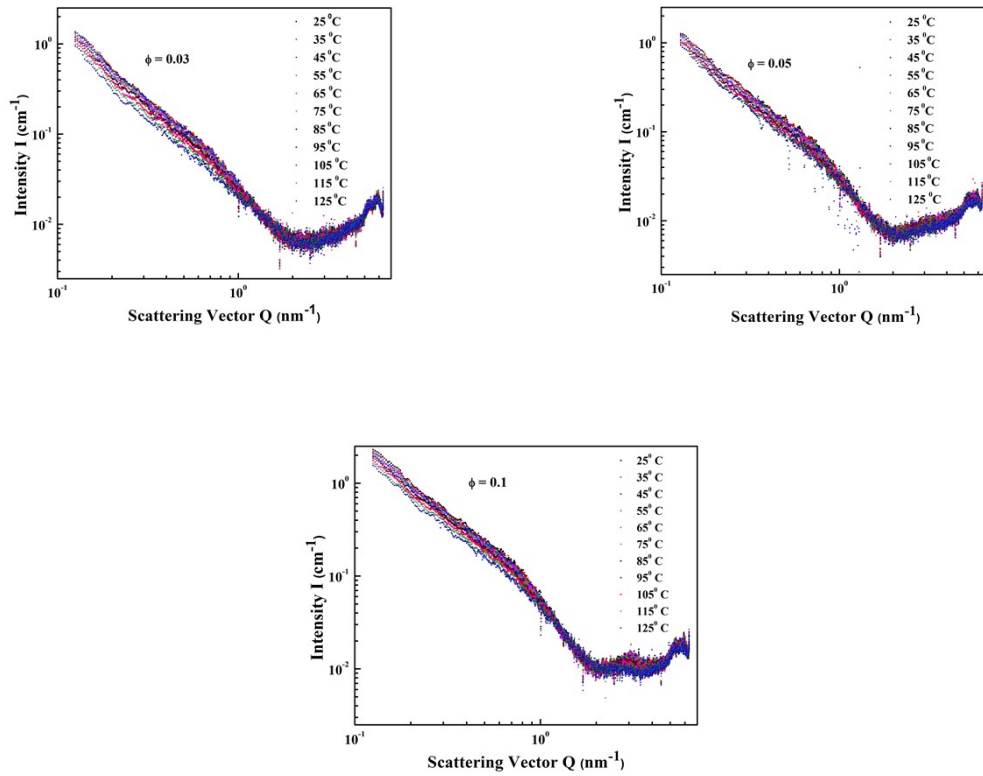
Figure S1. Small-angle X-ray scattering profiles of those binary mixtures which showed viscosity transitions.

Table S1: Fractal dimensions of most dominant mesostructures at different temperatures

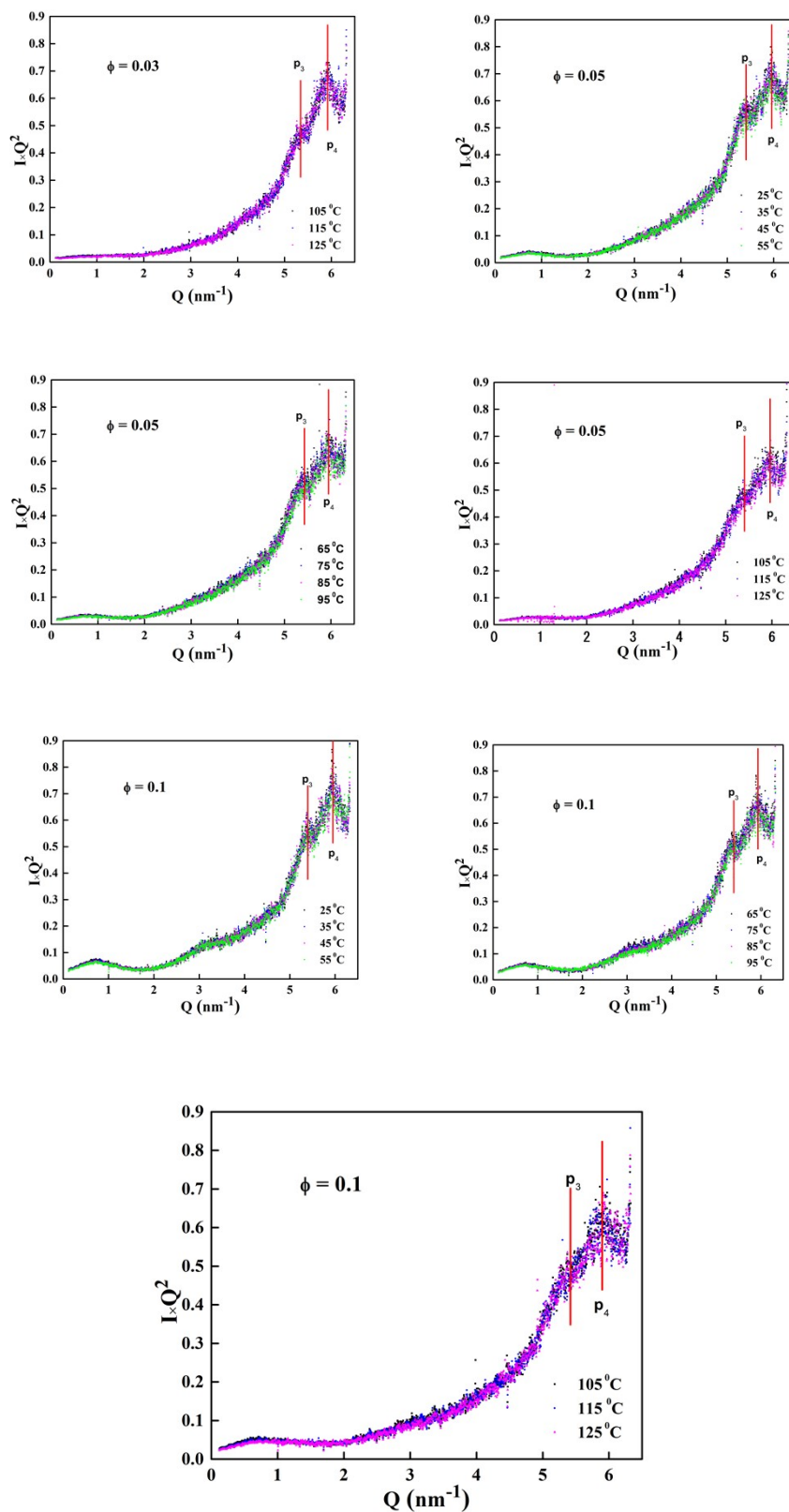| Fractal dimension/Temp. (^{0}C)	25^0	35^0	45^0	55^0	65^0	75^0	85^0	95^0	105^0	115^0	125^0
ϕ = 0.03	2.1	2.1	2.0	2.2	2.2	2.1	2.11	2.11	2.2	2.2	2.2
ϕ = 0.05	1.9	2.0	1.9	2.0	2.0	1.9	1.9	1.9	2.0	2.0	2.0
ϕ = 0.1	1.8	1.9	1.9	1.9	1.8	1.8	1.8	1.9	1.8	1.8	1.9
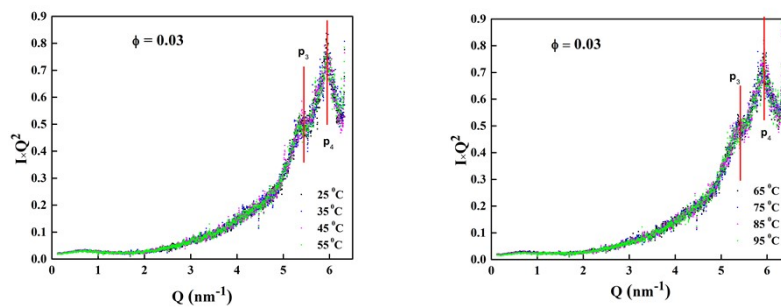
Figure S2: Lorenz plots of selected binary mixtures at different temperatures across the evolution path.

Table S2: Position of higher order peaks and corresponding interlamellar spacing

Parameters/Peaks	Peak position (nm^{-1})	2θ	d-spacing (nm)
p_2	3.0	4.2^0	2.1
p_3	5.5	7.7^0	1.2
p_4	5.9	8.4^0	1.1

Table S3. Parametric estimations from interface and correlation functions.

Particle mass fraction	Temperature (^{0}C)	Thickness of Lamellar Domain (nm)	Morphological parameters from correlation and interface functions	
			Long Period L_c (nm)	Long Period L_I (nm)
$\Phi=0.03$	35	8.84	2.47	2.49
	65	8.84	2.78	2.71
	95	8.84	2.78	2.62
	115	ambiguous*	2.78	2.57
$\Phi=0.05$	35	8.15	2.94	2.85
	65	8.37	3.00	2.89
	95	8.37	3.00	2.85
	115	ambiguous*	3.00	2.85
$\Phi=0.1$	35	8.48	3.10	2.89
	65	8.72	2.99	2.76
	95	8.72	3.00	2.80
	115	ambiguous*	2.93	2.70

*In these cases, the lamellar thickness could not be estimated due to the highly diffuse nature of peak p_1 so the peak maxima are not identifiable.

Table S4. Estimated relaxation time on tracing HN model to loss part of the dielectric function of binary mixture

Particle concentration	τ_{HN} (20^0 C)	τ_{HN} (40^0 C)	τ_{HN} (60^0 C)	τ_{HN} (80^0 C)	τ_{HN} (100^0 C)
$\phi = 0.03$	8.1E-3	3.5E-3	5.2E-3	4.4E3	Ambiguous
$\phi = 0.05$	3.7E-3	1.3E-3	5.6E-4	1.1E-3	3.9E-4
$\phi = 0.10$	3.1E-3	1.2E-3	6.2E-4	5.1E-4	Ambiguous

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