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Selective Location and Migration of Poly(methyl methacrylate)-Grafted Clay Nanosheets with Low Grafting Density in Poly(methyl methacrylate)/Poly(styrene-*co*-acrylonitrile) Blends

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Abstract: The location and migration of poly (methyl methacrylate)-grafted clay (clay-g-PMMA) nanosheets with low grafting density in a phase-separated polymer blend of poly (methyl methacrylate)/poly (styrene-*co*-acrylonitrile) (PMMA/SAN) was investigated. The grafting density and molecular weight for grafted PMMA chains on the surface of clay nanosheets was about 0.04 chains/nm² and 7.8×10⁴, respectively, indicating that the grafted chains might exhibit the mushroom-like distribution. With phase separation of PMMA/SAN blend matrix, the well-dispersed clay-g-PMMA nanosheets in the blend matrix were first located in the SAN-rich phase and then gradually migrated to the interface between PMMA and SAN. The

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first abnormal location of modified clay in the blend matrix might be attributed to the favorable interaction between clay-g-PMMA and SAN induced by the miscibility of grafted PMMA/surrounding SAN chains and the unfavorable interaction between clay-g-PMMA and PMMA without any interpenetration of grafted and matrix chains. The enhanced miscibility between grafted PMMA and surrounding SAN just began to be destroyed after being annealed for a long time, resulting in the final migration of clay-g-PMMA to the interface of PMMA/SAN (thermodynamic equilibrium state).

Keywords: Clay; Grafting; PMMA/SAN blend; Selective location

1. Introduction

The addition of nanoparticles (NPs) into a polymer matrix is an appealing strategy to obtain the desired materials with the enhanced strength and other novel properties such as optics, conductivity, magnetism, permeability, which have received a tremendous attention from the academic and engineering fields [1]. If the matrix is a polymer blend, the incorporation of NPs may bridge the morphology development of polymer blends, improve the compatibility for immiscible polymer blends and retard the coarsening of domain [2-10]. Due to different compatibility between the NPs and two components of blend matrix, the NPs may present different selective distribution states in the microcosmic heterogeneous polymer blends and migrate in the blend matrix under a certain thermodynamic and kinetic conditions. As a vital factor, the dispersion and distribution of NPs in the blend matrix may make significant difference on those ultimate properties.

1 In general, a fine dispersion of NPs in polymer matrix is prerequisite for excellent
2 mechanical and other properties. Furthermore, a controllable distribution of NPs can
3 also provide us some tunable properties, such as permeability or conductivity in a
4 large range [1, 11, 12]. The control for the selective distribution of NPs may facilitate
5 the optimization of morphology, structure and ultimate performance of
6 nanocomposites [13-18]. Due to large specific surface area and high surface energy of
7 NPs, they are easy to aggregate and difficult to disperse uniformly either in a unitary
8 polymer matrix or in a binary blend matrix. There have been several strategies to
9 control the NPs dispersion in a polymer matrix. Here, grafting polymer chains onto
10 the surface of NPs is one of the practically feasible strategies [19, 20]. Some
11 theoretical and experimental works on polymer-grafted NPs have shown that the
12 dispersion or aggregation (wetting-dewetting) state of NPs with the grafted chain
13 chemically identical to the matrix chain in the polymer matrix can be tuned by
14 changing the NPs size or curvature, graft density σ (mushroom to brush regimes) and
15 ratio of matrix to graft chain length [21-27]. When σ is below the allophobic limit, the
16 surface coverage of graft chains is so low that the interactions between NPs and
17 matrix chains are insufficiently screened and the grafted NPs still aggregate in the
18 matrix. When σ is above the autophobic limit, the matrix chains are completely
19 expelled and the grafted NPs also agglomerate. Only in the medium σ regime, the
20 matrix and graft chains interpenetrate, resulting in the repulsive interactions between
21 NPs and stable dispersions. As for the LCST (lower critical solution temperature)
22 blend matrix, the dispersion and distribution of grafted NPs in such blend matrix and

its effect on the thermodynamic miscibility in LCST blend matrix have not received much attention. Composto [23, 28] and Yu [3] et.al both coated silica (SiO_2) NPs with polystyrene brush, incompatible with two components of blend matrix, and varied the molecular weight of grafted PS to achieve different selective distribution of modified SiO_2 in poly (methyl methacrylate)/poly(styrene-*co*-acrylonitrile) (PMMA/SAN) blend matrix and different phase behaviors for the nanocomposites. It could be also found that SiO_2 with short grafted chains tended to aggregate in the interface, while SiO_2 with long grafted chains preferred to be located in the PMMA-rich phase. Recently, the reports on the control for the distribution of NPs have been mostly focused on the isotropic spherical NPs, such as SiO_2 [3, 23, 28] or gold [29] NPs. However, there are few related works on the distribution control for the two-dimensional anisotropic NPs, such as clay and graphene. Hence, the selective distribution and dispersion of grafted anisotropic NPs in the LCST blend matrix should be further explored.

In this work, the LCST-type PMMA/SAN blend is selected as binary blend matrix, in which the miscibility derives from the so-called “repulsion effect” [30]. In order to improve the dispersion of clay in PMMA/SAN blend matrix, PMMA chains are grafted on the surface of clay via soap-free emulsion polymerization [31]. The selective distribution and migration of clay-*g*-PMMA with the morphology evolution of blend matrix are investigated through transmission electron microscopy (TEM). The interactions between clay-*g*-PMMA and two components of blend matrix are detected by temperature-modulated differential scanning calorimeter (TMDSC).

Furthermore, the cause for the selective distribution and migration of clay-g-PMMA in PMMA/SAN blend is also explored and discussed.

2. Experimental Section

2.1 Materials

Poly (methyl methacrylate) (PMMA) (IF850, $M_n = 5.0 \times 10^4$, $M_w/M_n = 1.5$, LG Co. Ltd, South Korea) and poly (styrene-co-acrylonitrile) (SAN) (PN-127H, $M_n = 8.9 \times 10^4$, $M_w/M_n = 1.7$, Chimei Co. Ltd, Taiwan, China) with AN content of 32 wt% were both commercial products. Na-Montmorillonite clay (Na-MMT) (G105-PGV, Nanocor Co. Ltd, USA) with the cation exchange capacity of 145 mequiv/100 g and aspect ratio of 150-200 (data provided by the supplier) was used in our study. PMMA, SAN and clay were dried for 24 h at 80 °C in the vacuum oven before use to remove any moisture. MMA (Sinopharm Chemical Reagent Co. Ltd, China) was used before vacuum distillation to eliminate the inhibitor. 2-acrylamido-2-methyl propane sulfonic acid (AMPS), purchased from Aladdin, was used as a reactive emulsifier. Potassium persulfate (KPS), Tetrahydrofuran (THF), Methyl ethyl ketone (MEK), Hydrofluoric acid (40wt %) purchased from Sino pharm Chemical Reagent Co. Ltd, China, were used as received.

2.2 Synthesis of Clay-g-PMMA

Clay grafted with PMMA was prepared via soap-free emulsion polymerization reported by the literature [31] and the synthesis process was shown in Fig. 1a. The solution of Na-MMT, MMA, AMPS, and deionized water with the ratio of 2 g/5 g/2.5 g/126 g (Na-MMT/MMA/AMPS/water) was charged into a 500 mL four-neck reactor

1 equipped with a mechanical stirrer, a thermometer, a reflux condenser, a nitrogen
2 inlet, and a pressure-equalizing dropping funnel. The mixture was stirred at 200 rpm
3 for 30 min under a N₂ gas at an ambient temperature. The temperature of the reactor
4 was raised to 65 °C. 20 g of aqueous solution with 1 wt % initiator was injected into
5 the reactor and the polymerization was performed at 65 °C for 1 h. After the initial
6 polymerization was completed, 15 g of MMA was added dropwise in about 100 min.
7 Then the polymerization was carried out for additional 30min at the same temperature
8 of 65 °C. After the polymerization, the uniform emulsion product was cooled down
9 and centrifuged to demulsification at 12000 rpm and 20 °C for 30 min. Then the
10 supernatant liquid was discarded and the precipitation was dissolved by THF. The
11 above-mentioned centrifugation and dissolution procedures were repeated about ten
12 times to remove the untethered PMMA chains and surfactants. THF was subsequently
13 replaced by MEK to repeat those procedures three times and obtain the
14 clay-g-PMMA/MEK suspension. Here, it should be noted that MEK was the solvent
15 for the preparation of PMMA/SAN/clay-g-PMMA nanocomposites and the clay-g-
16 PMMA was dispersed in MEK without vacuum drying to avoid the formation of large
17 aggregates. The suspension was further sonicated for 2 h in an ice-water bath and kept
18 stewing for 72 h to remove some agglomerates. After the sonication for 1 h, a small
19 amount of translucent upper suspension was taken and the accurate solid content of
20 suspension was calculated to obtain the content of clay-g-PMMA.

21 To measure the molecular weight of PMMA end-tethered on clay, the clay in
22 clay-g-PMMA should be eliminated. Firstly, most MEK in the above-mentioned

suspension was volatilized at an ambient environment. The mash-like sample was obtained and added into hydrofluoric acid with being stirred for 10 min to etch the clay. The mixture was filtered to discard the liquid. Then the residual solid sample was rinsed with deionized water for three times and dried in the vacuum oven at 80 °C for 24 h to remove the water. Subsequently, the dried sample was dissolved into THF overnight and filtered again to remove the undissolved part. Hence, the residual molecules with the removal of THF corresponded to the PMMA grafted on the surface of clay.

2.3 Preparation of PMMA/SAN/Clay-g-MMA nanocomposites

PMMA and SAN at different weight ratios were dissolved into the above-mentioned clay-g-PMMA/MEK suspension to form the mixture solution at a weight fraction of 5 wt% by stirring for 24 h at room temperature. The mixture was ultrasonicated for 2 h in an ice-water bath to achieve the uniform dispersion of clay-g-PMMA in PMMA/SAN blend solution. Subsequently, the mixture solution was cast onto the cover glass at 30 °C. After the solvent evaporated at an ambient environment about 24 h, the samples were further dried at 90, 110 and 130 °C in a vacuum environment for 72 h to remove the residual solvent. The PMMA/SAN/clay-g-PMMA nanocomposites were denoted by A/B/x, where A and B represent the weight fraction of PMMA and SAN in the binary blend, respectively, and x is the weight fraction of clay (excluding the grafted PMMA) compared to the entire amount of polymers. As a control experiment, PMMA/SAN/Na-MMT nanocomposites were also prepared according to the abovementioned method. ~~The samples for rheological~~

1 ~~measurements were prepared in the same way as above with an adjusted mixture~~
2 ~~solution weight fraction of 10 wt% and the solutions were cast on the surface of~~
3 ~~horizontal glass plates to form the uniform films with the thickness of about 100 μm .~~
4 ~~Then these films were folded up and compression molded into the discs with the~~
5 ~~dimensions of 25 mm in diameter and 1.2 mm in thickness at 10 MPa and 130 °C.~~

6 *2.4 Characterization*

7 Fourier transform infrared (FTIR) was used to evaluate the clay grafted with
8 PMMA. Infrared spectra were recorded on a FTIR spectrometer (VECTOR22,
9 Bruker, Germany) with a nominal resolution of 4 cm^{-1} . The samples in powder form
10 were mixed with potassium bromide and compressed into transparent discs for FTIR
11 test. The change in the gallery distance of silicate layers was determined with a
12 scanning rate of 5 °/min by X-ray diffractometer(XRD, D/Max-2550 pc, Rigaku,
13 Japan) equipped with Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) using a generator voltage of 40
14 kV and a generator current of 300 mA. Thermo gravimetric analysis (TGA) was
15 carried out using a thermogravimetry analyzer (Q50, TA, USA) in a temperature
16 range from room temperature to 500°C with a heating rate of 10 °C/min under air
17 atmosphere to measure the graft mass ratio of clay-g-PMMA. The molecular weights
18 of raw PMMA, SAN and the residual molecules after hydrofluoric acid etching of
19 clay-g-PMMA were determined by using gel permeation chromatography (GPC,
20 Waters1515, Waters, USA) at a flow rate of THF 1.0 mL/min at 40 °C after
21 calibration with standard polystyrene samples. Transmission electron microscopy
22 (TEM) images of the samples were obtained by using a TEM (JEM1230, JEOL,

Japan). TEM specimens of clay-g-PMMA were prepared by casting one drop of clay-g-PMMA suspension at a concentration of 0.05 wt% on a copper grid with the support of carbon membrane and volatilize the solvent thoroughly. TEM specimens of the nanocomposites were prepared by embedding the samples in the epoxy resin (solidified at ambient temperature for 24 h) and ultramicro-toming them into the sections of 100 nm thick with a diamond knife.

The glass transition temperature and heat capacity of the filled and unfilled samples were determined by a differential scanning calorimeter (DSC, Q100, TA, USA) under temperature modulation mode. Reversing heat capacity signals were analyzed between 70 and 130 °C. Measurements were performed by using an underlying heating rate of 1 °C/min and a superimposed temperature modulation procedure with the amplitude of 1 °C and a period of 120 s under a dry nitrogen purge. Before any measurement, the heat capacity signal of the instrument was calibrated by using standard sapphire sample at the same above-mentioned testing condition. The contact angle measurement was conducted by Harke-SPCA instrument (Perkin Elmer Experimental Instrument Factory, Beijing, China). The surface tension γ can be determined by the contact angle of water and formamide according to the previous literature [32]. The sample film for contact angle measurements was molded at 10 MPa at room temperature. A mean contact angle value was averaged from results measured at eight different positions on each film.

3. Results and Discussion

3.1 Surface topography of Clay-g-PMMA nanosheets

FTIR spectrum may provide the evidence for the successful grafting of polymer chains onto the surface of clay. Fig. 1 (b) shows the FTIR spectra of pristine Na-MMT and clay-g-PMMA. In the spectrum of pristine Na-MMT, some characteristic absorbance bands occur in the following assignments: Si-O stretching vibration at 1033 cm^{-1} , Al-O stretching vibration at 520 cm^{-1} and Si-O bending vibration at 460 cm^{-1} . Besides these assignments, clay-g-PMMA also owns the following characteristic absorbance bands: C=O stretching vibration at 1732 cm^{-1} , C-H stretching vibration at 2950 cm^{-1} and 2995 cm^{-1} , indicating the successful grafting of PMMA on the surface of clay. In addition, the absorption peak of N-H bending vibration at 1542 cm^{-1} reveals the existence of AMPS. Chung et al. [31] reported that AMPS has amido and sulfonic acid contents in the molecule and strong

Fig. 1. (a) Schematic for synthesis of clay-g-PMMA by soap-free emulsion polymerization, (b) FTIR spectra and (c) TGA curves for pristine Na-MMT and clay-g-PMMA.

interaction of amido moiety with pristine Na-MMT may make the polymer end-tethered on the surface of clay. It should be noted that these abovementioned absorptions do not belong to the free PMMA chains but to grafted PMMA chains, because clay-g-PMMA was washed by THF and centrifuged for ten times before the FTIR test to get rid of the free PMMA chains and physically adsorbed PMMA chains. The quantitative analysis of the chemically grafted PMMA coverage on the clay surface can be determined by TGA measurements, as shown in Fig. 1 (c). The grafting mass ratio of PMMA chains is estimated as ~20 wt%, which is close to the results reported by Chung in the PMMA/Na-MMT nanocomposites via soap-free emulsion polymerization [31]. The number average and weight average molecular weights of the residual molecules after hydrofluoric acid etching of clay-g-PMMA are 7.8×10^4 and 1.9×10^5 , respectively. Furthermore, the specific surface area of Na-MMT was reported as $41.7 \text{ m}^2/\text{g}$ [33]. Hence, the grafting density of PMMA is estimated as $\sim 0.04 \text{ chains}/\text{nm}^2$.

The morphology and size distribution of pristine Na-MMT and clay-g-PMMA are disclosed from the high-magnification TEM micrographs, as shown in Fig. 2. It is found that pristine Na-MMT has smooth surface, clear boundary and multi-sheets structure, while clay-g-PMMA exhibits nearly single-sheet structure, shaggy surface and relatively blunt and coarse edges attributed to the encapsulation of grafted PMMA chains [34]. The grafted PMMA molecular chains on the surface of clay with low grafting density of $\sim 0.04 \text{ chains}/\text{nm}^2$ might exhibit a mushroom-like distribution, rather than a brush-like distribution.

Fig. 2. TEM images of (a) Na-MMT and (b) clay-g-PMMA.

3.2 Selective distribution of Clay-g-PMMA nanosheets in PMMA/SAN blend matrix

It was found in our previous study that with the evolution of phase separation in PMMA/SAN blend matrix, the clays modified with 25~30 wt% methyl-dihydroxyethyl hydrogenated tallow ammonium were first located at the boundaries between PMMA and SAN, and then gradually moved to the PMMA-rich domain, owing to the affinity of organically modified clay to PMMA [14]. In order to explore the dispersion and distribution variation of clay-g-PMMA and pristine Na-MMT during the phase separation of PMMA/SAN matrix intuitively, TEM observations were carried out for the samples subjected to annealing at 190°C for different time, as shown in Fig. 3. The clay-g-PMMA nanosheets are uniformly dispersed in the homogeneous 60/40 and 40/60 PMMA/SAN blend matrix and the nanocomposites have partially intercalated and partially exfoliated structure of clay-g-PMMA without the existence of large aggregates (Fig. 3(a1) and (b1)). However, the dispersion of pristine Na-MMT in the blend matrix is somewhat poor and the nanocomposites have mainly intercalated structure with the presence of some aggregates (Fig. 3(c1)). Such results indicate that the surface grafting of clay nanosheets may improve their dispersion in the blend matrix.

1 After being annealed at 190°C for just 50s, the blend matrices for three systems all
2 exhibit co-continuous morphology, indicating the emergence of phase separation
3 according to the spinodal decomposition mechanism. The poor dispersion of pristine
4 Na-MMT nanosheets results in the heterogeneity of domain size for the
5 phase-separated blend matrix. Namely, the local aggregation and distribution of
6 pristine Na-MMT just remarkably retard the phase separation of their adjacent region.
7 Here, the bright region refers to the PMMA-rich phase and the dark region refers to
8 the SAN-rich phase in the bright-field TEM micrographs. It could be found that the
9 clay-g-PMMA nanosheets are almost dispersed in the SAN-rich domain (dark region)
10 at the early stage of SD phase separation for PMMA/SAN (60/40) and (40/60) blend
11 matrices (Fig. 3(a2) and (b2)). With the evolution of phase separation and domain
12 coarsening, most clay-g-PMMA nanosheets are still located in the SAN-rich phase for
13 a long time and just a small amount of clay-g-PMMA nanosheets gradually migrate to
14 the boundary between PMMA and SAN (Fig. 3 (a3) and (b3)). With the further
15 extension of annealing time, all the clay-g-PMMA nanosheets migrate slowly to the
16 interface of PMMA and SAN in the PMMA/SAN (60/40) blend matrix (Fig. 3 (a4)),
17 while just most clay-g-PMMA nanosheets migrate to the interface of PMMA/SAN
18 (40/60) blend matrix (Fig. 3 (b4)). Here, the migration of clay-g-PMMA nanosheets
19 from SAN-rich domains to the interface happens at the very late stage of phase
20 separation accompanied with some aggregation of modified clay and hence the
21 decrease of surface area for clay-g-PMMA nanosheets may be related with the change
22 of interaction between clay-g-PMMA and SAN. However, the pristine Na-MMT

Fig. 3. TEM images of (a) PMMA/SAN/clay-g-PMMA (60/40/2), (b) PMMA/SAN/clay-g-PMMA (40/60/2) and (c) PMMA/SAN/clay (60/40/2) nanocomposites annealed at 190°C for different time.

nanosheets span over the PMMA-rich and SAN-rich phase at the early stage of SD phase separation due to their lateral size larger than the domain size (Fig. 3 (c2)).

1 With the extending of annealing time, the domain size increases and the pristine
2 Na-MMT nanosheets are located in the PMMA-rich phase (Fig. 3 (c3) and (c4)),
3 which is consistent with the results reported by Qazvini et al. [35] that Na-MMT
4 migrated to the PMMA-rich domains during phase separation. The location of
5 Na-MMT in the PMMA-rich phase may indicate that the interaction between
6 clay-g-PMMA and SAN should be related with the grafted PMMA chains, rather than
7 the surface nature of Na-MMT.

8 Here, the selective location and migration of clay-g-PMMA nanosheets in
9 PMMA/SAN blend matrix seem abnormal and interesting. Maybe the dispersion of
10 clay-g-PMMA nanosheets in the PMMA-rich phase is more reasonable. Composto et
11 al. [23, 28] observed different selective segregation of modified SiO₂ nanoparticles
12 with different grafted PMMA chain lengths at the interfaces of PMMA/SAN blends or
13 in the PMMA-rich phase. Yu et al. [3] also reported that in PS-grafted SiO₂ filled
14 PMMA/SAN system, the PS functionalized SiO₂ nanoparticles were also located at
15 the PMMA-rich phase or the interface, rather than SAN-rich phase, which was
16 thought as the interface tension for the PS-SAN pair higher than that for the
17 PS-PMMA pair. Pristine Na-MMT usually preferred to be dispersed in the PMMA
18 phase, which was verified by Qazvini et al. [35] that Na-MMT migrated to the
19 PMMA-rich domains during phase separation for the existence of strong hydrogen
20 bonding interaction. In our work, the surface of clay is grafted with PMMA molecules
21 in low grafting density, but the clay-g-PMMA nanosheets abnormally prefer to be
22 dispersed in the SAN-rich phase at the early and medium stage of phase separation for

PMMA/SAN blend matrix, rather than in the PMMA-rich phase. Here, the stronger interaction between SAN and clay-g-PMMA might exist and should be explored further to explain the abnormally selective location of clay-g-PMMA in the phase-separated PMMA/SAN blend matrix.

3.3 Dispersion of Clay-g-PMMA nanosheets in PMMA and SAN unitary matrix

The original purpose for the preparation of clay-g-PMMA is to improve the dispersion state of clay in polymer matrix. It could be found in Fig. 3 (a) that clay-g-PMMA nanosheets are dispersed uniformly in the homogeneous PMMA/SAN blend matrix. Here, the difference for the dispersion state of clay-g-PMMA in PMMA or SAN unitary matrix should be also further explored. The ratios of polymer and clay-g-PMMA chosen here are just consistent with the proportion of the above-mentioned PMMA/SAN/clay-g-PMMA (60/40/2) nanocomposites. Fig. 4 shows the TEM micrographs of PMMA/clay-g-PMMA (60/2) and SAN/clay-g-PMMA (40/2) nanocomposites with or without being annealed at 190 °C for 1 h. Conspicuously, the dispersion of clay-g-PMMA in SAN matrix is much better than that in PMMA, even better than that in homogeneous PMMA/SAN blend. Most clay-g-PMMA nanosheets in SAN matrix are in the exfoliated state, while most clay-g-PMMA sheets in PMMA are in the intercalated or aggregated state. Fig.5 shows the XRD curves of pristine Na-MMT, PMMA/clay-g-PMMA (60/2) and SAN/clay-g-PMMA (40/2) nanocomposites with or without being annealed at 190 °C for 1 h. The characteristic (001) peaks of pristine Na-MMT and PMMA/clay-g-PMMA (60/2) nanocomposite appear at $2\theta = 6.60^\circ$ and 5.10° , respectively,

Fig. 4. TEM micrographs of (a), (b) PMMA/clay-g-PMMA (60/2) and (c), (d) SAN/clay-g-PMMA (40/2) nanocomposites. The samples of (b) and (d) are both annealed at 190°C for 1h, while the samples of (a) and (c) are without annealing.

while the visible diffraction peaks disappear in the XRD pattern of SAN/clay-g-PMMA (40/2) nanocomposite, indicating that the clay-g-PMMA nanosheets are exfoliated in SAN matrix and intercalated in PMMA matrix, respectively. Such abnormal phenomenon just coincides with the selective location of clay-g-PMMA in SAN-rich phase with the phase separation of blend matrix. It is well known that there exist strong hydrogen bonding interactions between the hydroxyl groups of pristine Na-MMT and the carbonyl groups of PMMA [36, 37]. The particular preference of clay-g-PMMA to SAN phase indicates that there might be some interactions between clay-g-PMMA and SAN. Furthermore, after being annealed at 190 °C for 1 h, the

Fig. 5. XRD curves of pristine Na-MMT, PMMA/clay-g-PMMA (60/2) and SAN/clay-g-PMMA (40/2) nanocomposites with or without being annealed at 190°C for 1h.

aggregation of clay-g-PMMA in PMMA (Fig. 4(b)) is much more obvious than that in SAN (Fig. 4(d)), while the characteristic peak (001) of PMMA/ clay-g-PMMA (60/2) nanocomposite becomes more remarkably and just a very weak peak appears in the XRD pattern of SAN/clay-g- PMMA (40/2) nanocomposite, as shown in Fig. 5. Such results also confirm the existence of some interactions between clay-g-PMMA and SAN. The increase of agglomeration for clay-g-PMMA in SAN matrix upon annealing indicates that their interaction might be destroyed to a certain extent at high annealing temperature. On the other hand, although the molecular weight of grafting chains is a little larger than that of matrix chains, the grafting density (~ 0.04 chains/nm²) of clay-g-PMMA is too low to completely shield the interactions between the clay nanosheets, resulting in obvious agglomeration of clay-g-PMMA in PMMA matrix [22, 24, 25].

For a further understanding on the bewildering dispersion of clay-g-PMMA in PMMA and SAN matrix, the interaction between nanoparticles and polymer matrix should be explored completely. MDSC is used to investigate the confine effect of filler on the polymer chains by detecting the change of heat capacity [38, 39]. Wunderlich et al. [40] introduced the concept of rigid amorphous fraction (RAF) to determine the crystallinity for semicrystalline polymers via the value of reversing heat capacity, ΔC_p , at the glass transition stage. Then the RAF is expanded to polymer nanocomposites to determine the immobilized fraction according to [38]

$$\text{RAF} = 1 - \text{filler content} - \Delta C_p / \Delta C_{p, \text{pure}} \quad (1)$$

where ΔC_p and $\Delta C_{p, \text{pure}}$ are the increments of reversing heat capacity at the glass transition for the nanocomposite and pure polymer, respectively. The reversing component of heat capacity includes the contributions of polymer and nanoparticles. Fig. 6 shows the reversing heating capacity of PMMA/clay-g-PMMA and SAN/clay-g-PMMA nanocomposites with different filler loadings during glass transition. It is obvious that the reversing heat capacity value of clay-g-PMMA is much lower than those of PMMA and SAN. Hence, the specific reversing heat capacity of the nanocomposites C_p is mainly contributed by that of polymer matrix $C_{p, \text{polymer}}$. The measured C_p of the nanocomposites can be calculated according to mass balance

$$C_{p, \text{polymer}} = C_p / (1 - x_{\text{clay}}) \quad (2)$$

where x_{clay} is the mass fraction of clay-g-PMMA. The glass transition temperature T_g is determined at the inflection point of the curves in Fig. 6 and the ΔC_p at T_g is calculated from the distance between the two tangents to the data in the glassy and

Fig. 6. Reversing heat capacity of (a) PMMA/clay-g-PMMA and (b) SAN/clay-g-PMMA nanocomposites with different filler contents during glass transition.

Table 1 Glass transition temperature T_g and heat capacity ΔC_p of PMMA/clay-g-PMMA and SAN/clay-g-PMMA nanocomposites.

x_{clay} (%)	PMMA/clay-g-PMMA		SAN/clay-g-PMMA	
	T_g (°C)	$\Delta C_{p, \text{PMMA}}$ (J·g ⁻¹ ·°C ⁻¹)	T_g (°C)	$\Delta C_{p, \text{SAN}}$ (J·g ⁻¹ ·°C ⁻¹)
0	95.4	0.334	105.9	0.466
2.5	95.3	0.333	105.7	0.458
5	94.9	0.335	105.8	0.448
7.5	95.2	0.336	105.2	0.441
10	95.1	0.340	105.1	0.428

rubbery states away from the transition. The detailed data are listed in Table 1. In the PMMA/clay-g-PMMA nanocomposites, the $\Delta C_{p, \text{PMMA}}$ at T_g hardly changes with the increasing x_{clay} , suggesting that PMMA in the nanocomposite might behave like the pure polymer. However, in the SAN/clay-g-PMMA nanocomposites, the $\Delta C_{p, \text{SAN}}$ at T_g remarkably decreases with the increasing x_{clay} , indicating that a considerable fraction of SAN is immobilized. In all nanocomposites, the variation of T_g induced by the incorporation of clay-g-PMMA is less than 1 °C with increasing x_{clay} up to 10% and no additional glass or secondary transitions could be observed in all the nanocomposites, which tends to approve the two-phase model assuming an

immobilized glassy layer without detectable T_g surrounding the NPs [38]. The slight decline of T_g should be ascribed to the increase of free volume for polymer matrix, which might be induced by the mushroom surface of clay-g-PMMA.

Fig. 7 (a) shows the $\Delta C_{p, \text{ sample}}$ values of different samples normalized by the $\Delta C_{p, \text{ pure}}$ values of the pure polymers. According to Eq. (1), the blue line in Fig. 7 (a) represented the case when no RAF is present. The $\Delta C_{p, \text{ sample}}/\Delta C_{p, \text{ pure}}$ values for PMMA/clay-g-PMMA nanocomposites are close to this line. For SAN/clay-g-PMMA nanocomposites, the decrease of the normalized relaxation strength is much steeper than the blue line. The difference between the measured values and the blue line represents the immobilized fraction (RAF), while the difference between the blue line and the black dotted line corresponded to the filler fraction.

Fig. 7. (a) Calorimetric relaxation strength and (b) interfacial layer amount as a function of clay content for PMMA/clay-g-PMMA and SAN/clay-g-PMMA nanocomposites.

The immobilized fraction of polymer Φ_{imm} , or the glassy layer encircling NP, can be determined according to [38]

$$\text{RAF}_{\text{polymer}} = \Phi_{\text{imm}} = 1 - \Delta C_{p, \text{ polymer}} / \Delta C_{p, \text{ pure}} \quad (3)$$

assuming that the density of the immobilized and free polymer fractions is equal. Fig. 7 (b) shows Φ_{imm} as a function of x_{clay} . The Φ_{imm} values for PMMA/ clay-g-PMMA nanocomposites are very close to zero, indicating that no RAF is present. However, the Φ_{imm} values for SAN/clay-g-PMMA nanocomposites are approximately proportional to x_{clay} , suggesting that the decrease of SAN chain mobility should be attributed to the interaction between SAN and PMMA grafted on the surface of clay. Hence, the good dispersity of clay-g-PMMA in the SAN matrix from the TEM micrographs could be easily understood and the immobilized SAN chains on the surface of clay-g-PMMA could hinder the aggregation of modified clay. Besides the confined effect of SAN chains surrounding clay-g-PMMA nanosheets, there may exist another possible contribution for the decreasing $\Delta C_{\text{p, SAN}}$ and the constant $\Delta C_{\text{p, PMMA}}$ values with the increase of x_{clay} , which comes from different chain conformations of grafted PMMA (different ratio of loops to tails) near the surface of nanosheets under different interaction environments with surrounding polymer chains (PMMA or SAN). In SAN/clay-g-PMMA nanocomposites with favorable interaction, the grafted PMMA chains near the surface of nanosheets may mainly present the tail conformation, while they may present the loop conformation in PMMA/clay-g-PMMA nanocomposites.

3.4 Cause for selective distribution and migration of Clay-g-PMMA nanosheets in the blend matrix

The interaction of clay-g-PMMA and SAN inferred by the results of MDSC and TEM should be further explored to understand the cause for selective distribution and

1 migration of clay-g-PMMA nanosheets in the phase-separated blend matrix. SAN is a
 2 random copolymer of styrene and acrylonitrile. To further clarify the origin of such
 3 mysterious interaction, PMMA/PAN/clay-g-PMMA and PMMA/PS/clay-g-PMMA
 4 nanocomposites were also prepared by solution casting and annealed at 190 °C for
 5 different time. Fig. 8 shows the TEM micrographs for PMMA/PAN/clay-g-PMMA
 6 and PMMA/PS/clay-g-PMMA nanocomposites with and without annealing. Here, the
 7 bright region also refers to the PMMA phase and the dark region refers to the PAN or
 8 PS phase in the bright-field TEM micrographs. It can be found that PMMA/PAN and
 9 PMMA/PS blend matrices without annealing are both inhomogeneous and the
 10 clay-g-PMMA nanosheets all prefer to be located in the PMMA phase of two
 11 abovementioned heterogeneous blend matrices with or without annealing, indicating

13
 14 **Fig. 8.** TEM images of (a) PMMA/PAN/clay-g-PMMA (60/40/2) and (b)
 15 PMMA/PS/clay-g-PMMA (60/40/2) nanocomposites annealed at 190 °C for different
 16 time: (1) 0s, (2) 30min, (3) 24h. The bright phase corresponds to the PMMA domains,
 17 and the gray phase corresponds to PAN or PS domains.

1 that the interaction between clay-g-PMMA and PMMA might be stronger than those
2 of clay-g-PMMA/PAN and clay-g-PMMA/PS. Hence, such interaction between
3 clay-g-PMMA and SAN should be attributed to the grafted PMMA and the SAN
4 copolymer, rather than styrene or acrylonitrile. It could be deduced that the interaction
5 of clay-g-PMMA and SAN might be derived from the miscibility induced by the
6 so-called “repulsion effect” of the grafted PMMA with SAN matrix [30].

7 At the early and medium stages of phase separation for PMMA/SAN blend matrix,
8 the clay-g-PMMA nanosheets prefer to be located in the SAN-rich phase due to the
9 abovementioned miscibility of PMMA end-tethered on the clay and SAN induced by
10 the repulsion effect. However, at the late stage of phase separation, the clay-g-PMMA
11 nanosheets gradually migrate to the interface, which may be induced by the phase
12 separation of the grafted PMMA chains and surrounding SAN. It is well known that
13 the localization of NPs in an immiscible or partially miscible blend matrix always
14 depends on many factors, such as the affinity of NPs to each polymer, mixing
15 sequence, mixing time, interfacial tension and viscosity of two polymers [41].
16 However, the equilibrium localization of NPs in the blend matrix should be governed
17 by their thermodynamics and the minimization of the interfacial energy is the
18 thermodynamic driving force for the NPs to localize in a specific phase or at the
19 interface [42, 43]. A quantitative estimation of wetting coefficient may give the idea
20 about the equilibrium selective location of clay-g-PMMA in the phase separated blend
21 matrix driven by the thermodynamic forces, providing the surface free energy of the
22 components. According to the Young’s equation, the location of filler in a polymer

blend matrix can be also predicted by evaluating the wetting coefficient ω [44]

$$\omega_a = \frac{\gamma_{\text{filler-A}} - \gamma_{\text{filler-B}}}{\gamma_{\text{A-B}}} \quad (4)$$

where γ_{i-j} is the interfacial tension between the components pair i and j . The fillers are predicted to locate in the A-rich phase when $\omega_a < -1$, at the interface between two phases when $-1 \leq \omega_a \leq 1$ and within the B-rich phase when $\omega_a > 1$. Here, the interfacial tension between two components can be calculated from the surface tensions of components using the geometric mean equation [45, 46]:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \times \gamma_2^d} - 2\sqrt{\gamma_1^p \times \gamma_2^p} \quad (5)$$

where γ_i is the surface tension of components i ; γ^d and γ^p are the dispersive part and polar part of the surface tensions of components i , respectively. Here, the surface tensions of PMMA and SAN are extrapolated to the investigated temperatures using the temperature coefficients ($-d\gamma_{\text{PMMA}}/dT=0.076$, $-d\gamma_{\text{SAN}}/dT=0.053$) extracted from the literatures [42, 43]. Furthermore, the surface tension of clay-g-PMMA is obtained as 43.34 mN/m by contact angle measurements at room temperature, which is approximate to those of commercial organically modified clays (Cloisite 20A and Cloisite 15A) from Southern Clay Products, Inc., USA [47]. It is obvious that all the ω_a values in Table 2 in the investigated temperature region are between -1 and 1, suggesting that clay-g-PMMA should be located at the interface of PMMA/SAN in the thermodynamic equilibrium state. Such predictions are just consistent with our TEM results for the samples after being annealed at 190°C for 48 h. ~~It takes a long time for clay-g-PMMA to migrate from the SAN-rich phase at the early and medium stages of phase separation for PMMA/SAN blend matrix into the interface in the~~

~~thermodynamic equilibrium state (at the late stage of phase separation).~~

Table 2 Interfacial tension and wetting coefficient according to the geometric mean equation

Temperature (°C)	Interfacial tension (mN/m)			Wetting coefficient ω_a	Location prediction
	$\gamma_{\text{PMMA-clay}}$	$\gamma_{\text{SAN-clay}}$	$\gamma_{\text{PMMA-SAN}}$		
170	0.073	0.168	0.200	0.476	Interface
190	0.076	0.158	0.214	0.383	Interface

~~Based on the abovementioned results, we can infer that there should exist a certain amount of immobilized SAN chains on the surface of clay g-PMMA nanosheets detected through MDSC method might be both induced by the miscibility between the grafted PMMA chain and surrounding SAN their miscibility. It should be noted that the MDSC results are detected at the glass transition stage of PMMA or SAN matrix and the temperature ranges are both far below the phase separation temperature of PMMA/SAN blends. In general, the relaxation behavior of polymer chains grafted to the solid surface is distinct from that of free or entangled chains and is strongly influenced by the embedded particle [48-50]. Furthermore, besides a small population of SAN chains dynamically immobilized to form a thin adsorption layer surrounding nanosheets, another population of SAN chains is dynamically restricted and the according translational diffusion of chains could be completely suppressed irrespective of the unaffected segmental dynamics, resulting in the enhancement of miscibility between grafted PMMA chains and surrounding SAN chains [51, 52]. should be enhanced and there should exist homogeneous nanoscale regions of PMMA/SAN blend adjacent to the surface of clay nanosheets, which may correspond to the immobilized fractions in SAN/ clay g-PMMA nanocomposites~~

~~through MDSC measurement~~ On the other hand, low grafting density of PMMA
 end-tethered on the surface of clay can hardly shield the interactions among the clay
 nanosheets and further hardly hinder the aggregation of such clay-g-PMMA
 nanosheets in the PMMA matrix, indicating that there exist unfavorable (repulsive)
 interactions between PMMA and clay-g-PMMA, although the matrix and grafted
 chains have the same chemical composition. Namely, the PMMA matrix and grafted
 chains might hardly interpenetrate, resulting in no immobilized PMMA chains in
 PMMA/clay-g-PMMA nanocomposites detected through MDSC measurements.
 Hence, it is easy to understand different dispersion states of clay-g-PMMA nanosheets
 in the PMMA or SAN matrix without annealing in Fig. 4 (a) and (c). When the
 samples are annealed at 190 °C for 1 h, the unfavorable interactions between PMMA
 and clay-g-PMMA aggravate the aggregation of clay-g-PMMA nanosheets in neat
 PMMA matrix, while the miscibility of grafted PMMA chains and surrounding SAN
 chains should be destroyed and the homogeneous nanoscale regions of PMMA/SAN
 blend near the surface of clay-g-PMMA nanosheets may gradually disappear,
 resulting in some agglomeration of clay-g-PMMA nanosheets in neat SAN matrix.

~~When PMMA/SAN/clay-g-PMMA nanocomposites are thermally annealed above~~
~~the phase separation temperature, the well-dispersed clay-g-PMMA nanosheets in the~~
~~homogeneous matrix preferentially migrate into the SAN-rich phase for the~~
~~unfavorable interactions between PMMA and clay-g-PMMA and the enhanced~~
~~miscibility of grafted PMMA chains and surrounding SAN chains.~~ Similarly, the
 clay-g-PMMA nanosheets at the late stage of SD for the blend matrices gradually

1 migrate from the SAN-rich phase to the interface due to the destruction of enhanced
 2 ~~with the extending of annealing time, the domain size of blend matrix increases~~
 3 ~~remarkably and the~~ miscibility of grafted PMMA chains and surrounding SAN chains
 4 ~~is gradually destroyed~~. Namely, the phase separation of grafted PMMA/surrounding
 5 SAN occurs later than that of blend matrix for the restrained diffusion of grafted
 6 PMMA chains ~~on the nanosheets~~ and surrounding SAN chains. After being annealed
 7 for a long time, the clay-g-PMMA nanosheets gradually migrate from the SAN-rich
 8 phase to the interface (thermodynamics equilibrium state) ~~between PMMA and SAN~~
 9 very slowly, owing to the relatively high viscosity of SAN/clay-g-PMMA and the
 10 weak mobility of clay-g-PMMA nanosheets with relatively large size and weight. ~~The~~
 11 ~~abovementioned two factors may hinder the clay-g-PMMA nanosheets to reach the~~
 12 ~~distribution state and hence most clay-g-PMMA nanosheets gradually migrate to the~~
 13 ~~interface of two PMMA/SAN matrices.~~

14 For spherical NPs silica SiO₂, Composto et al. [23, 28] grafted SiO₂ with PMMA
 15 brushes having different molecular weights at fixed grafting density and then
 16 investigated the location of modified NPs in a phase-separated PMMA/SAN blend.
 17 With the increase of brush length, the PMMA-grafted SiO₂ NPs were found to
 18 segregate to the PMMA/SAN interface, partition between the interface and PMMA
 19 phase, or locate in the PMMA phase, respectively. Hence, the surface and interfacial
 20 energy of polymer grafted NPs are thought to be determined by chain conformation
 21 (entropic) and the density of end groups (enthalpic). Other spherical gold NPs were
 22 also densely coated with varying graft length of PS and then introduced into PS/poly

(vinyl methyl ether) (PVME) blend [29]. Gold NPs grafted with short PS chains were located in the PVME phase due to the exclusion from the PS phase with the grafted chains shorter than the matrix chain and the enthalpic interaction between PVME and gold core with insufficient screening of large core by small PS shell, while the localization of gold NPs grafted with long PS chains in the PS phase was facilitated by the favorable matrix/graft interactions. However in our study, the screening of nanosheets by low grafting density of PMMA is also far from sufficient and the interaction between clay-g-PMMA nanosheets and SAN originates from the enhanced miscibility of the grafted PMMA chains and SAN, rather than that of the clay nanosheet and SAN. Hence, we may provide a promising and simple method to control the selective location of NPs in the blend matrix (in one phase or interface), in virtue of the miscibility transition for a chemically dissimilar graft-matrix polymer chain that exhibits LCST behavior. Furthermore, the grafting of PMMA onto the surface of clay can also significantly improve the loading and dispersion stability of filler in SAN matrix and the chemically dissimilar matrix may be further extended to the polymers which can be partially or completely miscible with grafted chains.

4. Conclusions

In summary, the clay-g-PMMA nanosheets with low grafting density of ~ 0.04 chains/nm² prepared by soap-free emulsion polymerization were incorporated into PMMA/SAN blend matrix and the dispersion of clay-g-PMMA nanosheets in the phase-separated blend matrix was investigated. The mushroom-like distribution of grafted PMMA chains on the surface of clay nanosheets can hardly shield the

interactions between the clay nanosheets, resulting in obvious agglomeration of clay-g-PMMA nanosheets in unitary PMMA matrix and no RAF layer between clay-g-PMMA and PMMA. However, the uniform dispersion of clay-g-PMMA nanosheets in unitary SAN matrix and the detectable immobilized SAN chains around the modified clay may indicate the favorable interaction between clay-g-PMMA and SAN induced by the miscibility of grafted PMMA and surrounding SAN chains. Hence, with phase separation of PMMA/SAN blend matrix, the well-dispersed clay-g-PMMA nanosheets in the blend matrix are first located in the SAN-rich phase and then gradually migrate to the interface between PMMA and SAN. The enhanced miscibility between grafted PMMA and surrounding SAN may result in the distribution of clay-g-PMMA in the SAN-rich phase at the early and medium stages of phase separation for blend matrix. Such miscibility may be destroyed with further annealing for a long time and the migration of clay-g-PMMA to the interface of PMMA/SAN may be the thermodynamic equilibrium distribution state, which is verified by the prediction of wetting coefficient. Hence, we may provide a promising and simple strategy to control the selective location of NPs in the blend matrix (in one phase or interface), in virtue of the miscibility transition for a chemically dissimilar graft-matrix polymer chain that exhibits LCST behavior.

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1 Graphical Abstracts

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4 The selective location of clay-g-PMMA nanosheets with low grafting density in
5 PMMA/SAN blend matrix can be controlled by the miscibility variation for the
6 grafted PMMA chains/SAN matrix chains.

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