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Description	

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Selective Migration of Silica Particles between Rubbers

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Abstract:

The migration of silica nanoparticles in the laminated sheets of poly(butadiene) (BR) and poly(styrene-co-butadiene) (SBR) rubbers is investigated. Laminated rubber sheets are subjected to various annealing conditions beyond their glass transition temperatures. After separation, the surface morphologies of separated sheets are observed by scanning electron microscopy. The transfer of particles occurs from SBR to BR during annealing, but not from BR to SBR. Since SBR exhibits a higher viscosity than BR under the experimental conditions, the transfer direction is determined by interfacial tension. Silica particles without any surface modification prefer to reside in BR. The diffusion distance is predicted from the Stokes-Einstein equation. Differential scanning calorimetric measurements show that BR crystallization is enhanced by the silica particles immigrated from the SBR sheet, because of their favorable nucleating ability. This study allows the prediction of silica particle localization in BR and SBR blends.

Keywords: Interphase transfer, Silica, Poly(butadiene), Poly(styrene-*co*-butadiene)

Introduction

Silica nanoparticles have applications in rubber nano-composites, because of their high reinforcing capability. Silica particles are known as a petroleum-free eco-friendly material, and are relatively economic to prepare compared with other fillers. Adding nanofillers into a rubber typically reduces the mobility of polymer chains, and increases the viscosity and elastic modulus. Silica nanoparticles also affect the viscoelastic properties of the polymer matrix [1-3].

Silica nanoparticles have become a promising candidate for replacing carbon blacks in tire applications. Waddell et al. [4,5] reported that adding silica particles enhanced tear strength, cut-growth resistance, elongation at break and the ultimate strength of the rubber. They also found that it affected the rolling resistance and wet grid performance. Rubber composites with silica particles exhibit lower hysteresis energies than composites containing carbon blacks at ~50 ^{O}C, which is the typical working temperature of tires [6-8].

Poly(styrene-*co*-butadiene) (SBR) and poly(butadiene) (BR) rubbers are common materials in tire applications [1]. SBR imparts favorable wet-skid and traction properties, and the low glass transition temperature T_g of BR renders it useful in winter tires. Moreover, BR imparts good abrasion resistance, tread wear performance and high elasticity. SBR and BR are often blended to meet the requirements of final applications. Fujimoto and Yoshimiya [9] suggested that SBR/BR blends prepared by mill-mixing exhibited a homogeneous structure. Marsh et al. [10] used electron microscopy to observe the morphology of rubber blends, and reported a similar result. Ougizawa et al. reported recently that SBR is thermodynamicaly immiscible with BR [11], and surface-modified silica particles have since been reported to enhance the compatibility between SBR and BR [12,13], similarly to other nanofillers [14,15].

The distribution and migration of fillers plays an important role in the structure and properties of polymer composites [1,16-32], and much research has focused on the distribution of silica nanoparticles

in polymer blends. Liu et al. [21] studied the effect of silica particle surface properties on the morphology and properties of polyamide 6 (PA6) and acrylonitrile-butadiene-styrene terpolymer (ABS) blends. Hydrophilic silica particles were concentrated within the PA6 matrix, whereas hydrophobic ones tended to preferentially reside at the interphase, leading to a reduction in ABS domain. The distribution state of silica particles strongly affects the rheological and mechanical properties of composites. Maiti et al. [23] evaluated the dynamic mechanical properties to estimate the distribution of silica particles in blends of natural rubber (NR) and epoxidized natural rubber (ENR). Silica particles preferentially migrated to ENR because of the interaction between silanol groups in silica and epoxidized groups in the matrix. Ziegler and Schuster [24] found that untreated silica particles preferred residing in ENR to BR, while after surface treatment, silica localized in the BR phase. Le et al. [25] reported that the selective localization of silica particles occurred in ternary blends of NR, SBR and ethylene-propylene rubber, and silica localization was strongly affected by the wetting behavior of the rubber. Lee et al. [26] investigated the effect of silica on the morphology of PP and polyolefin elastomer (POE) blends with co-continuous structure. Silica particles preferentially localized in the PP phase, leading to a morphology change from co-continuous to island-matrix, in which elongated POE particles were dispersed in the PP matrix. Kawazoe and Ishida [27,28] found that the selective absorption of acrylonitrile-butadiene rubber (NBR) on the silica surface was responsible for the localization of silica particles in the NBR phase of SBR/NBR blends. Few studies have been published on SBR/BR blends filled with silica particles, in spite of their industrial importance [14,15,29]. The interphase transfer behavior of silica in this blend also remains unresolved, and controlling the distribution of silica in the SBR/BR blend for tire applications remains a challenge.

In this study, the transfer of silica nanoparticles between BR and SBR is investigated. Our previous studies on the transfer of carbon nanotubes [30], nanofibers [31], and tackifier [32] between immiscible

polymer pairs are consulted to understand the experimental process. A recent study regarding the nucleating ability of silica particles on BR [33] is also considered to evaluate the transfer.

Experimental

Materials

All materials used in this research are commercially available. The average molecular weight of rubbers was determined by gel permeation chromatography with a polystyrene standard, and the values are summarized in Table 1. The *cis*- and vinyl contents in BR are 94.8 and 0.5%, respectively. The styrene and vinyl contents in SBR are 27 and 59%, respectively. Silica nanoparticles were used without surface modification (Zeosil, 115GR), and are hereafter referred to as Silica. Their diameter is ~16 nm. Aromatic process oil (Idemitsu Kosan, Diana Process Oil AH) was also used.

[Table 1]

Sample preparation and transfer experiment

Rubbers were blended with Silica and process oil with a conventional two-roll mill. The rubber/Silica/oil blend ratio was 100/70/10 (weight fraction), which is typical of industrial tire compositions. Sample sheets 1 mm thick were used for transfer experiments without vulcanization. Pure rubber samples were also compressed into flat 1 mm thick sheets.

For transfer experiments, a rubber sheet containing Silica was laminated with a sheet of another without Silica, under light pressure to adhere them. These laminated sheets were annealed at 50 ^{o}C for 1.5, 6, 24 and 100 h in an oven. Annealing temperature was determined to obtain information on

interphase transfer at typical working temperatures. Laminated sheet samples were also ‘annealed’ at room temperature, to evaluate the effect of annealing temperature.

Sheets were separated after cooling so that morphology observations at the boundary could be made by SEM. A small section of the laminated sheet boundary region was cut out with a microtome for DSC measurements. The thickness of each layer for the DSC measurement was ~30 μm. The procedure is illustrated in Figure 1.

[Figure 1]

Measurements

The morphologies of rubber/Silica composites and the surface of separated sheets were observed by scanning electron microscopy (SEM, Hitachi, S4100). Specimens were pre-coated with Pt-Pd using a sputter coating machine.

The thermal properties of laminated sheets before and after annealing were analyzed by differential scanning calorimetry (DSC, Mettler, DSC820) under a nitrogen atmosphere. Approximately 10 mg of sample was encapsulated in a standard Al pan. Samples were cooled from room temperature to -80 ^{O}C at a rate of 5 ^{O}C/min, to evaluate the crystallization behavior.

The frequency dependence of oscillatory shear moduli for the pure rubbers were measured by a parallel plate rheometer (TA Instruments, AR-2000ex) at 25, 50, 70 and 100 ^{O}C under a nitrogen atmosphere. The plate diameter was 25 mm, and the gap between plates was ~1 mm.

Results and Discussion

Rheological properties of rubbers

Master curves of the frequency dependence of oscillatory shear moduli for BR and SBR are shown in Figure 2. The reference temperature (i.e., that used for the transfer experiments) is 50 ^{o}C.

[Figure 2]

The time-temperature superposition principle is applicable to both BR and SBR, demonstrating that both polymers are fully amorphous in the experimental temperature range. The shift factors a_T obey the Williams-Landel-Ferry (WLF) equation [34]:

$$\log a_T = \frac{-c_1(T - T_r)}{c_2 + (T - T_r)} \quad (1)$$

where T_r is the reference temperature, and c_1 and c_2 are the WLF parameters.

Since SBR has a higher T_g than BR, a_T values are strongly dependent upon temperatures (25-100 ^{o}C).

The master curves of BR and SBR are typical in the terminal and rubbery regions. The loss modulus *G"* shows a maximum, which can be approximated to the inverse of average relaxation time; 0.1 and 10 s for BR and SBR, respectively.

Interphase transfer behavior of Silica between rubbers

Prior to transfer experiments, the distribution of Silica in each rubber was investigated by SEM. Figure 3 shows SEM images for the cut surfaces of the BR and SBR composites.

[Figure 3]

Silica is distributed homogeneously in each rubber. The size of dispersed Silica is about 20-30 nm. This value is similar to the diameter of individual particles, indicating that little agglomeration occurs.

The transfer of Silica between the rubbers was investigated following the method shown in Figure

1. Although the rubber sheets are sticky, they are easily separated after cooling. Observation by the naked eye suggested that particles are not removed from the sheets during separation. Figure 4(a) shows SEM images of the BR sheet surface after separation from the SBR/Silica sheet, while Figure 4(b) shows that of the SBR sheet surface after separation from BR/Silica.

[Figure 4]

Silica migrates from SBR to BR, and accordingly Silica is found on the BR surface. The cut surface of the boundary region in the laminated sheets is also observed by SEM. However, the migration into the BR phase is not clearly detected. Because the sample preparation, i.e., cut at the boundary region, is not so easy, and therefore, it is not clearly observed by SEM.

As seen in Figure 4(a), the particle size of Silica on the BR surface is smaller than the average size in the SBR composite, indicating that only small particles can transfer. It is reasonable because the Brownian motion is the main driving force for the movement of dispersed nanoparticles. In contrast, no Silica is detected on the SBR surface, suggesting that the migration of Silica from BR to SBR does not occur.

The diffusion constant D of a spherical particle in a liquid is described by the Stokes-Einstein equation [35]:

$$D = \frac{k_B T}{6\pi\eta_0(T)R} \tag{2}$$

where k_B is the Boltzmann constant, R is the particle radius, and $\eta_0(T)$ is the zero-shear viscosity of the medium at the experimental temperature T.

The zero-shear viscosity at T, $\eta_0(T)$, is expressed by the shift factor and the zero-shear viscosity at reference temperature T_r. [36]

$$\eta_0(T) = a_T \eta_0(T_r) \tag{3}$$

The zero-shear viscosity is defined by

$$\eta_0 = \int_{-\infty}^{\infty} H(\tau)\tau d\ln\tau \quad (4)$$

where $H(\tau)$ is the relaxation spectrum and τ is the relaxation time.

The zero-shear viscosity of SBR is 100 times as high as that of BR, assuming the distribution of relaxation times is the same for both rubbers. Considering that SBR has a broad molecular weight distribution, the viscosity ratio will be larger than 100. Consequently, the diffusion constant of Silica in SBR is, at least, 100 times smaller than that in BR.

Samples containing Silica are prepared by compression-molding, so a thin surface layer of a rubber without Silica must exist. In support of this, Silica is not detected by SEM on the surface of the composite sheet. Therefore, Silica must diffuse through this surface layer to attach at the neighboring sheet, prior to the transfer into the other rubber. Since the diffusion rate of Silica in BR is significantly higher than that in SBR, diffusion through the surface layer occurs more quickly in BR. However, Silica transfer from BR to SBR is not detected, indicating that the compatibility between Silica and rubber determines the interphase transfer. Considering that there is no chemical interaction between Silica and rubbers, interfacial tension between BR and Silica is lower than that between SBR and Silica.

BR is a semi-crystalline polymer and exhibits crystallization during cooling [33,37]. Even a tiny amount of Silica (e.g., 0.01 parts per hundred of rubber) exhibits a marked nucleating ability on the crystallization of BR [33]. Therefore, the transfer of Silica into the BR phase can be confirmed by thermal analysis.

Figure 5 shows DSC cooling curves of samples taken from the interface of laminated sheets of the SBR composite and pure BR, before and after annealing. Curves of the laminated sheets annealed at room temperature are also shown.

[Figure 5]

The sample prior to annealing exhibits the BR crystallization peak at ~-40.5 ^{o}C. This peak

temperature is unchanged after annealing for 1.5 and 6 h at 50 ^{O}C. The results indicate that Silica does not transfer into BR during the early stages of annealing. The endothermic peak shifts to higher temperature upon annealing of 24 h or more. This suggests the Silica originating from SBR acts as a nucleating agent and enhances BR crystallization. Silica requires time to migrate through the rubber layer at the SBR surface and attach to BR. Equation 2 indicates that the diffusion constant of Silica in SBR at 50 ^{O}C is ~2 x 10^{-21} m^2/s. As a result, the diffusion distance at 50 ^{O}C after 24 h is estimated to be ~30 nm, which is approximately the thickness of the surface layer. The calculated distance also indicates that the Silica diffusion inside of BR is not easily detected by SEM.

Figure 5 also shows that the endothermic peak is unchanged after 24 h at 25 ^{O}C, and the peak shift is detected after 10 days. The zero-shear viscosity of SBR at 25 ^{O}C is ~10 times higher than that at 50 ^{O}C. Thus, the diffusion constant at 25 ^{O}C of Silica in SBR is at least 10 times smaller than that at 50 ^{O}C, which is in a good agreement with the DSC results in Figure 5.

Conclusion

The transfer of Silica between the immiscible BR and SBR rubbers employed in the tire industry, was studied by SEM and DSC. SEM images suggest that Silica migrates from SBR to BR. Silica is found to be localized on the BR sheet surface, after separation from the SBR composite sheet. In contrast, migration from BR to SBR does not occur, which indicates that the compatibility between Silica and rubber is the driving force for the transfer. Silica prefers to be localized in the rubber that has lower interfacial tension. Silica transfer from SBR to BR is confirmed by DSC measurements, by investing the crystallization of BR. Silica must diffuse through the surface layer of the composite sheet prior to transfer, and so takes some time to migrate to the other sheet. The annealing time required for transfer is greatly affected by the annealing temperature, and can be predicted by the diffusion and WLF equations.

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Figure Captions

Figure 1 Illustration of the transfer experiment between rubbers.

Figure 2 Master curves of frequency dependence of oscillatory shear moduli such as (closed symbols) storage modulus G' and (open symbols) loss modulus G" for (a) BR and (b) SBR at 50 ^{O}C.

Figure 3 SEM images of cut surface for (a) BR composite and (b) SBR composite

Figure 4 SEM images of (a) BR surface after separation from the SBR composite and (b) SBR surface after separation from the BR composite.

Figure 5 DSC cooling curves of the interfacial layer in the laminated sheets of the pure BR and the SBR composite after annealing for various times at 50 ^{O}C and 25 ^{O}C.

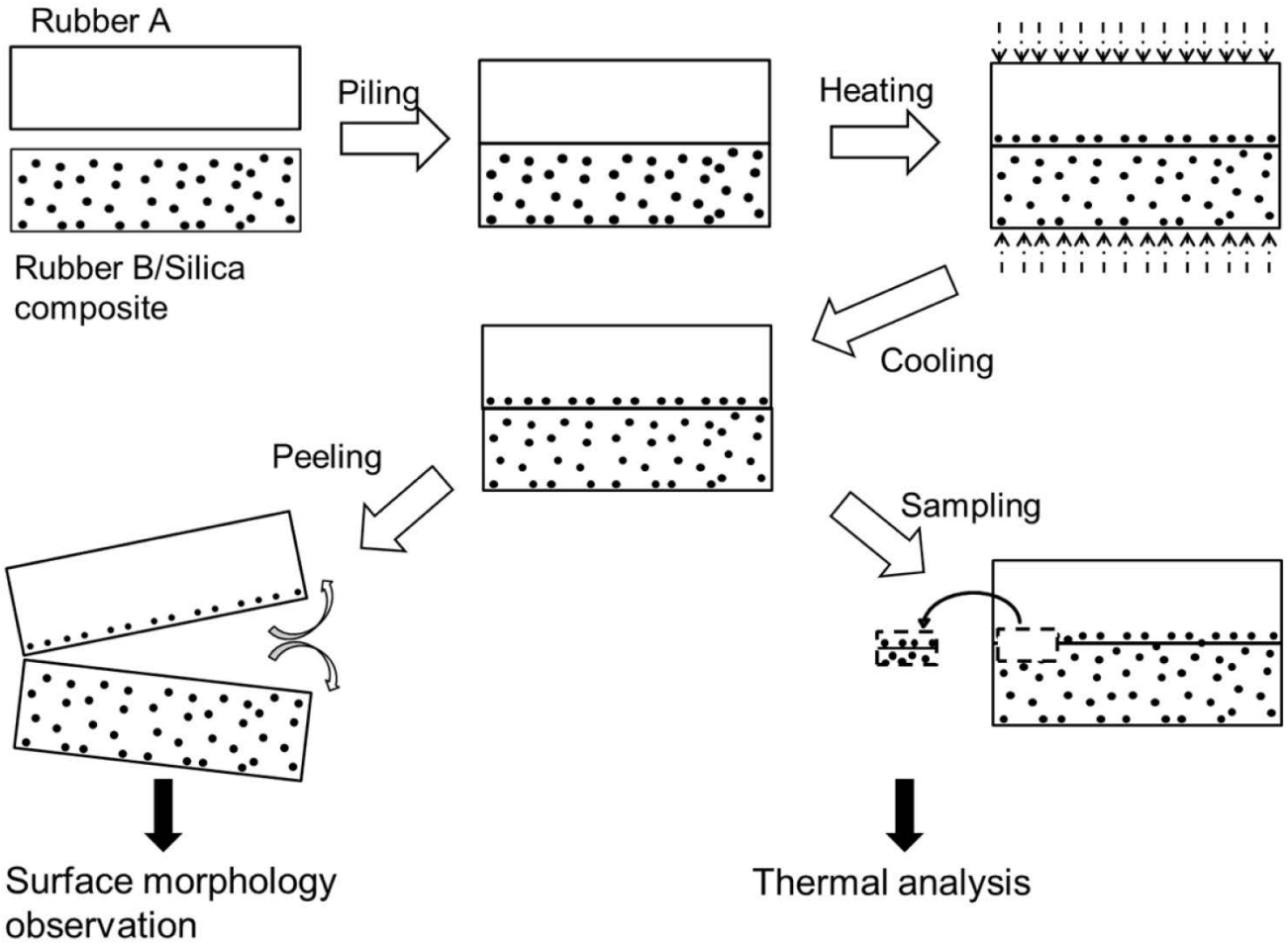
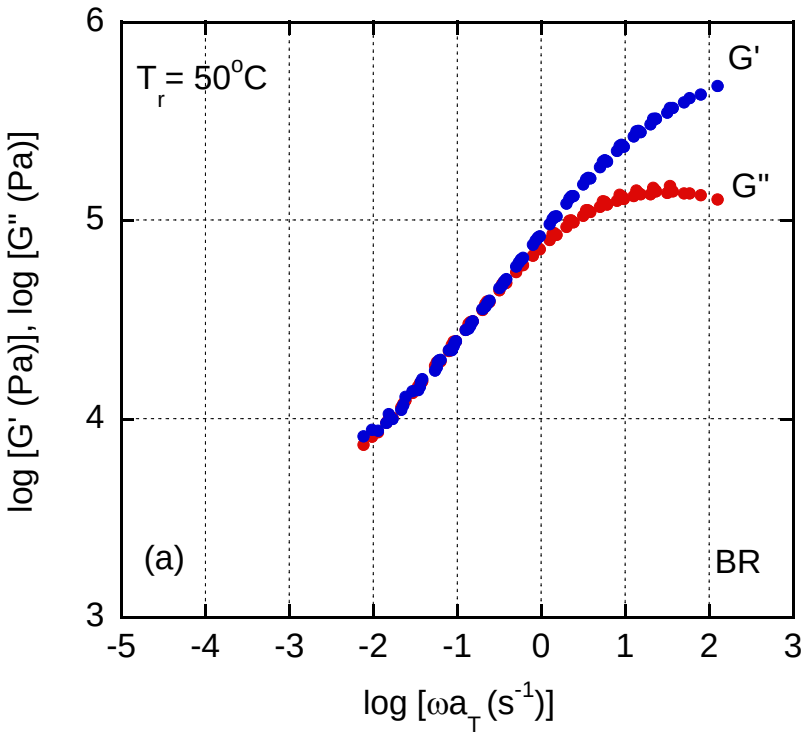

Rubber A
Rubber B/Silica composite
Piling
Heating
Cooling
Peeling
Sampling
Surface morphology observation
Thermal analysis

Figure 2


T_r = 50°C
G'
G"
(a)
BR
log [G' (Pa)], log [G" (Pa)]
log [ωa_T (s^-1)]
6
5
4
3
-5
-4
-3
-2
-1
0
1
2
3

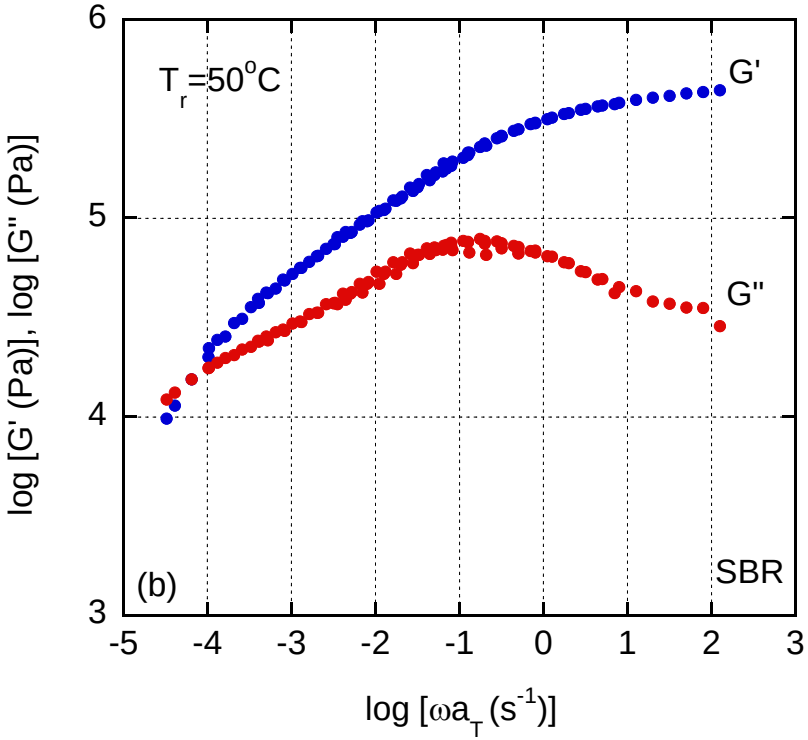

T_r =50°C
G'
G"
(b)
SBR
log [G' (Pa)], log [G" (Pa)]
log [ωa_T (s^-1)]
6
5
4
3
-5
-4
-3
-2
-1
0
1
2
3

Figure 3

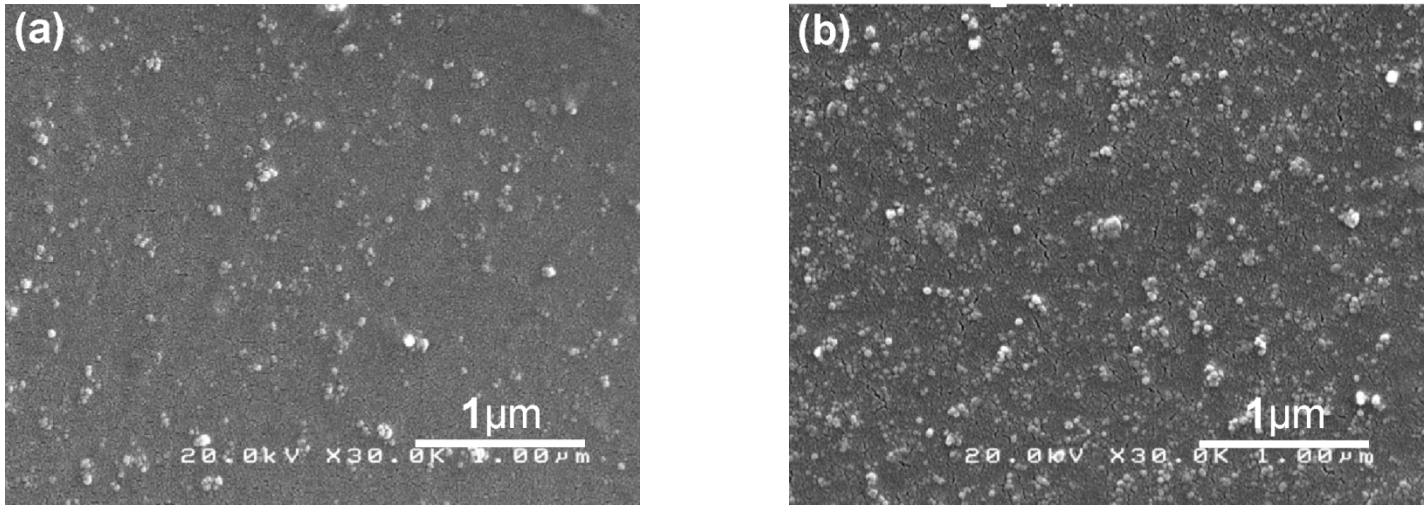
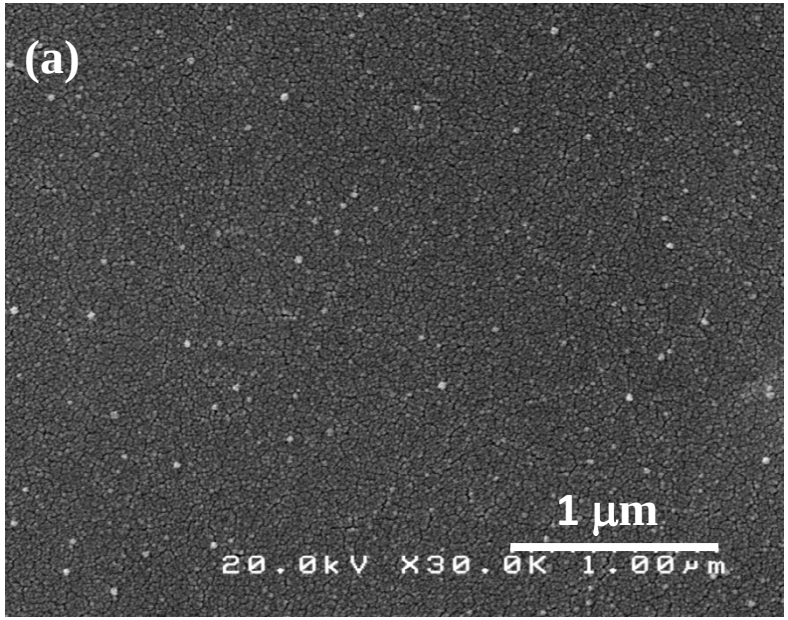


Figure 4



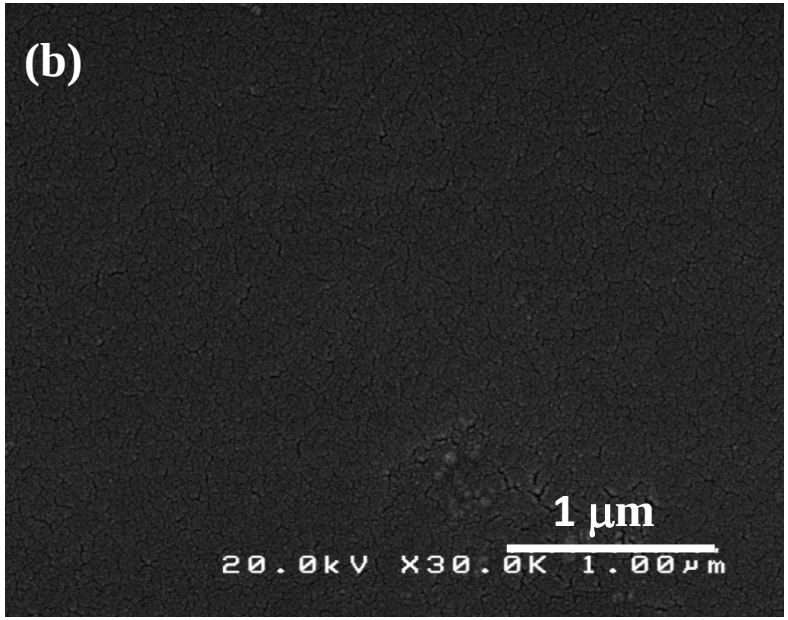
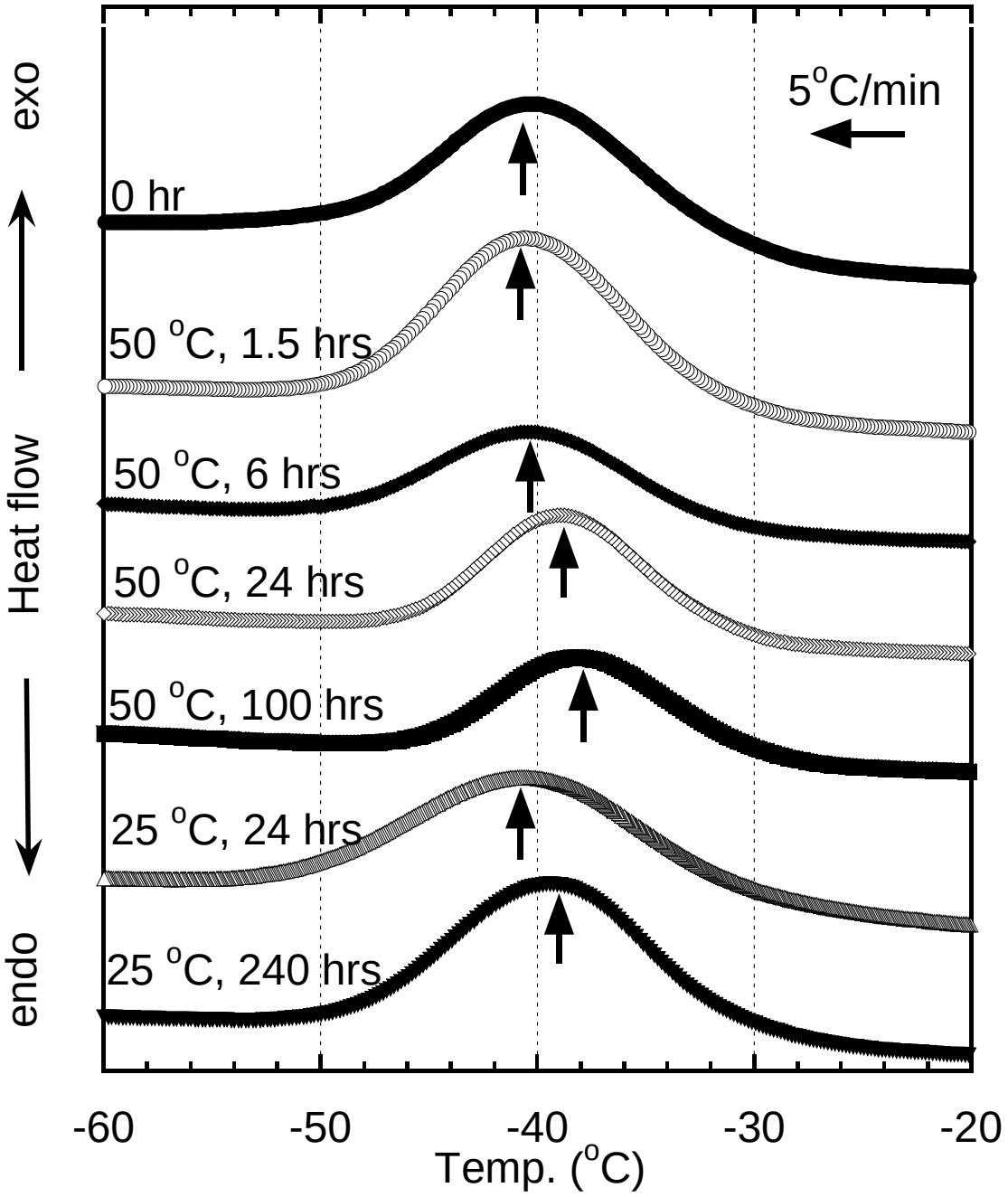


Figure 5


exo
Heat flow
endo
5°C/min
0 hr
50 °C, 1.5 hrs
50 °C, 6 hrs
50 °C, 24 hrs
50 °C, 100 hrs
25 °C, 24 hrs
25 °C, 240 hrs
-60
-50
-40
-30
-20
Temp. (°C)