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RHEOLOGY OF NANOSILICA FILLED POLYETHYLENE

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ในการศึกษานี้ ฟูมซิลิกา ขนาด 7 และ 14 นาโนเมตร ถูกใช้เติมในพอลิเอทิลีน อย่างละสองน้ำหนักโมเลกุล ทั้งแบบสายโซ่ตรง (H) และแบบสายโซ่กิ่ง (L) ปริมาณที่เติมคือ 0, 0.5, 1, 3, 5 และ 10 เปอร์เซ็นต์โดยน้ำหนัก คอมโพสิตระหว่างนาโนซิลิกา/พอลิเอทิลีนถูกเตรียมโดยการหลอมผสมในเครื่องบดผสมภายใน ชิ้นตัวอย่างถูกขึ้นรูปโดยเครื่องขึ้นรูปแบบกดอัด สมบัติด้านวิสโคอีลาสติกเชิงเส้น ภายใต้การทดลองเชิงกลพลวัตที่ความเครียดต่ำ อุณหภูมิอ้างอิงเท่ากับ 160 องศาเซลเซียส ของพอลิเอทิลีนและนาโนคอมโพสิตถูกตรวจสอบ และศึกษาสัณฐานวิทยาของนาโนคอมโพสิต โดยอาศัยเทคนิคกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน จากผลด้านวิสโคอีลาสติกเชิงเส้น พบว่าระหว่างสายโซ่ตรงและสายโซ่กิ่ง ที่ค่าความหนืดที่อัตราเฉือนเข้าสู่ศูนย์เดียวกัน สายโซ่กิ่งแสดงค่าเวลาผ่อนคลายที่นานกว่าแบบสายโซ่ตรง โครงสร้างกิ่งเป็นตัวเพิ่มกระบวนการผ่อนคลายของสายโซ่ การเติมอนุภาคนาโนซิลิกา เพิ่มค่ามอดูลัสสะสม มอดูลัสสูญเสียและความหนืดเชิงซ้อนของพอลิเอทิลีนเมทริกซ์ การเติมนาโนซิลิกาที่มากกว่าหรือเท่ากับร้อยละ 5 โดยน้ำหนัก นาโนคอมโพสิตแสดงพฤติกรรมคล้ายของแข็งในช่วงความถี่ต่ำ บ่งบอกว่าเกิดโครงสร้างร่างแหขึ้นที่ปริมาณนาโนซิลิกาดังกล่าว นาโนซิลิกาทั้งสองขนาดแสดงผลทางด้านกระแสวิทยาและสัณฐานวิทยาที่คล้ายคลึงกัน มันอาจเป็นไปได้ว่า อนุภาคฟูมซิลิกาเกิดการเกาะกลุ่มกัน จนมีขนาดรูปร่างใกล้เคียงกัน สังเกตได้จากเทคนิคกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน

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RATCHANOK THANAMAN : RHEOLOGY OF NANOSILICA FILLED POLYETHYLENE. THESIS ADVISOR : ASST. PROF. CHANTIMA DEEPRASERTKUL, Ph.D., 78 PP.

POLYETHYLENE/MOLECULAR WEIGHT/MOLECULAR CHAIN STRUCTURE /NANOSILICA SIZE/NANOSILICA CONTENT/ RHEOLOGY/ MORPHOLOGY

In this study, 7 and 14 nm hydrophilic fumed silica were used to fill linear (H) and branched (L) chain structure at two molecular weights of polyethylene (PE). The contents were 0, 0.5, 1, 3, 5 and 10 wt%. Nanosilica/PE composites were prepared by melt mixing using an internal mixer. The specimens were molded using a compression molding machine. The linear viscoelastic properties [under small amplitude oscillatory shear (SAOS) measurement] at the reference temperature of 160°C of the neat polyethylenes and nanocomposites were investigated. Morphology of the nanocomposites were also studied using transmission electron microscopy (TEM). The LVE results revealed that at the same zero shear viscosity, the branched PE showed longer relaxation time than the linear structure. The branching caused the additional mode of relaxation process. The presence of nanosilica increased the moduli and complex viscosity of the polyethylene matrix. At the nanosilica content of ≥ 5 wt%, the filled polyethylene melts showed the solid-like behavior in the terminal (low frequency) region. It indicated that the network-like structure formed at these contents. Both nanosilica sizes display the similar results in the rheological and morphological properties. It could be that the fumed silica nanoparticle can aggregate to the same size by particle-particle interactions as observed in transmission electron microscopy (TEM).

School of Polymer Engineering Student's Signature ______________________

Academic Year 2012 Advisor's Signature ______________________

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SYMBOLS AND ABBREVIATIONS

L = Branched structure

τ_c = Characteristic time

G^* = Complex modulus

η^* = Complex viscosity

Mc = Critical molecular weight

ωc = Crossover frequency

cm^3 = Cubic centimeter

°C = Degree celsius

η' = Dynamic viscosity

ETC = Environmental testing chamber (controlled convection/ radiant-heating)

Tg = Glass transition temperature

g = Gram

H08 = High density polyethylene (MFI=0.8 g/10min)

H14 = High density polyethylene (MFI=14 g/10min)

HDPE = High density polyethylene

$[\eta]$ = Intrinsic viscosity

kV = Kilovolts

G'' = Loss modulus

LDPE = Low density polyethylene

LLDPE = Linear low density polyethylene

SYMBOLS AND ABBREVIATIONS (Continued)

L30 = Low density polyethylene (MFI=14 g/10min)

LCB = Long chain branching

LVE = Linear viscoelastic

L5 = Low density polyethylene (MFI=5 g/10min)

τ_d = Longest relaxation time

H = Linear chain structure

M = Molecular

Mw = Molecular weight

Me = Entanglement molecular weight

Φ_m = Maximum-packing volume fraction

MFI = Melt flow index

nm = Nanometer

min = Minute

mm = Millimeter

η'' = Out-of-phase component of complex viscosity

ω = Oscillation frequency

wt% = Percent by weight

Pa = Pascal

PP = Polypropylene

PS = Polystyrene

PE = Polyethylene

SYMBOLS AND ABBREVIATIONS (Continued)

Pa.s = Pascal second

Rg = Radius of gyration

Rad/s = Radian per second

s = Second

SiO_2 = Silicon dioxide

G' = Storage modulus

SAOS = Small amplitude oscillatory shear

TEM = Transmission electron microscopy

Φ = Volume fraction

η = Viscosity of suspension

η_s = Viscosity of solvent

WLF = Williams-Landel-Ferry equation

η_0^* = Zero complex viscosity

CHAPTER I

INTRODUCTION

1.1 General Introduction

Polymer nanocomposites has been one of the most widely used materials as it could provide high strength at relatively low filler contents compared to conventional composites. For nanocomposite, the size of the polymer is comparable to or larger than the particle size (Pryamitsyn and Ganesan, 2006). Reduction of the particles or filler size down to the order of nanometers can lead to substantial difference in the various properties of filled melts compared to complex fluids, reinforced with micron sized particles. The particles can influence the properties of system because it has an extremely large specific surface area than microcomposites at similar filler volume fractions (Haghtalab and Marzban, 2011).

By adding nanofiller to polymers, one of a direct consequence is the change in the polymer rheology. A rheological study of molten polymer nanocomposites is important to assess their processability. Moreover, viscoelastic properties of nanocomposites in the molten state are generally useful to understand the relationships between structure and property. The filler - filler and filler – polymer interactions can strongly influence both linear and nonlinear viscoelastic responses. Melt rheology is thus useful for the investigation of the polymer nanocomposites.

The basic theory about filled melts is based on Einstein’s equation. In case of Newtonian fluids, at very low volume fraction ($\phi < 0.03$), the shear viscosity (η) of a suspension of hard spheres can be predicted by the simple formula of Einstein, calculated from the viscous dissipation produced by the flow around a single sphere. Thus, Einstein's formula as shown in equation (1.1) is only valid when the suspension is dilute enough that the flow field around one sphere is not appreciably influenced by the presence of neighboring spheres (Einstein, 1906).

$$\eta = \eta_s(1 + 2.5\phi) \tag{1.1}$$

where η and η_s are viscosity of suspension and viscosity of medium respectively and ϕ is volume fraction of the particles.

For suspensions, equation (1.1) fails at non-dilute solutions such as large particle size, high volume fraction and aggregation of particles. Therefore, the modified Einstein-type equations were developed hereafter. For example, the Krieger-Dougherty equation as shown in equation 1.2 was proposed for suspensions of particles of spherical or other shape (Krieger and Dougherty, 1959).

$$\eta = \eta_s[1-(\phi/\phi_m)]^{-[\eta]\phi_m} \tag{1.2}$$

where $[\eta]$ is an intrinsic viscosity and ϕ_m is maximum-packing volume fraction. Generally, as the particle aspect ratio increases, $[\eta]$ increases and ϕ_m decreases, while the product $[\eta]\phi_m$ usually remains in the range 1.4-3 (Barnes, Hutton and Walters, 1989).

According to equations (1.1) and (1.2), the viscosity increases with increasing the nanoparticle volume fraction. In addition to an increase in viscosity, Zhang and Archer (2002) found that the stress relaxation was dramatically slowed down because of physisorption between polyethylene oxide (PEO) and silica nanocomposites. They indicated that bare particle-particle jamming contacts were not likely the source of slowing down of stress relaxation but because of hydrogen bonding. The onset of shear thinning was shifted to lower shear rates when adding nanofillers. These results mean implicitly that the particle interactions increase the non-Newtonian range and cause it to occur at a lower shear rate than the unfilled polymer melt. Filled polymers have a higher viscosity at low shear rates, and yielding may occur with increased filler concentration.

On the contrary, adding nanoparticles causing faster relaxation of chains based on different explanation were reported. Zhang, Lippits and Rastogi (2006) found that the storage modulus or viscosity of single-walled carbon nanotubes filled broad ultrahigh molecular weight polyethylene decreased with increasing mass or volume fraction of particles. They attributed the decrease in viscosity to the selective adsorption of the high molar mass fraction onto the nanoparticles surface. In addition, Mackay et al. (2003) found the decrease in the cross-linked polystyrenes nanoparticles filled polystyrene viscosity and the glass transition temperature (T_g) because of the increase in free volumes as well as the change in certain configuration to the linear polymer. They proposed that this is due to the nanoparticle confinement effects where the interparticle half-gap is less than or equal to radius of gyration (R_g).

Many previous works have shown that the presence of nanoparticles in polymer melts could either increase or decrease the viscosity (Sarvestani, 2008; Zhang, Lippits and Rastogi, 2006). The general behavior reported in the literature for oscillatory shear rheological measurements at low frequencies is that the linear rheological properties evolve from a liquid-like behavior to a solid-like behavior as the nanoparticle concentration increases. In the case of viscosity reduction which is not common, one of the proposed criteria is that the size of the particle should be comparable to or smaller than the polymer molecular size (Mackay et al.,2003; Zhang, Q., Lippits, D. R., and Rastogi, S., 2006).

In recent years, inorganic nanoparticles especially fumed silica (SiO_2 is a multi-functional ceramic material) has been used in various industries to improve surfaces and mechanical properties of diverse materials. It is used as a filler, performance additive, rheological modifier or processing aid in many product formulations, such as plastics and synthetic rubber. By using appropriate reaction conditions and surface modifications, wide range of hydrophilic and hydrophobic grades of fumed silica can be obtained. Surface chemistry of fumed silica can be found in the siloxane and silanol groups on the surface properties. The silanol groups account for the hydrophilic behaviour of untreated fumed silica.

Besides nanoparticle content and size, the rheological properties also depend on the polymer matrix. Here the effect of polymer chain structure is focused as well as the effect of nanoparticles.

1.2 Research objectives

This research is aimed to study the rheological properties of nanosilica filled polyethylene melts. The main objectives of this research are;

(i) to study the effect of molecular chain structure of polyethylene (linear versus branched) on rheological properties of nanosilica filled melts.

(ii) to study the effect of length scale of nanosilica size in comparison to molecular size of polyethylene through molecular weight of HDPE and LDPE on rheological properties of nanosilica filled melts.

(iii) to investigate the effect of nanosilica content on rheological properties of nanosilica filled melts.

1.3 Scope and limitation of the study

Nanosilica filled polyethylene melts were prepared using an internal mixer. High density (linear chain) and low density (branched chain) polyethylenes with two molecular weights were used. To investigate the effect of nanoparticle size and content, hydrophilic nanosilica (fumed silica) with the size of 7 and 14 nm added at 0, 0.5, 1, 3, 5 and 10 wt% were chosen. Specimens for testing were arranged by compression. Linear viscoelastic properties of samples were investigated by small amplitude oscillatory shear measurements. The possible morphology and silica aggregation of nanocomposites were analyzed using transmission electron microscopy (TEM).

CHAPTER II

LITERATURE REVIEW

The rheological properties of suspension, solid particles dispersed in Newtonian fluids are rather complex itself. With the polymer melt the rheology of filled melts is expected even more complicated. Rheology of filled melts is governed by the diverse properties of polymer melts and the polymer-particle interaction. Therefore, studies on polymeric fluids are mostly carried out whice complex fluids, often show strong viscoelastic effects.

2.1 Rhelology of polymer melts

2.1.1 Effect of molecular weight

It is well-known that for linear flexible polymer chains, the zero shear viscosity (η_0) scales with the molecular weight (M) as $\eta_0 \sim M^x$ where x depends on M (Berry and Fox, 1968). Below the critical molecular weight (M_c), the zero shear viscosity is found to depend roughly linearly on molecular weight i.e. $\eta_0 \sim M^{1.0}$. Above M_c, it rises with a much higher power-law exponent where x = 3.4 i.e. $\eta_0 \sim M^{3.4}$.

2.1.2 Effect of molecular chain structure

The effect of chain branching is one of the most challenging molecular structure and rheology relationships. The rheological behavior of branched chains is generally different from linear chains depending on type of flow. The effect of long chain branching [LCB or the branches are longer than molecular entanglement (M_e)] for shear flow, the viscosities as a function of shear rate of both linear and branched are similar. This suggests that long-chain branching can have little effect on viscosity of melts. For extensional flow, strain hardening behavior is present in LCB melts (Bishko, Mcleish, Harlen and Larson, 1997; Yang, Chung, Webber and Wollny, 2009). Consequently, in case of LCB, the equation $\eta_0 \sim M^x$ can be applied under shear.

2.2 Rheology of filled melts

2.2.1 Effect of mass or volume fraction

The sizes of polymer (radius of gyration) are smaller than particle sizes in case of micro-particles. Based on Einstein and Krieger-Dougherty equations, with increasing the volume fraction of particle increased in the viscosity of filled suspensions. At low loading ($\Phi \geq 0.05$) of non-aggregating spherical shape of particles filled in a polymer melt, the viscosities of filled melts were closed to the melt. At high loading ($\Phi \geq 0.2$), it was found that the yield stress was developed. The result of this system is similar to high concentration of particles with attractive interactions (Lobe and White, 1979 quoted in Lason, 1999).

Comparisons with the size of nano-particles, the sizes of radius of gyration are higher than particle sizes. Because of this, the present of rheological properties depended upon the nature of the nanoparticle-polymer interactions. The possible rheological properties of nanoparticles filled melts are enormous differentiation from micron size of particles. Both increasing and decreasing in modulus or viscosity of nanocomposites are reported. Based on different explanation, the systems can not be considered as held part on the nanoparticle surfaces. Therefore, a faster polymer dynamics were observed relative to the neat systems and were associated with a increase in the polymer mass (Osman, Atallah, Schweizer and Ottinger, 2004). On the other hand, in inviting interactions, the slowing of polymer dynamics observed was associated with a dramatic reduction in mobility of adsorbed polymer segments along the nanoparticle surface (Zhang and Archer, 2002). These explain the cause of the increased viscosity.

In case of reduction in viscosity because of nanoparticle, various mechanisms have been proposed to explain this behavior. Cho and Paul (2001) found the decrease in viscosity of Nylon with the addition of organoclay. They suggested that the viscosity decrease could be a result of polymer degradation and slip at wall of particles. Later, Jain (2005) presented an argument against Cho and Paul about the explanation. He proved the argument through the molecular weight of the polypropylene by size exclusion chromatography. His results confirmed that no molecular degradation occurred. To proof about the slip at the wall of nanoparticles, measurements were performed by changing the gap or thickness between the plates and same results were obtained. This rules out that the observed viscosity effect is due to the slip at wall. Moreover, Mackay et al. (2003) found that fumed silica induced disruption of polymer chain packing and an accompanying subtle increase in free volume through which molecular transport occur. This result cause decreasing in the viscosity of the intramolecular cross-linking of single polystyrene chains filling the suspended polystyrene. Jain also presented argument against Mackay. He proved and confirmed that the silica nano-particles act as nucleating agent. Polypropylene chains start to crystallize on silica, so the depletion layer cannot be formed around silica. Therefore, silica does not increase the free volume in the system and the explanation based on increase in free volume does not hold for the decrease in the viscosity. From these results, Jain proposed the selective physisorption to be the cause of decreasing in the viscosity of nanocomposites. But decreasing of the viscosity with increasing nanoparticle volume fractions failed when particles volume fractions more than the critical volume fraction were added. This is because of the strong interaction between particles. (Mackay et al., 2003; Zhang et al., 2006).

2.2.2 Effect of particles size

Yield stresses are generally observed in dispersions with fine particle having a high specific surface area. This is because the smaller particle size can lead to the stronger interaction between polymer-particle or particle-particle interactions. Increasing filler surface area has a pronounced effect on the rheology of the filled systems. Viscoelastic properties of polymer composites are particle size dependent (Barnes, Hutton, and Walters, 1989; Larson, 1999). In addition, polymer adsorption on the particles' surface results in a transient filler–polymer network and slow dynamics of the bound polymer, which contribute to the moduli of the complex fluid. The sum of all these factors leads to gradual increase in moduli and to a shift of the crossover frequency to lower values (Osman and Atallah, 2006). In the case of viscosity reduction, one of the proposed criteria is that the size of the particle should be comparable to or smaller than the polymer molecular size (Mackay et al., 2003).

In the study of diffusion, Roberts et al. also suggested that the smaller silicate particle acted as a solvent where the larger particle reinforced the polymer (Roberts, Cosgrove, Schmidt, and Gordon, 2001).

CHAPTER III

EXPERIMENTAL

3.1 General Background

The expeimental details in this chapter aimed to investigate the effect of molecular characteristics and silica nanoparticles on viscoelastic properties of filled polyethylene melts. High density (H) and low density (L) polyethylenes were supplied by Thai Polyethylene Co., Ltd. Their specification are comparable in density and different in melt flow index (MFI) as H08 = 0.8 g/10min, H14 = 14 g/10min, L5 = 5 g/10min and L30 = 30 g/10min. Hydrophilic fumed silica (SiO_2) nanoparticles with an average size of 7 and 14 nm were used. Both were purchased from Aldrich.

3.2 Experimental

3.2.1 Preparation of nanosilica

Before mixing, nanosilica was put into aluminum tray by thin layer with approximate thickness of 2 mm. It was dried in an oven at 70 °C overnight. After drying, it was mixed with polyethylene immediately.

3.2.2 Sample Preparation

Melt-mixing and solution mixing were used. An internal mixer (Haake Rheomix 600p) was employed to mix PE and silica using a rotor speed of 50 rpm at 160 °C. Contents of fumed silica in the range of 0, 0.5, 1, 3, 5 and 10

% by weight were used. For dissolution mixing, ultrasonic processing has been used for 2 hrs. and xylene was used as a solvent. After ultrasonication, xylene was evaporated out at room temperature for ~ 1 week. The disk-like samples with a diameter of 25 mm for oscillatory shear measurement were prepared by compression molding (Lab tech engineering Co., Ltd. Model LP20-B) using a temperature of 160 ˚C under pressure for 10 minutes.

3.2.3 Rheological Testing

Oscillatory shear measurements were performed using an AR-G2 rheometer. Measurements were carried out using parallel plate geometry at a temperature range of 120-200 ˚C under nitrogen atmosphere by environmental test chamber (ETC mode). The disk-like samples with a diameter of 25 mm was placed on the parallel plate then closed the chamber. The gap between parallel plate is set at 1 millimetre. Frequency sweep with an angular frequency in the range of 0.1-100 radian/second at low strain of 2% was applied. Master curve at temperature of 160 ˚C was constructed using WLF equation.

3.2.4 TEM Sample Preparation and Testing

In this study, transmission electron microscopy (TEM) was used to examine the filler dispersion. Some fumed silica nanoparticles filled PE melts were microtomed to thin sections (~130-150 nm) using the Ultramicrotome with a diamond knife at -80 ˚C. Sections were placed flat on a copper grid coated with carbon. The samples were then brought up to room temperature. TEM was performed on the FEI Iecnai G^{2}20 (FEI Co., Eindhoven, Netherlands) at Khon Kaen university. In this experiment, Lanthanum Hexaboride (LaB_6) filament was used to generate the electron beam. The instrument was operated at an accelerating voltage of 200 kV. TEM micrograph was captured by TEM camera connected to computer. TEM images were also measured at Suranaree University of Technology by using Hitachi JEOL 2010 at the various accelerating voltage between 80-200 kV. Pure hydrophilic fumed silica particles were diluted by methanol and placed into the ultrasonic mixer for 5 minutes. The test tube of two silica particles were dropped on the copper grid immediately (Mesh no. 100). The sample was then dried at the room temperature before TEM testing. For fumed silica nanoparticles filled PE, some samples were tested.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, rheological properties of LDPE and HDPE melts will be firstly discussed in terms of molecular weight and molecular chain structure. Then effects of silica content and size on the rheology of these polyethylene melts will be delineated.

4.1 Rheology of polyethylene melts

Small amplitude oscillatory shear (SAOS) measurements were conducted in the temperature range of 120-200°C. The linear viscoelastic (LVE) results at various temperature were shifted to 160°C by the Williams–Landel–Ferry equation (WLF equation). Master curve of storage and loss moduli, (G' and G") of neat L5 at temperature of 160°C is plotted in Figure 4.1. It shows a typical LVE behavior in the terminal region i.e. the moduli scale with angular frequency (ω) where $G' \sim \omega^2$ and $G'' \sim \omega^1$. The angular frequency at which G' crosses over G", so-called the crossover frequency (ω_c) is determined. The characteristic time (τ_c) is then calculated from the inverse of ω_c, $\tau_c = 1/\omega_c$. This τ_c can relate to the longest relaxation time of the polymer chain. So, in this work the frequency range below and beyond ω_c was considered the terminal region and rubbery region respectively. Complex modulus (G*) and complex viscosity (η*) are also presented as obtained from the equations 4.1-4.4 below. As seen, the η* is constant in the terminal region and decreases as the ω increases. Similar to the Newtonian region in the steady shear measurement, the constant η^* is thus called the zero complex viscosity (η_0^*). At the higher ω, the shear-thinning behavior is observed as η^* decreases.

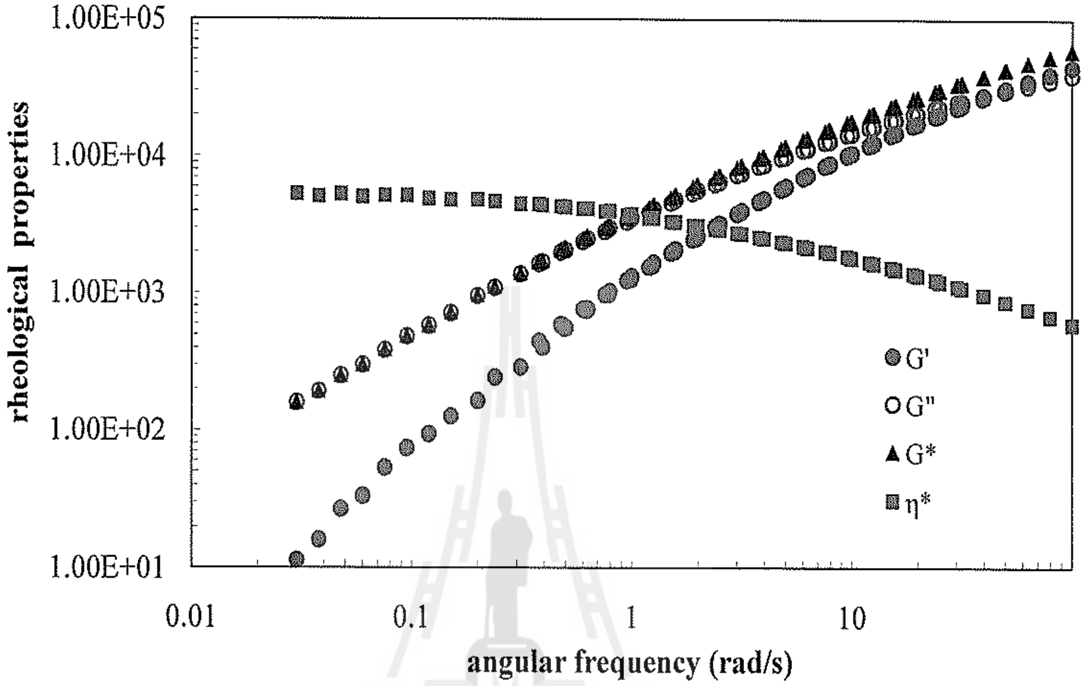


Figure 4.1 Typical LVE behavior in the terminal region of polymer melts (here is neat L5 at temperature of 160°C).

The moduli interrelate with viscosities via following equations (Bird, Armstrong and Hassager, 1987).

$$G^* = G' + iG'' \tag{4.1}$$

$$\eta^* = \eta' - i\eta'' \tag{4.2}$$

$$G'(\omega) = \eta''\omega \tag{4.3}$$

$$G''(\omega) = \eta'\omega \tag{4.4}$$

where G^*, G', G'' are complex modulus, storage modulus and loss modulus respectively. η^*, η', η'' are complex viscosity, dynamic viscosity, out-of-phase component of η^* and ω is angular frequency. The dynamic viscosity (η') corresponds to dissipation or energy loss, while the out-of-phase component of η^* (η'') reflects energy storage. In the low frequency limit, η' approaches the zero shear viscosity, η_0.

Figure 4.2 presents the plot of complex viscosity against frequency of all the neat polyethylenes used. As expected, the viscosity of H08 is higher than H14, and L5 is higher than L30. Also, it is seen that the constant viscosity (η_0) at low frequency (Newtonian behavior) was clearly obtained in the low density (L) polyethylene melts. The onset of shear-thinning of L5 was observed at lower frequency than L30. In the high density (H) polyethylene melts, only relatively small constant viscosity region could be observed. The constant viscosities of these polyethylenes are listed in Table 4.1.

Table 4.1 List of melt flow index, zero complex viscosity and characteristic time of polyethylenes used.

PE	MFI (g/10min)	η_0^* (Pa.s)	τ_c x10^3 (s)
H08	0.8	27.32 x10^3	16
H14	14	2.62 x10^3	3.2[a]
L5	5	5.0 x10^3	25
L30	30	0.9x10^3	1.3

[a]: extrapolated data

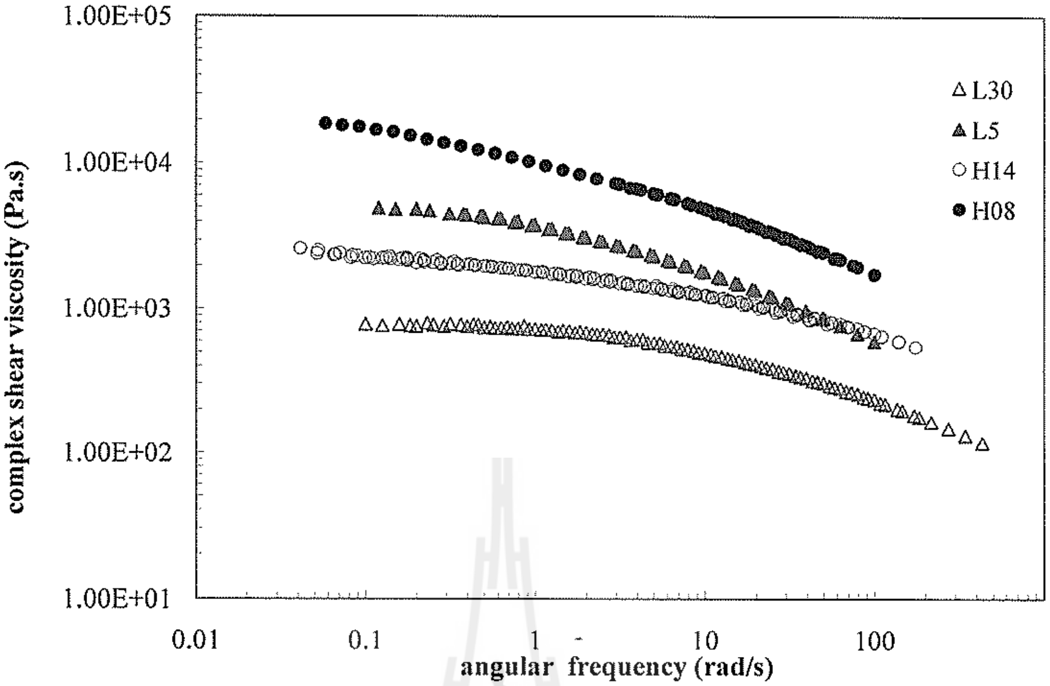


Figure 4.2 The complex viscosity versus angular frequency for polyethylene melts at the reference temperature of 160°C.

The master curve of storage and loss moduli as a function of frequency of these polyethylenes at 160 °C is presented in Figure 4.3. It is known that in the terminal zone only the longest relaxation times contribute to the viscoelastic behavior, the G' and G" would scale with frequency as G' ~ ω^2 and G" ~ ω^1. As also pointed out in the complex viscosity plot, only low density polyethylene melts could show this terminal behavior. The crossover frequency (ω_c) of these polyethylenes except H14 was obtained. Experimentally, H14 was solidified at low temperature before the crossover frequency could be reached. The ω_c was thus extrapolated. The characteristic time (τ_c) was then calculated and also listed in Table 4.1. For the same chain structure the polyethylenes with the higher zero viscosity (i.e. higher molecular weight) show longer τ_c. It means that H08 takes longer time to relax than H14, and L5 longer than L30.

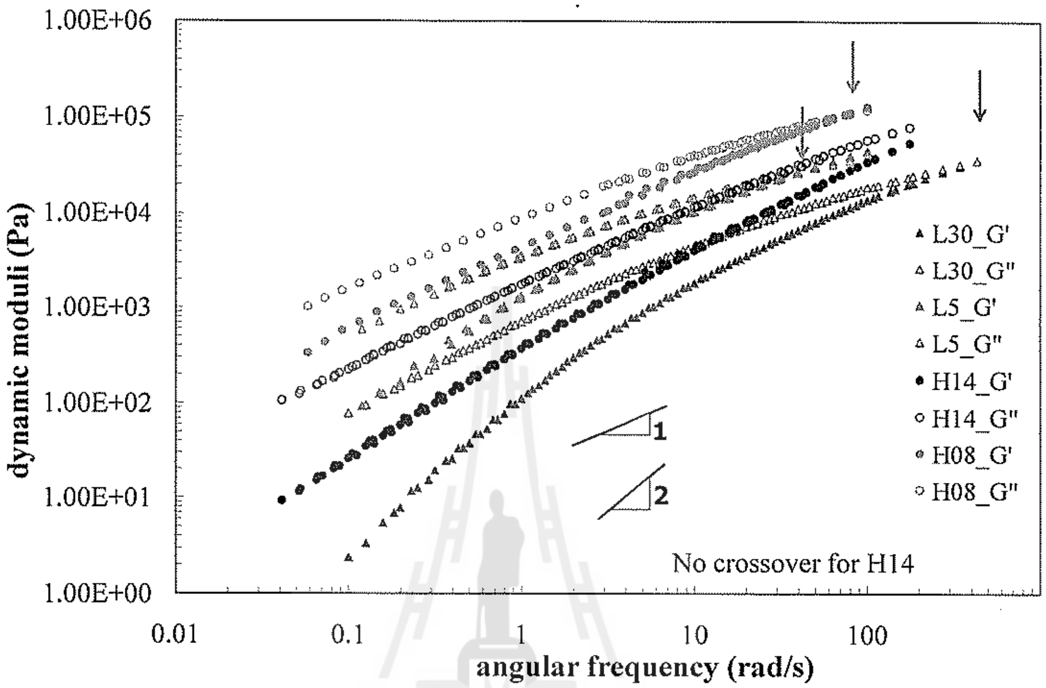


Figure 4.3 Master curve of dynamic moduli versus frequency of long-chain branched (L30 and L5) and linear (H14 and H08) polyethylenes at the reference temperature of 160°C.

According to linear viscoelasticity theory (de Gennes, 1971; Doi and Edwards, 1986), both the zero shear viscosity and the longest relaxation time (τ_d) of linear polymer chain scale with the molecular weight to the same power of 3.0, $\eta_0 \sim M^{3.0}$ and $\tau_d \sim M^{3.0}$. Log-log plot of characteristic time scale versus zero complex viscosity of all polyethylene used is presented in Figure 4.4. The slopes of LDPE and HDPE are compared. The slope of LDPEs is 1.747 which significantly differs from 0.690 of HDPE. If the scaling between η_0 and Mw and τ_d and Mw were taken to be the same. The slope of the plot η_0 versus τ_d represents the coefficient which significantly differs between linear and branched chains.

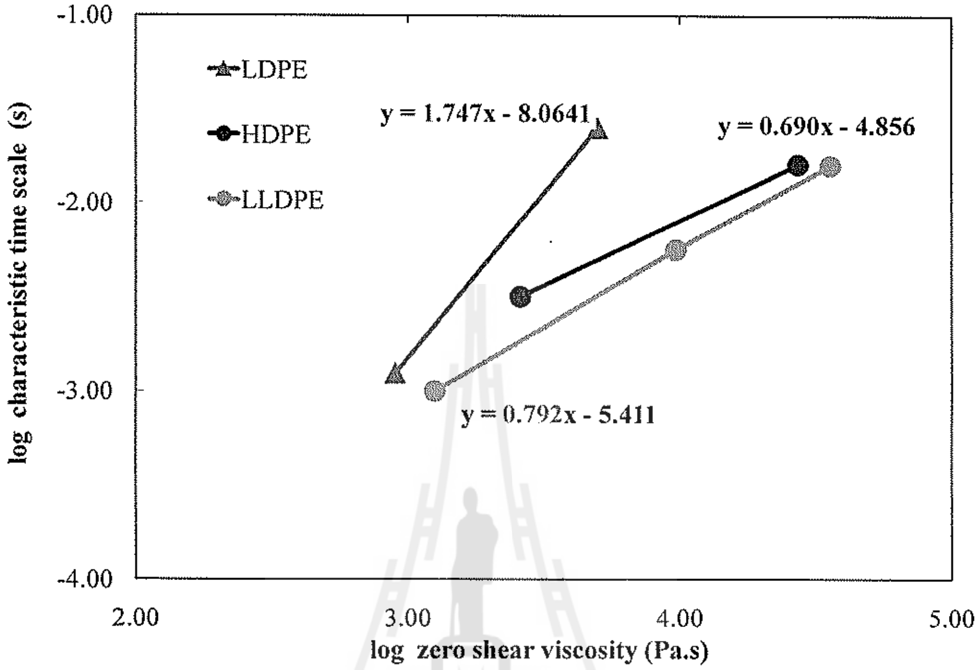


Figure 4.4 Log-log plot of characteristic time scale versus zero shear complex viscosity of polyethylenes

However, it was propose that η_0 of branched structure scales with Mw stronger than linear counterparts. Three LLDPEs were tested and their η_0 and τ_d were plotted in Figure 4.4. It is shown that the slope of LLDPEs is close to HDPE. In any case, for the same viscosity, the relaxation in branched structure (L) takes longer time than in linear chain structure (H). It could be explained that branching has additional modes of relaxation at low frequency that are not present in the linear chain structure. The observed large differences are the result of the high friction concentrated at the branch points in H-shaped polymers. As nicely explained by

McLeish (1999), the rapidly fluctuating arms provide drag that far outweighs the sum of monomeric drags along the backbone. Trapped between the two branch points, the main chain backbone or crossbar remains practically immobile, and it is only after very long times that arms have completely retracted that relaxation of the crossbar takes place via renormalized reptation in a dilated tube. The additional branch point friction caused by the dangling arms has a profound effect on the relaxation processes of the H-shaped molecules and its segmental dynamics (McLeish, 1999).

4.2 Rheology of fumed silica filled polyethylene melts

Size and contents of the fumed silica were considered in LDPE and HDPE, respectively.

4.2.1 The effects of fumed silica size and content on filled LDPE melts

The rheological measurements of fumed silica filled polyethylene melts were carried out using small amplitude oscillatory shear (SAOS). By using the fumed silica with 7 nm and 14 nm in size and the filler loadings at 0.5, 1, 3, 5 and 10 wt %, the SAOS results are presented.

Figure 4.5 and Figure 4.6 present the results of L5 and L30 at low loading respectively, both G' and G" moduli of the filled melts increase with increasing ω and in the low frequency region G" is larger than G', displaying the viscous nature. The slope of G" (ω) is smaller than that of G' (ω) and with increasing ω the two curves cross each other at ω_c (the crossover frequency). This characteristic frequency (where G' = G") marks a transition from viscous (G" > G') to rubbery or solid-like behavior (G' > G") response.

With increasing the filler loading, the moduli increased over the whole frequency range by which the increase was more pronounced in the low frequency region and in G' more than in G". It was also noticed that the crossover frequency (ω_c) was shifted to lower values, indicating an increase in the longest relaxation

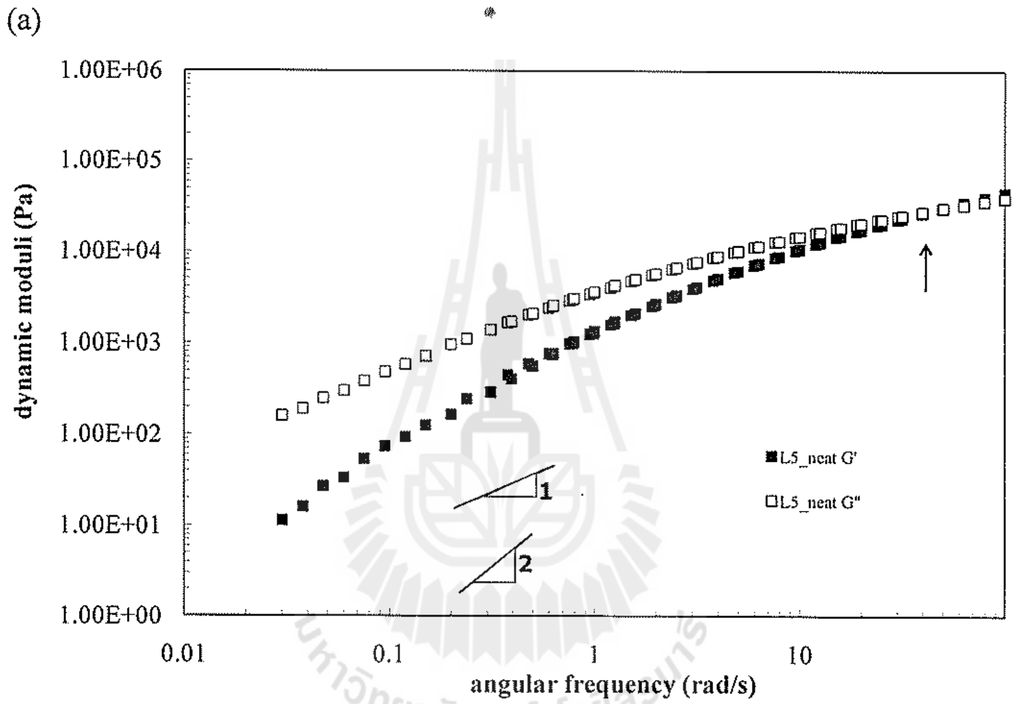


Figure 4.5 Storage and loss moduli of the fumed silica (7 and 14 nm) filled L5 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160°C.

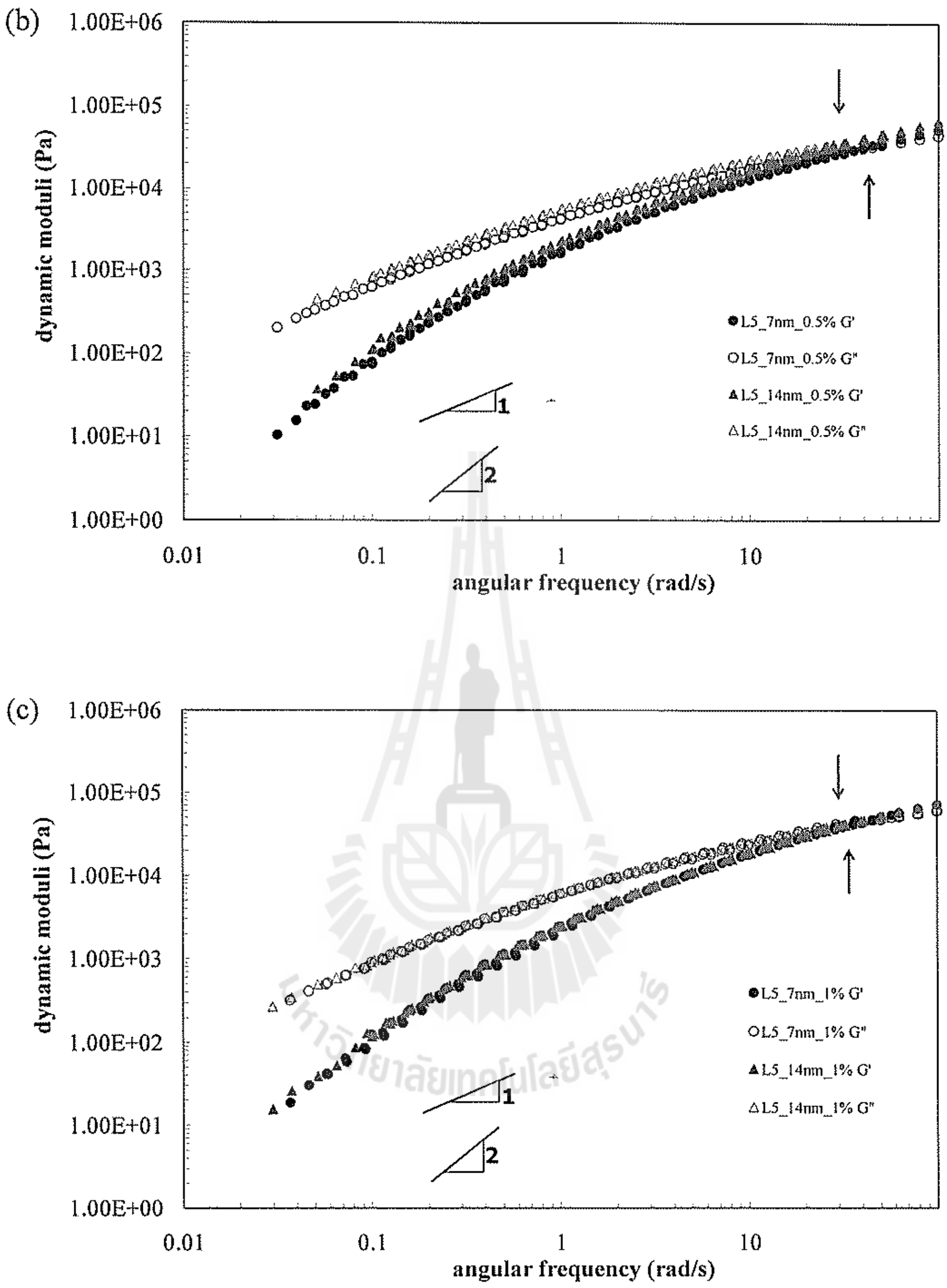


Figure 4.5 Storage and loss moduli of the fumed silica (7 and 14 nm) filled L5 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160°C (continued).

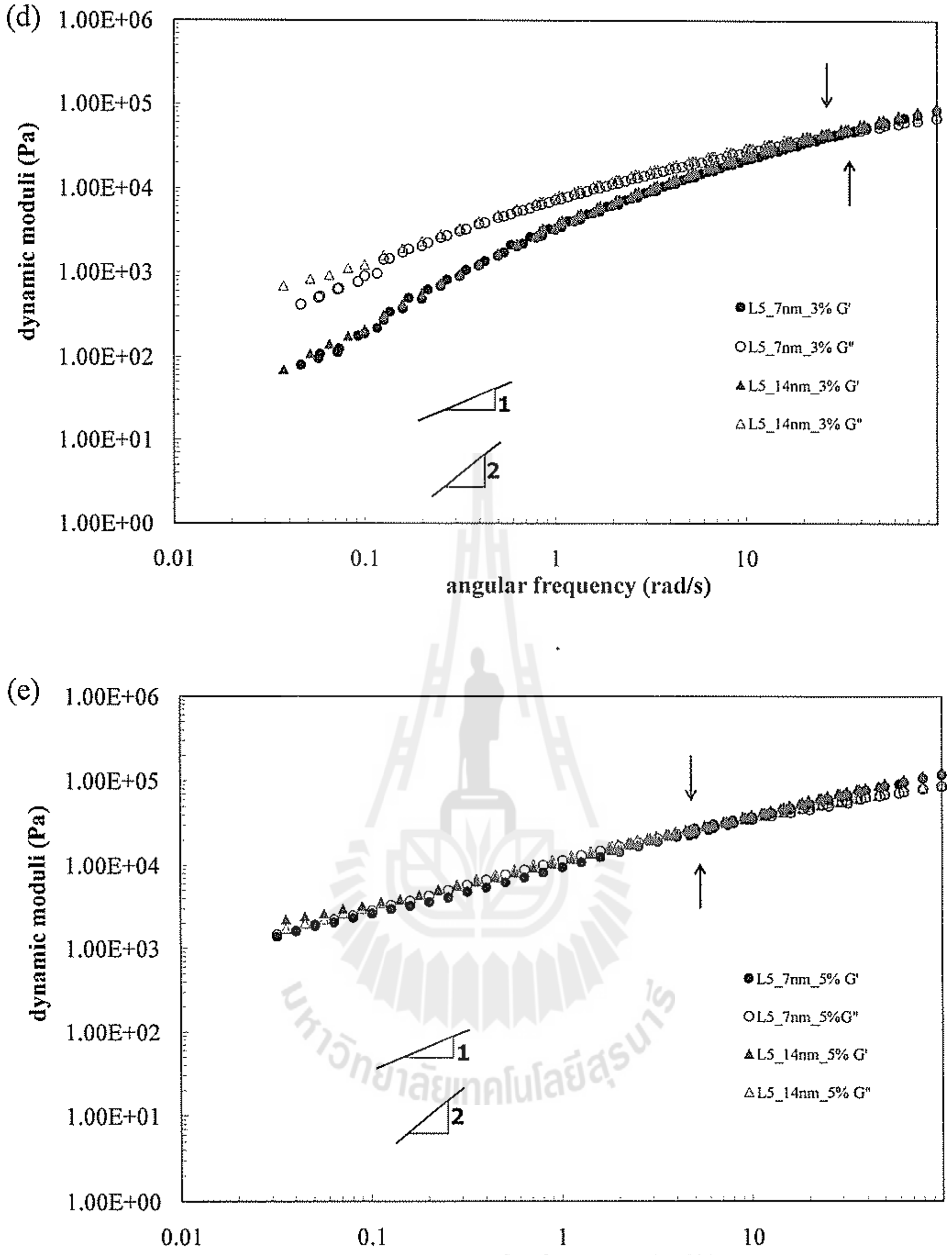


Figure 4.5 Storage and loss moduli of the fumed silica (7 and 14 nm) filled L5 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160°C (continued).

(f)

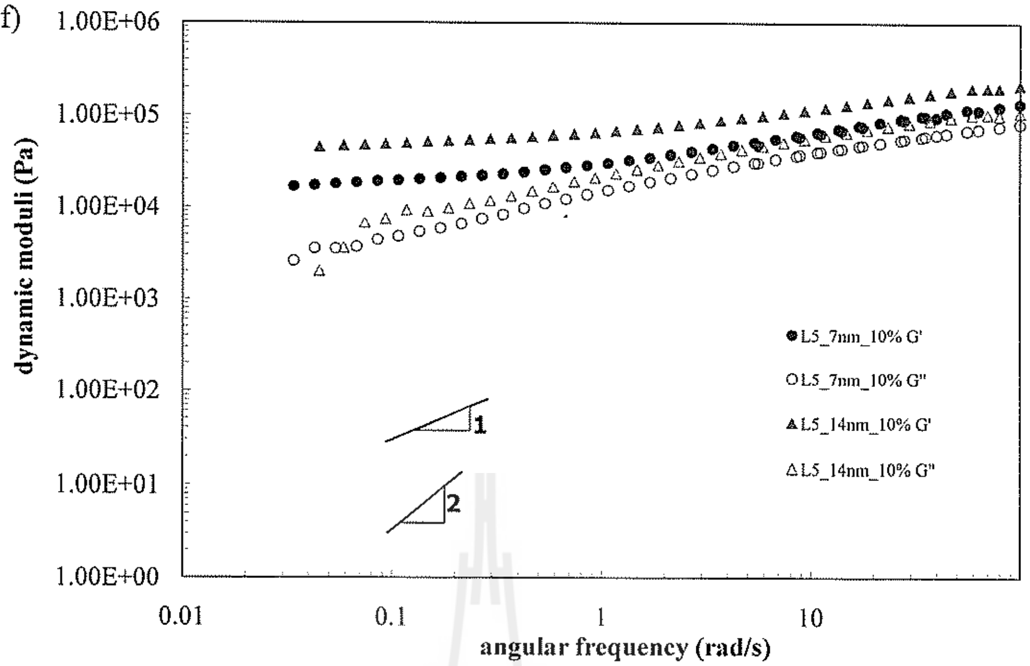


Figure 4.5 Storage and loss moduli of the fumed silica (7 and 14 nm) filled L5 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160°C (continued).

time (ω_c is approximately equal to the inverse of the fluid characteristic relaxation time τ_c, roughly the longest relaxation time). It could mean that the presence of fumed silica contributes to the elasticity of the polyethylene melts. At 5 wt% loading for both L5 and L30, G' nearly became larger than G" over the measured angular frequency range and ω_c was hard to observe. The samples can be described as a viscoelastic solid. At 10 wt% loading for both L5 and L30 , both G' and G" became almost frequency independent (log–log plot).

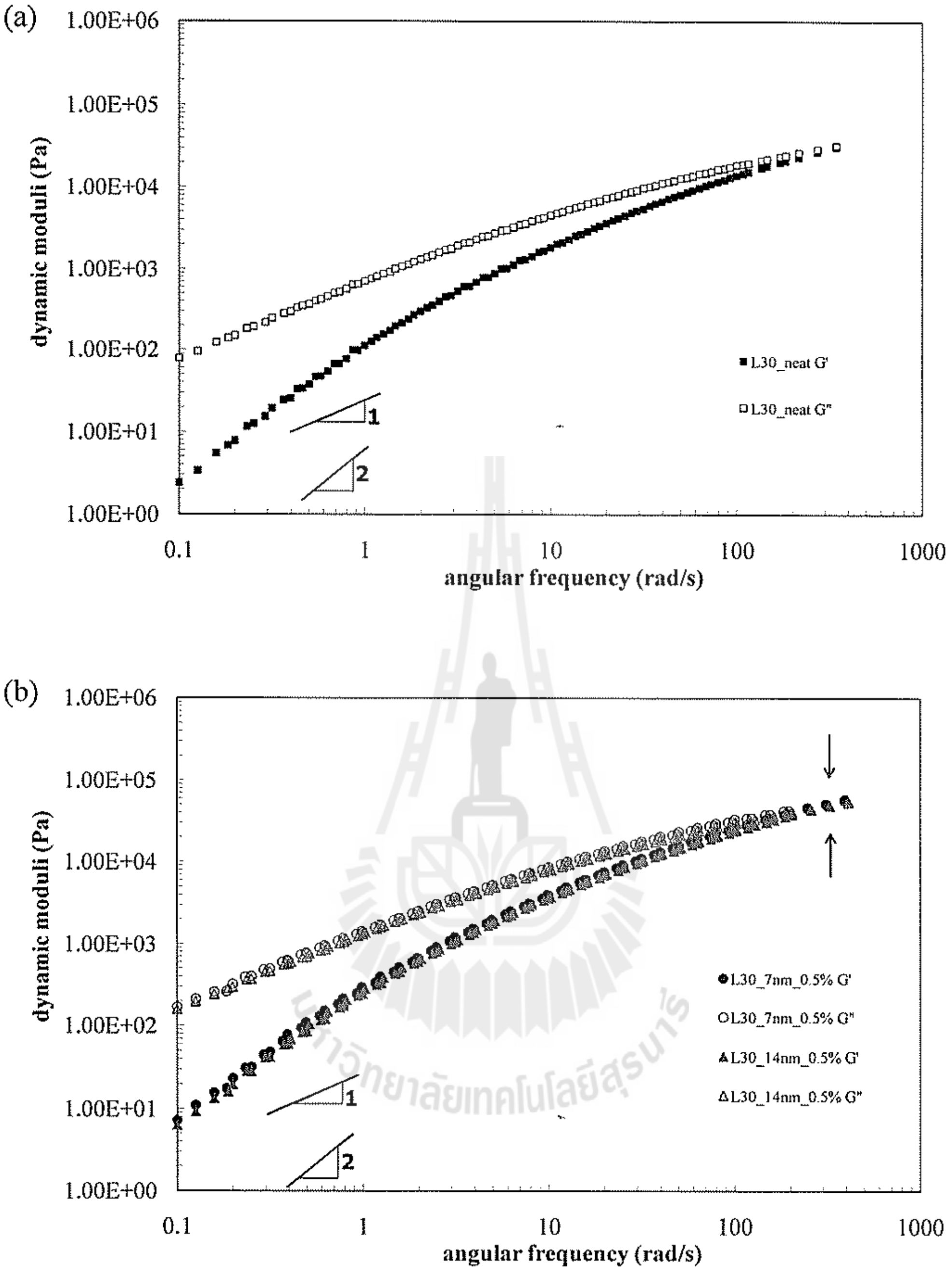


Figure 4.6 Storage and loss moduli of the fumed silica (7 and 14 nm) filled L30 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160°C.

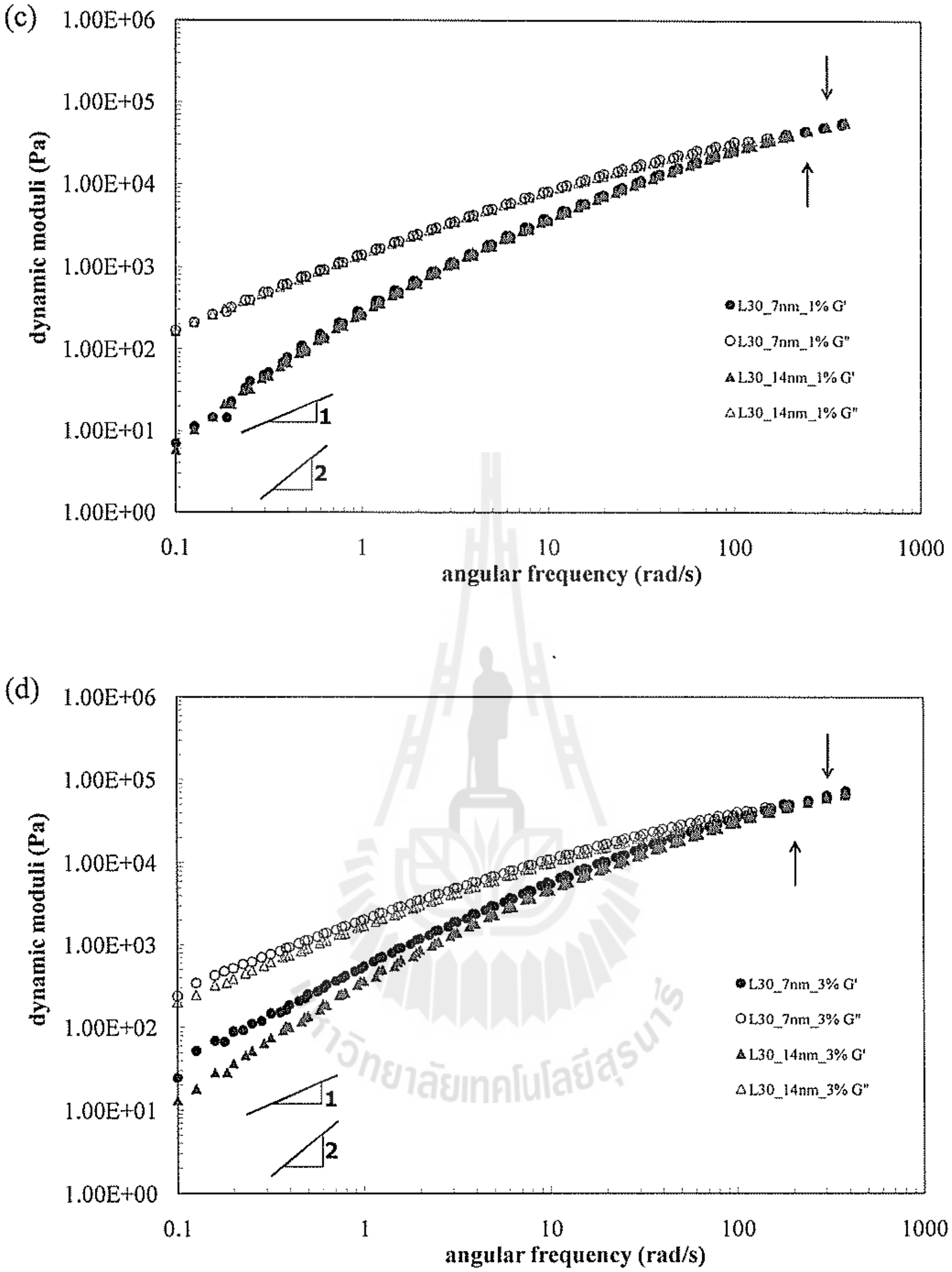


Figure 4.6 Storage and loss moduli of the fumed silica (7 and 14 nm) filled L30 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160°C (continued).

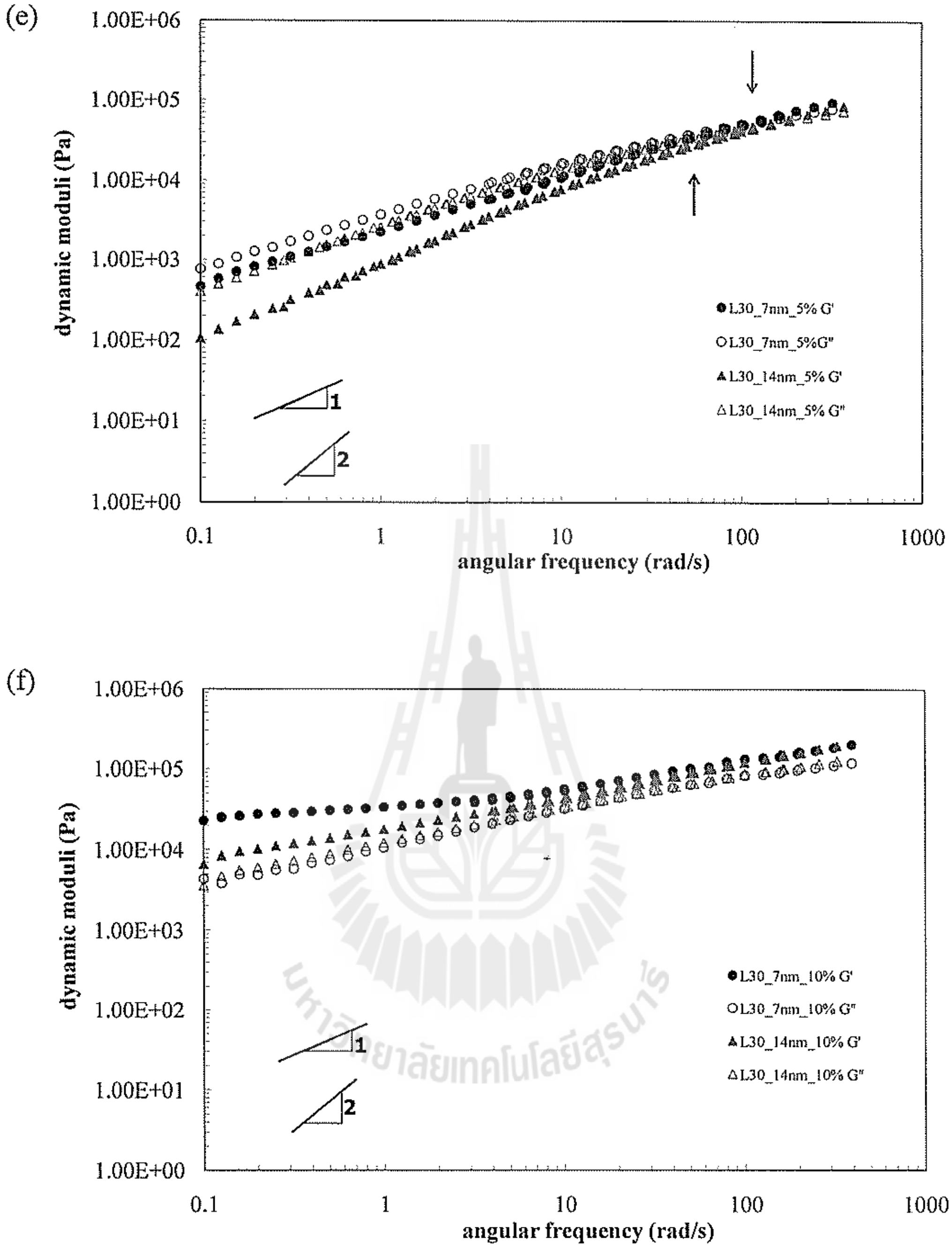


Figure 4.6 Storage and loss moduli of the fumed silica (7 and 14 nm) filled L30 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160°C (continued).

Figure 4.5 and Figure 4.6 also present the effect of silica size on L5 and L30 melts. It is seen that both size generally gave similar behaviors on the filled LDPE melts. It could be that the fumed silica nanoparticles can aggregate to the same size as will be observed in transmission electron microscopy (TEM).

In particular, G' and G" curves deviated from the relationship founding for the neat in case of filled melts. Sternstein and Zhu (2002) proposed the particle surfaces serve as contact points and verified the "bridging' and "training" of polymer chains between and along particle surfaces that effectively increased the entanglement distribution.The bridging segments have a low mobility and, therefore, generate the higher relaxation time. This result is especially revealed at low frequencies where a plateau region in G'(ω) function is seen corresponding to characteristic times of the order of magnitude of the relaxation time of the bridges. It should be noted that this situation seems to be similar to the process taking place during cross-linking (Winter and Chambon, 1986) and grafting (Castellani and Lomellini, 1994), where a plateau in the storage modulus at low frequencies also appears upon gelation. Such a strong indication for network formation can be observed. Especially for the 10 wt% loading, displays as G' values are higher than G" whole angular frequencies or is called gel-behavior. This is indicative of solid-like behaviors at higher particle volume fractions.

Besides the viscoelastic moduli, the complex viscosity of the neat and the filled LDPEs is plotted. Figure 4.7 and Figurer 4.8 display the complex viscosity versus frequency at various filler loadings. As shown, at low filler loadings all the samples show a frequency-independent behavior in the low

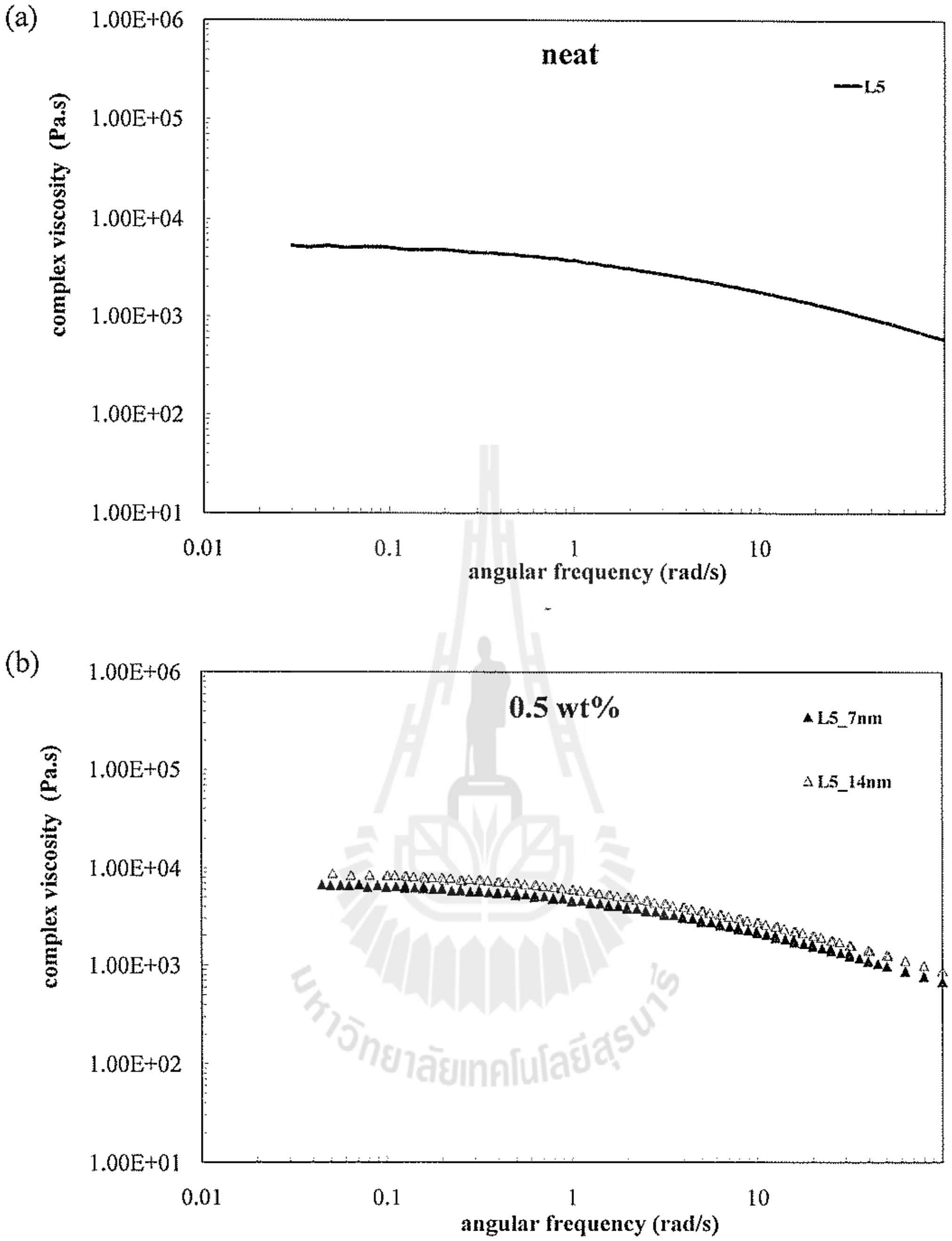
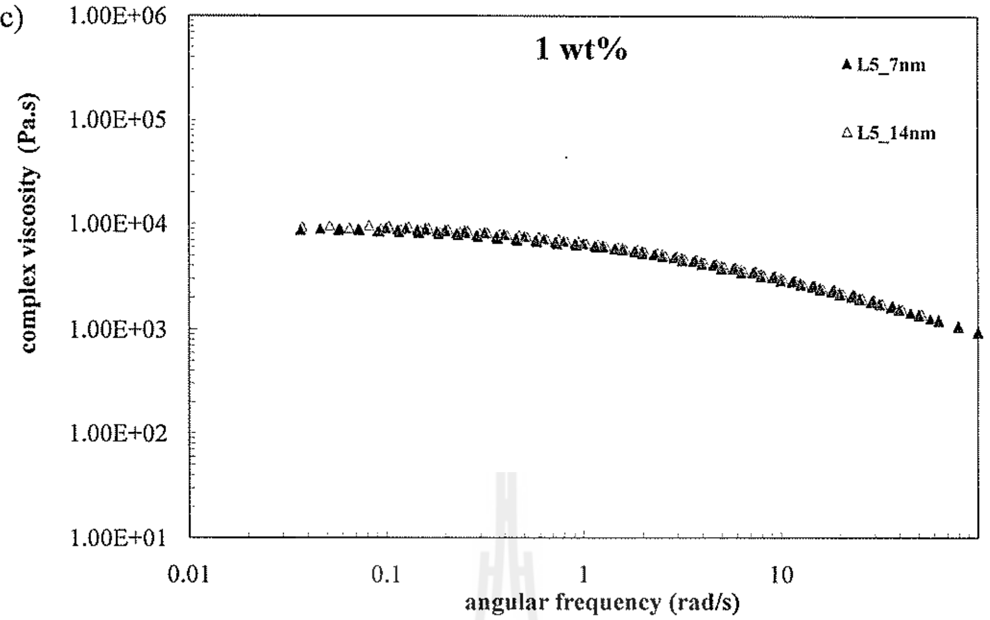


Figure 4.7 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled L5 at constant filler loadings of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160°C.

(c)



(d)

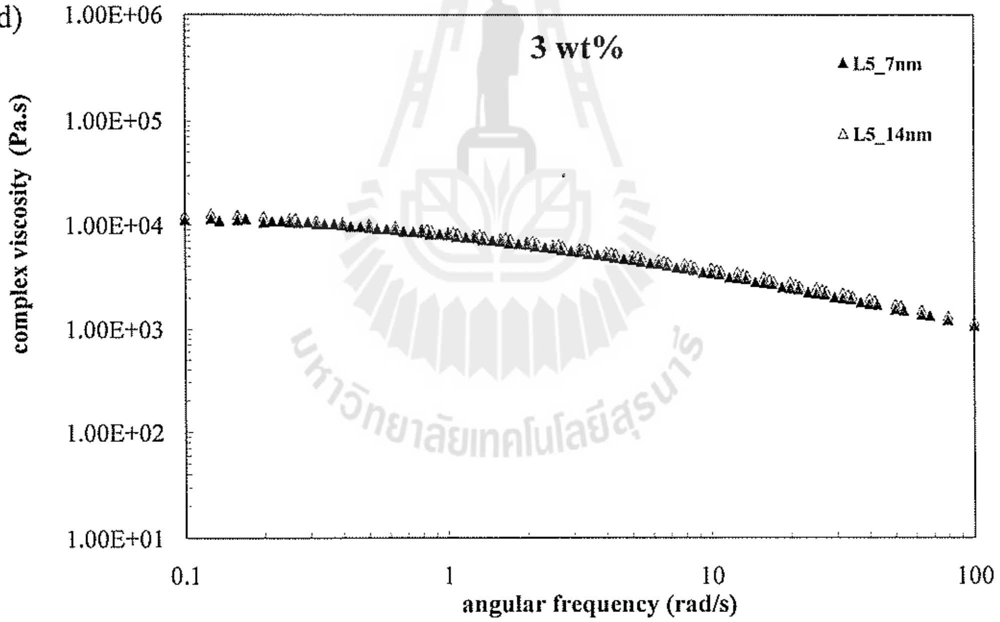


Figure 4.7 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled L5 at constant filler loadings of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160°C (continued).

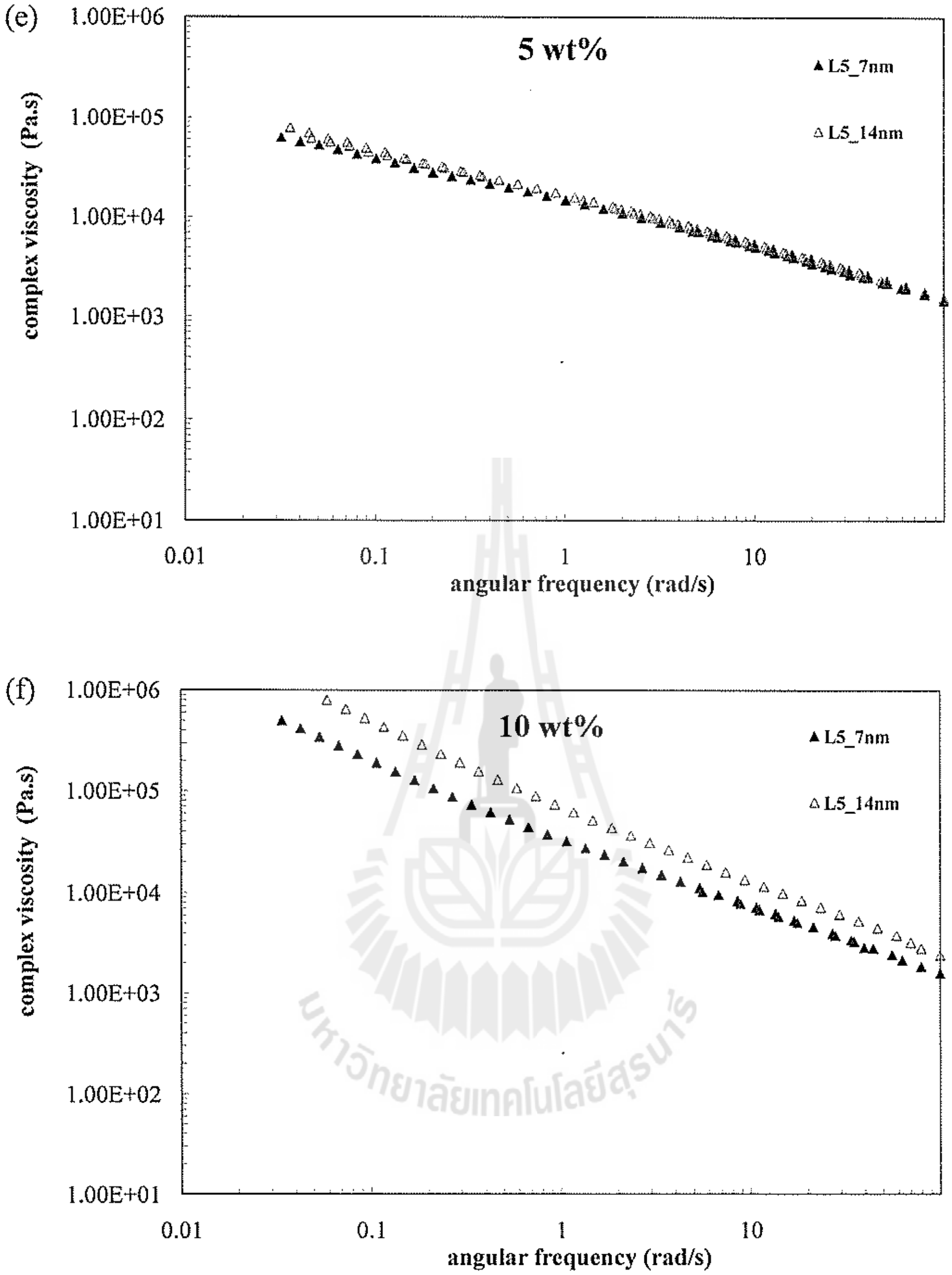


Figure 4.7 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled L5 at constant filler loadings of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160°C (continued).

frequency region, whereas at high loadings the viscosity diverges. This diverge corresponds to the solid-like behavior observed in the storage modulus.

(a)

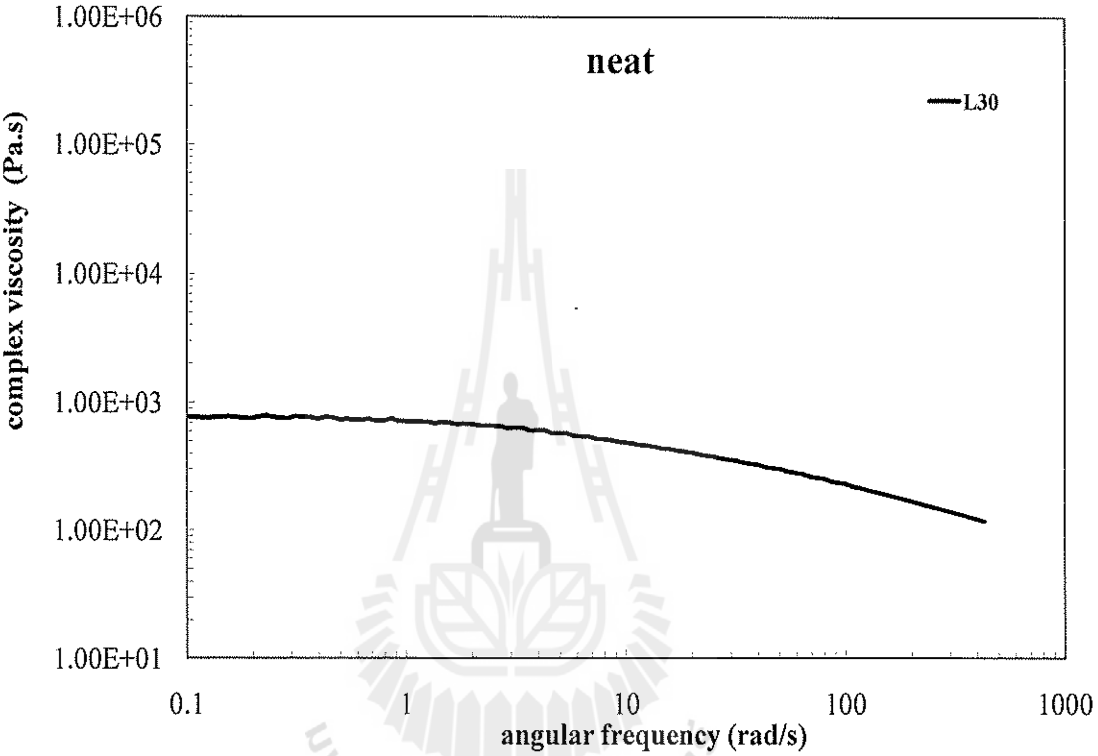


Figure 4.8 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled L30 at constant filler loadings of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160°C.

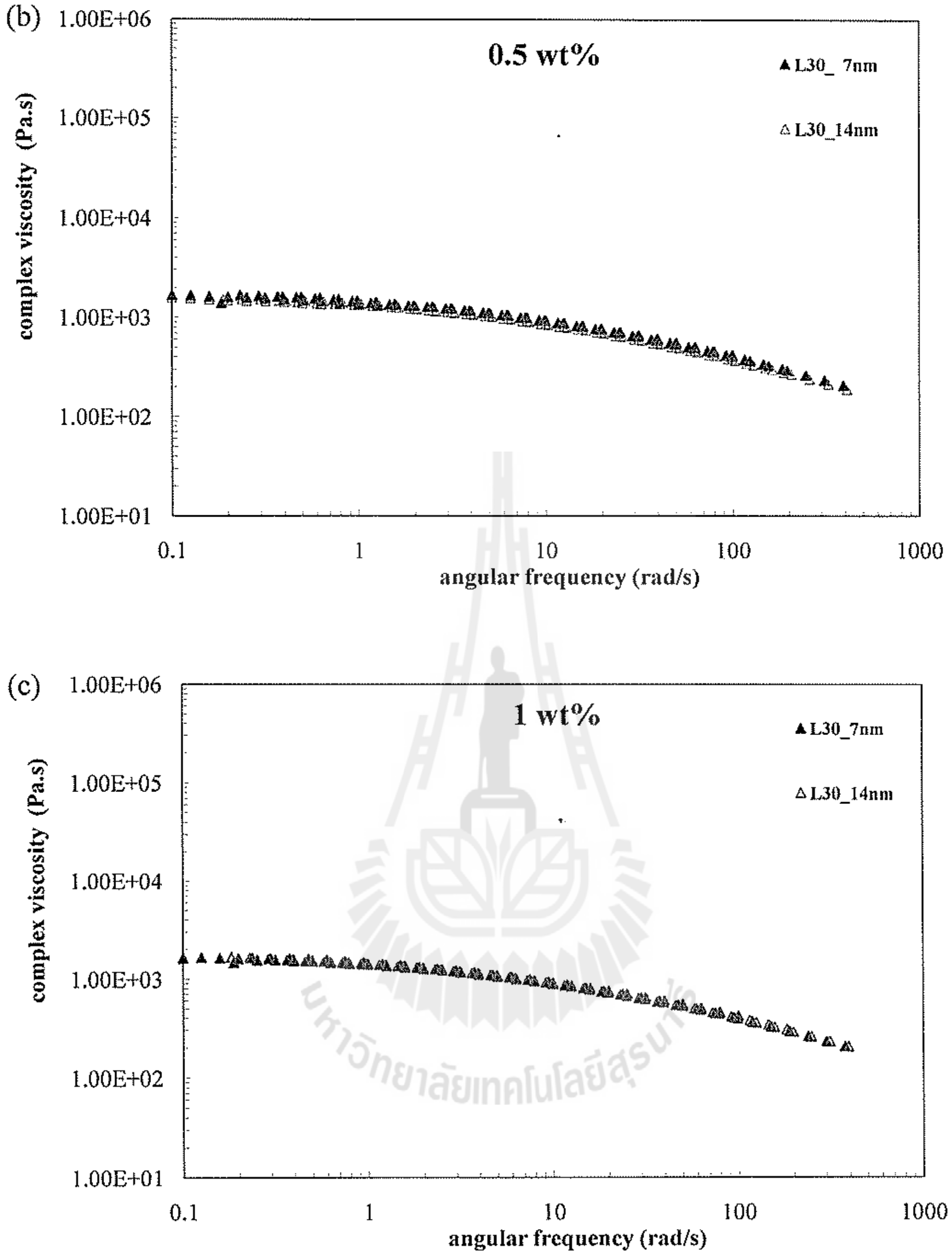
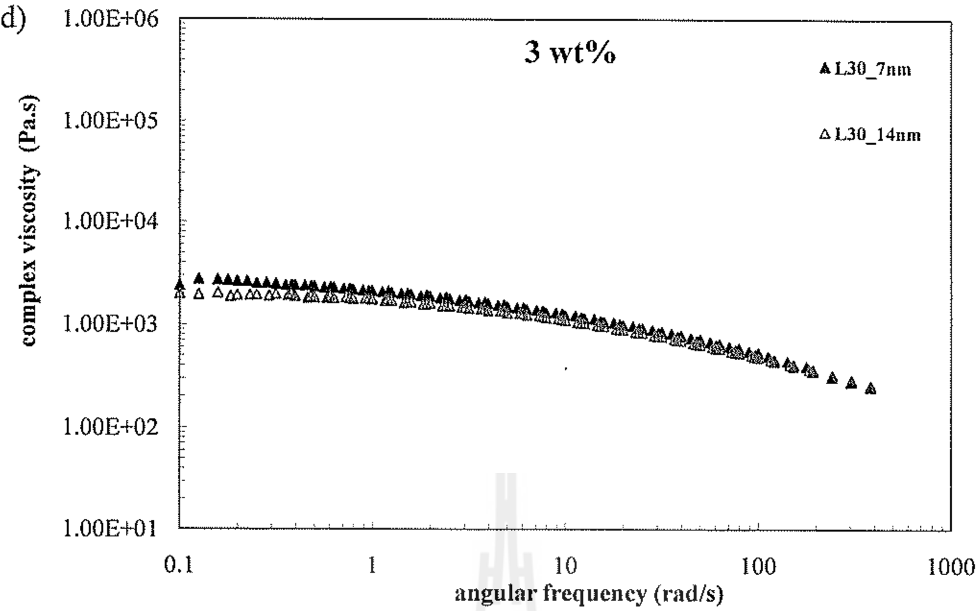


Figure 4.8 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled L30 at constant filler loadings of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160°C (continued).

(d)



(e)

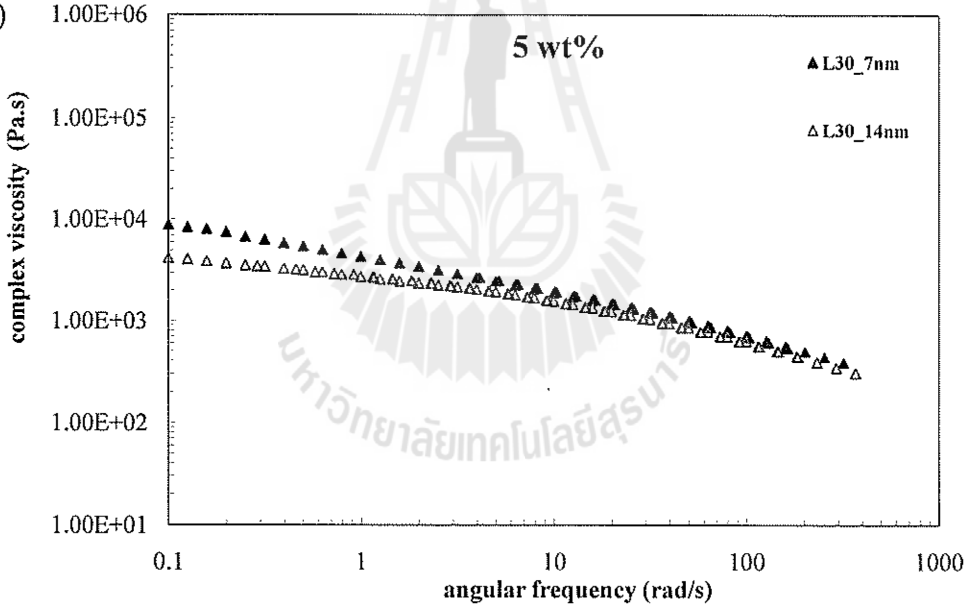


Figure 4.8 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled L30 at constant filler loadings of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160°C (continued).

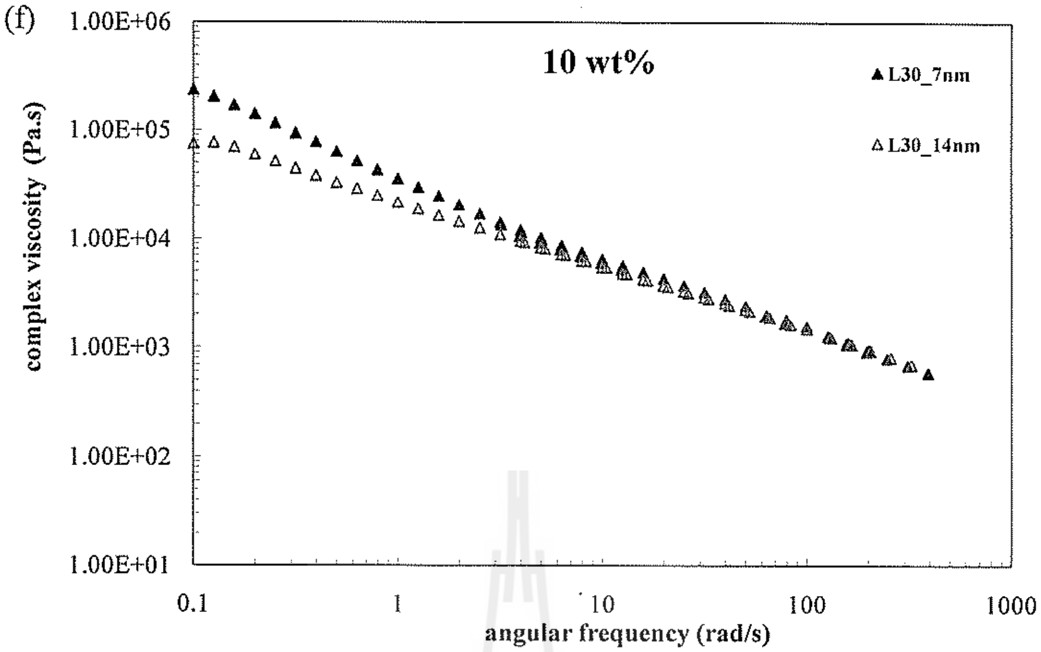


Figure 4.8 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled L30 at constant filler loadings of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160°C (continued).

4.2.2 The effects of fumed silica size and content on filled HDPE melts

High density polyethylene mainly differs from low density polyethylene in chain structure, not in chemical structure. Rheological studies on the effect of branch structure reveal the significant difference in viscosity and molecular weight relation from the linear chain (McLeish, 1988, 1999; Yan, Wang and Zhu, 1999; Liu et al., 2004; Tian, Yu and Zhou, 2006).

Similar to LDPE, the storage and loss moduli of both H08 and H14 were increased in the presence of nanosilica particles as presented in Figure 4.9 and Figure 4.10 respectively. At 10 wt% loading, the G′ in the terminal region was clearly independent of the frequency.

a)

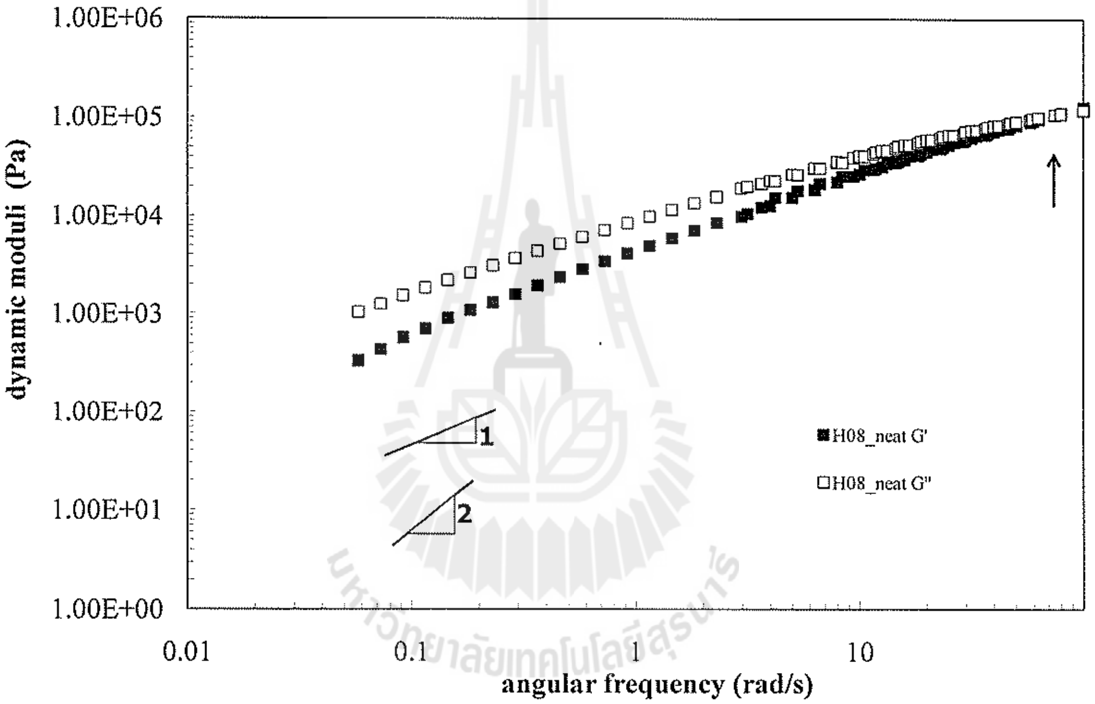


Figure 4.9 Storage and loss moduli of the fumed silica (7 and 14 nm) filled H08 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160 °C.

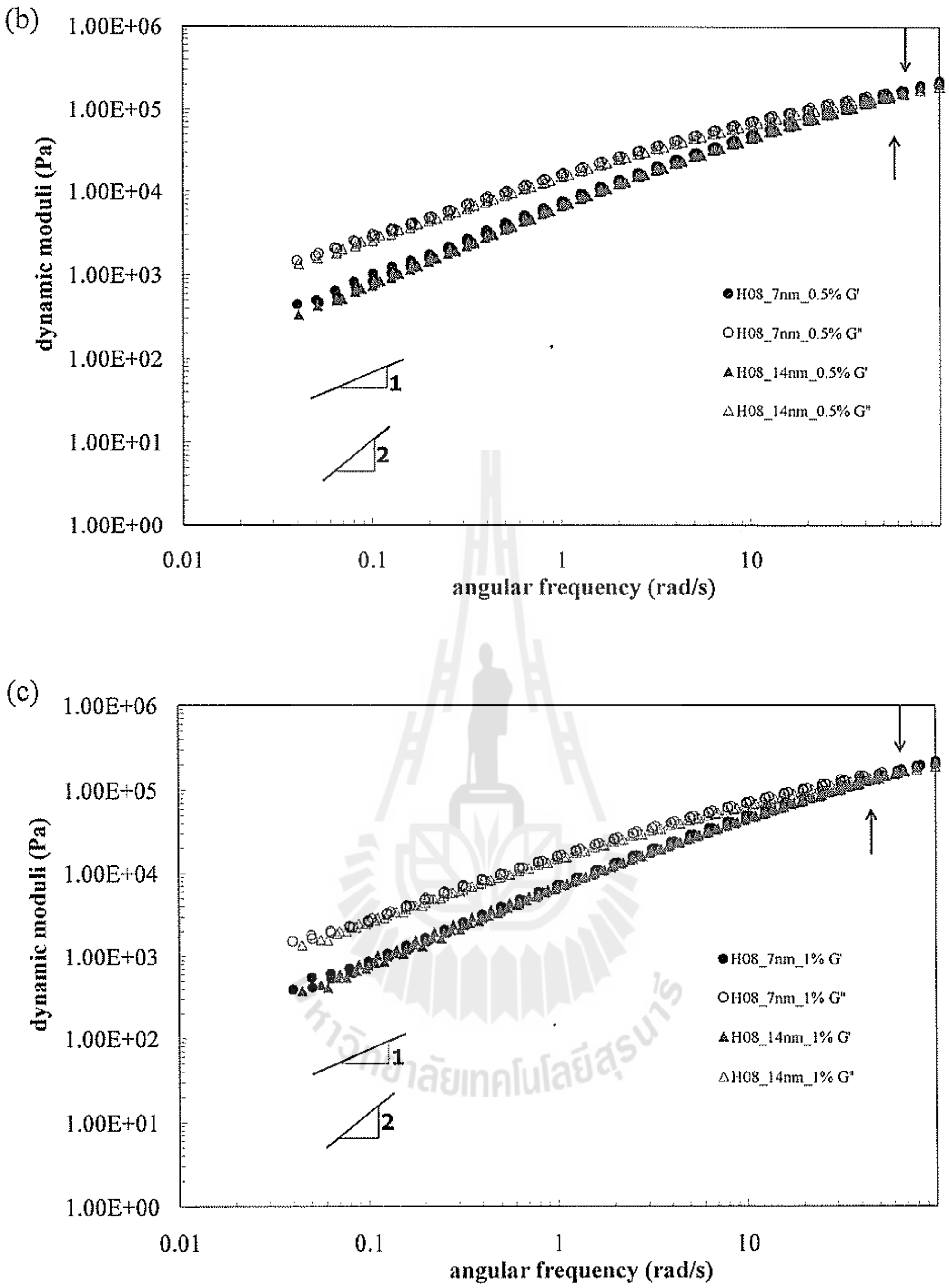


Figure 4.9 Storage and loss moduli of the fumed silica (7 and 14 nm) filled H08 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160 °C (continued).

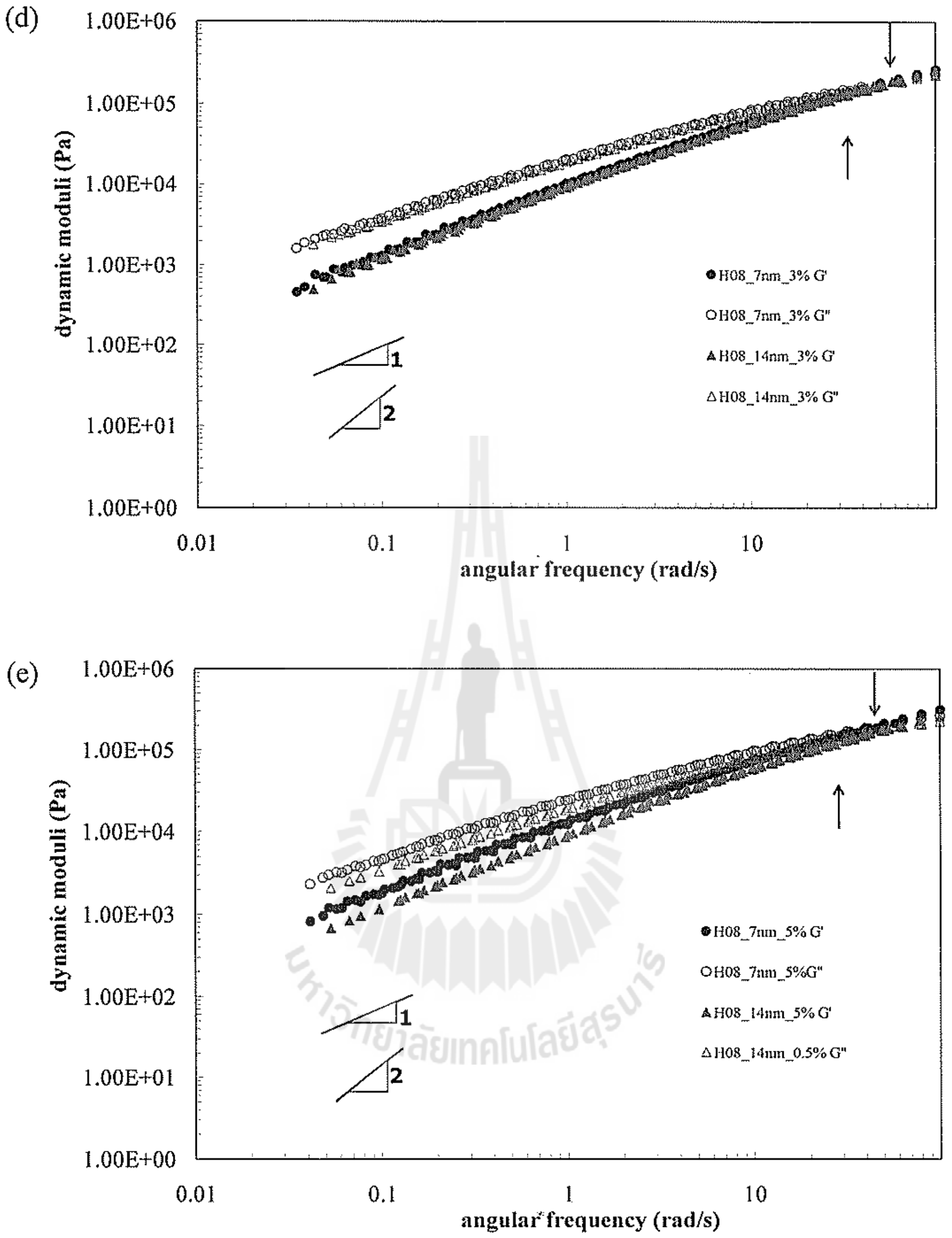


Figure 4.9 Storage and loss moduli of the fumed silica (7 and 14 nm) filled H08 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160 °C (continued).

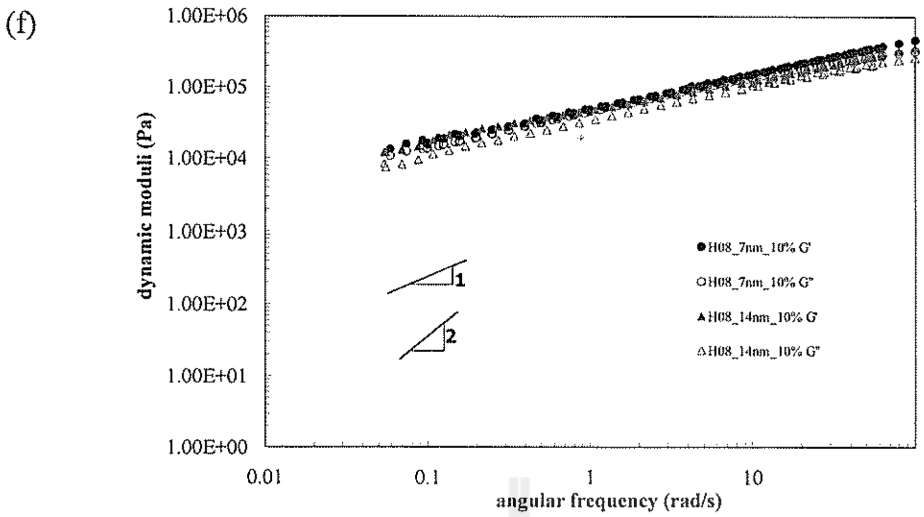


Figure 4.9 Storage and loss moduli of the fumed silica (7 and 14 nm) filled H08 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160 °C (continued).

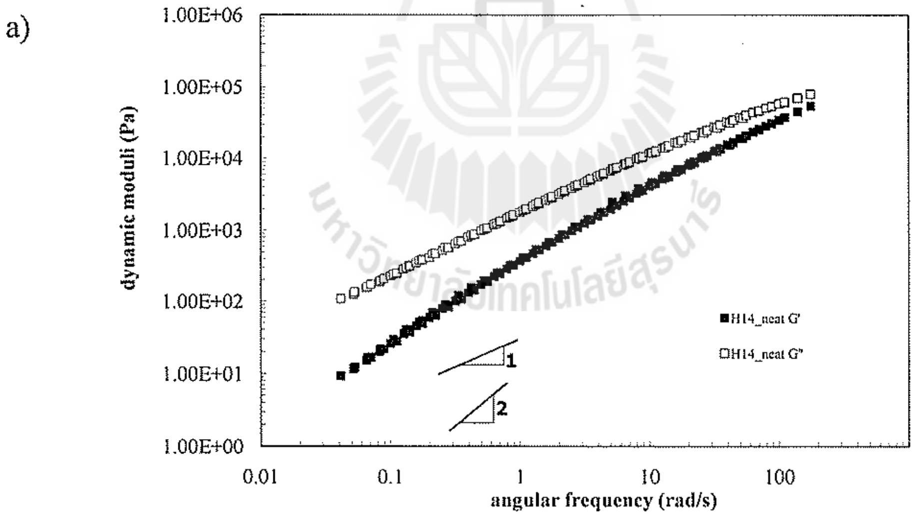


Figure 4.10 Storage and loss moduli of the fumed silica (7 and 14 nm) filled H14 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160 °C.

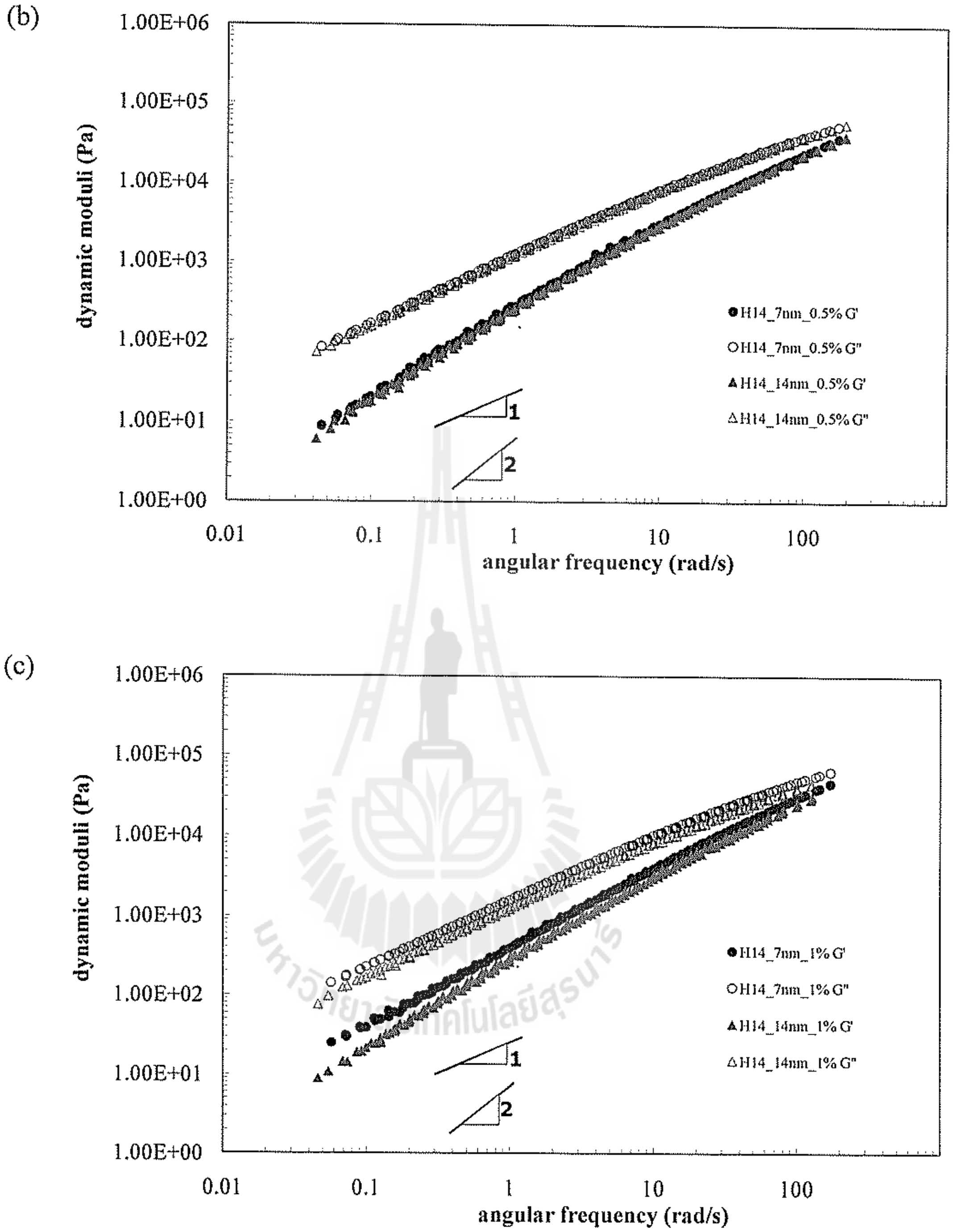


Figure 4.10 Storage and loss moduli of the fumed silica (7 and 14 nm) filled H14 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160 °C (continued).

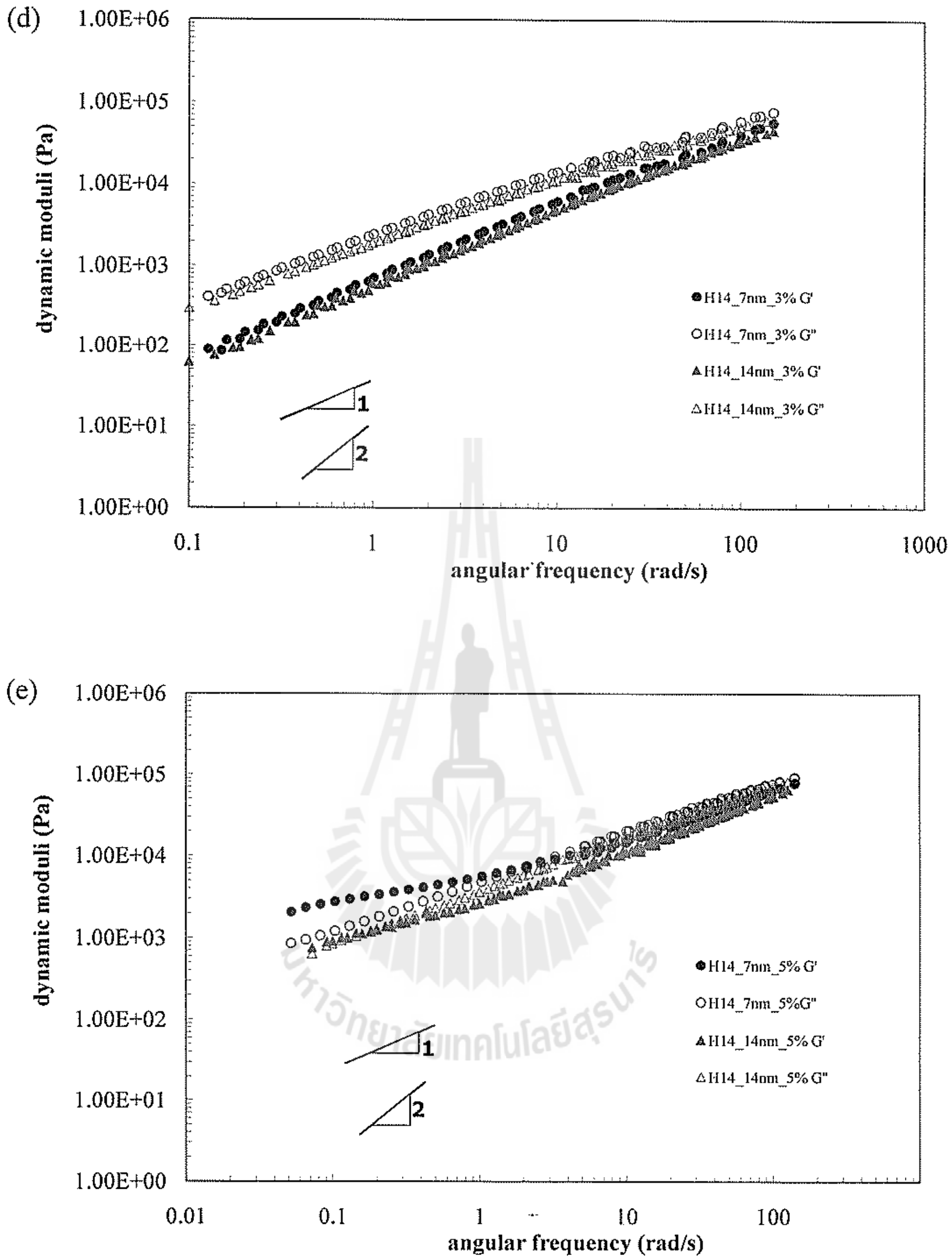


Figure 4.10 Storage and loss moduli of the fumed silica (7 and 14 nm) filled H14 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160 °C (continued).

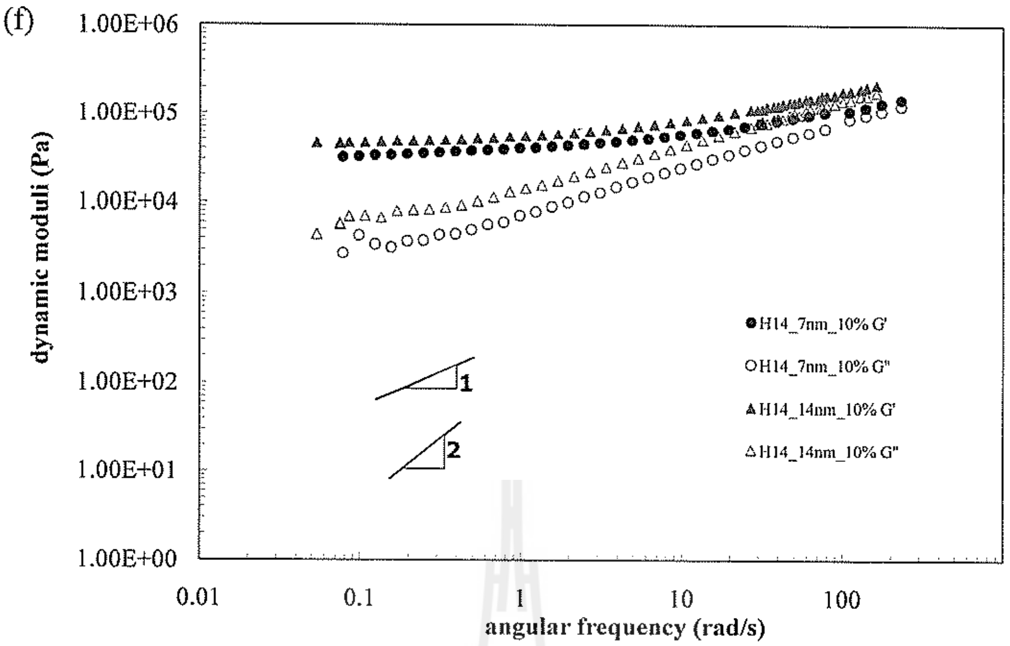


Figure 4.10 Storage and loss moduli of the fumed silica (7 and 14 nm) filled H14 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160 °C (continued).

Figure 4.11 and 4.12 presents the complex viscosity against frequency for the filled HDPE melts with different particle size at each nanosilica loading. The neat HDPE showed Newtonian behavior as the complex viscosity was relatively constant at low frequency range. The decrease of the complex viscosity was observed at higher frequency. In the presence of the small silica loadings (≤ 3wt%), the complex viscosities were nearly identical for both particle sizes (7 and 14 nm) at each loading. At higher loadings (≥ 5wt%), the filled melts showed the complex viscosities increased significantly.

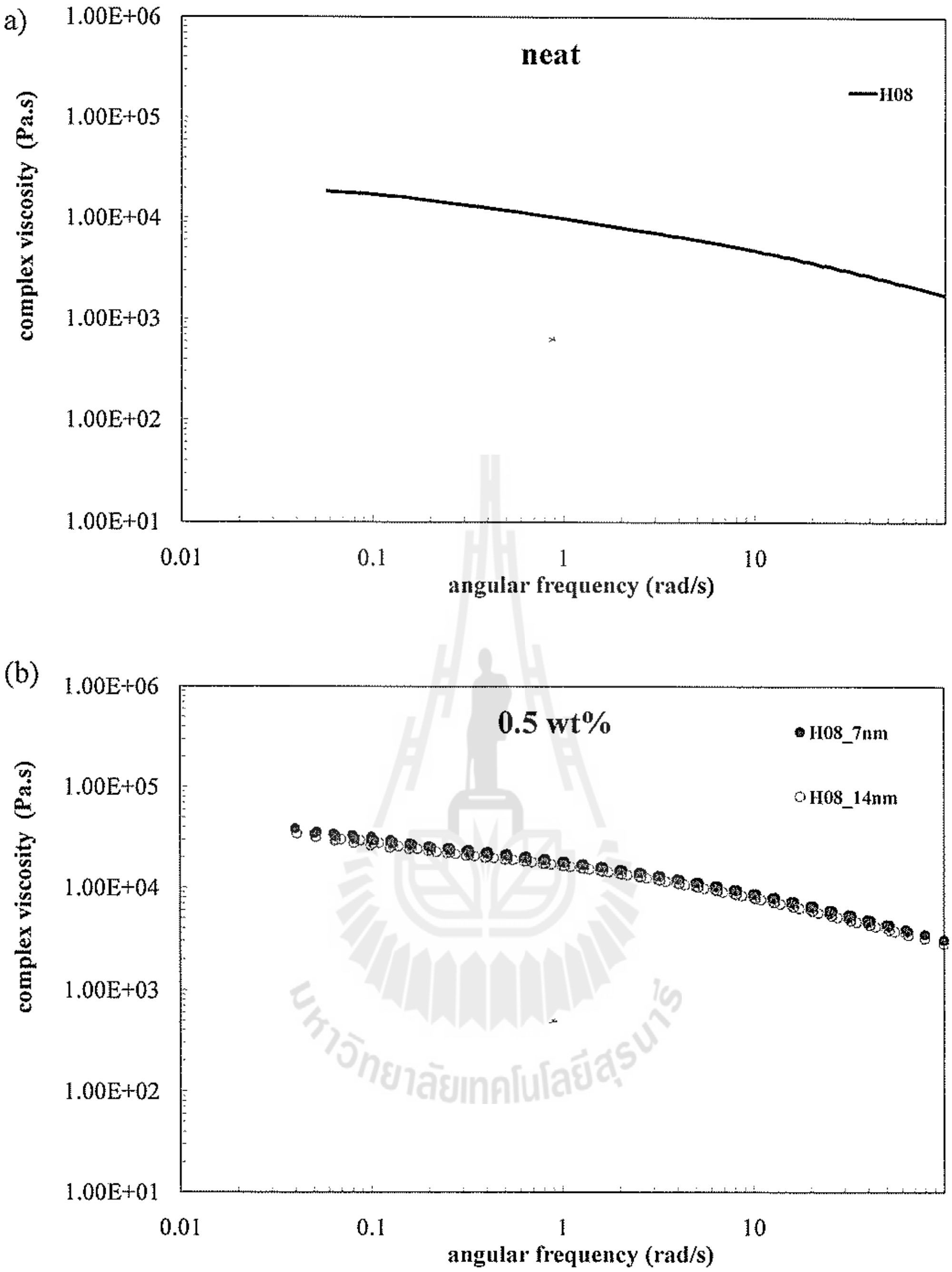


Figure 4.11 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled H08 at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C.

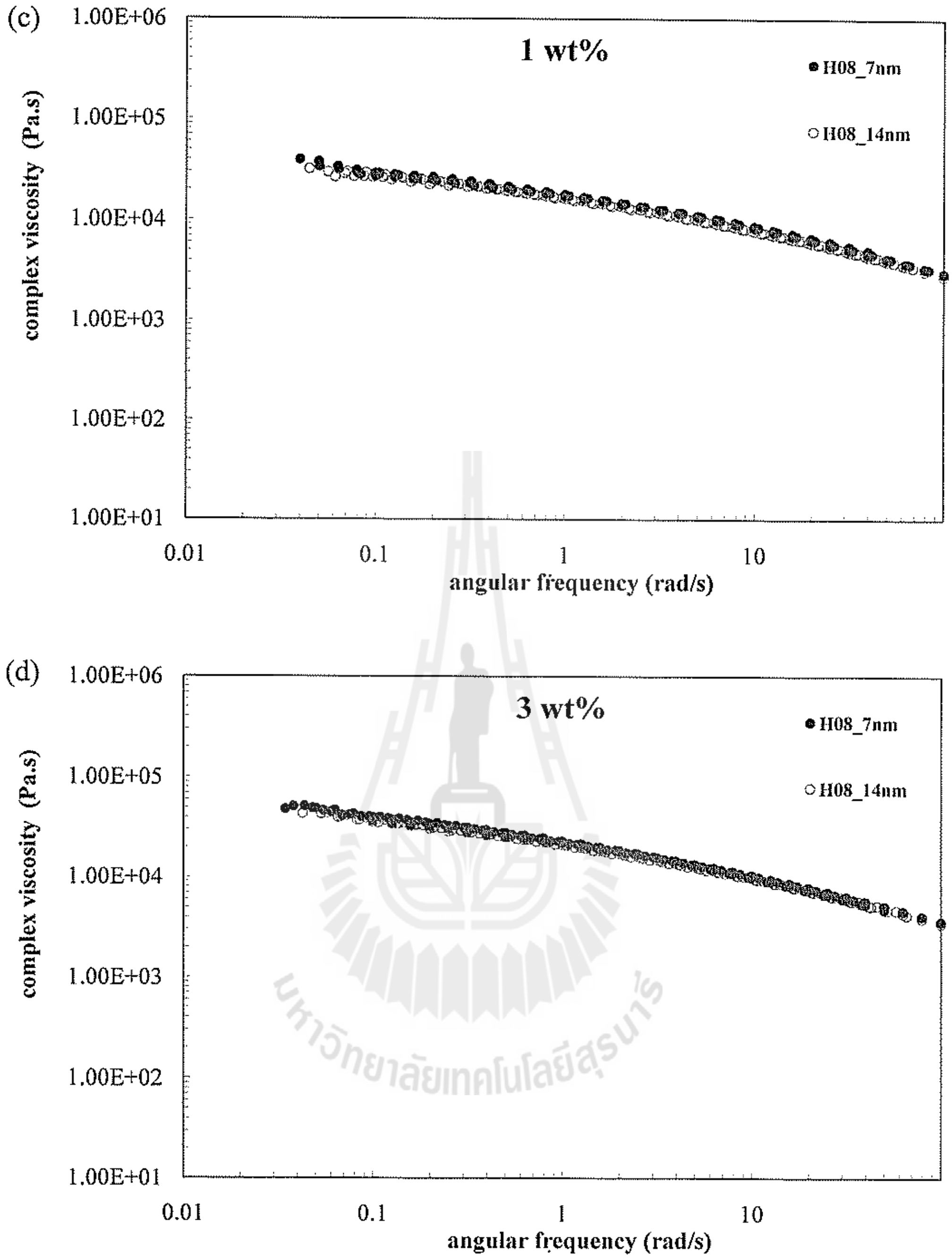
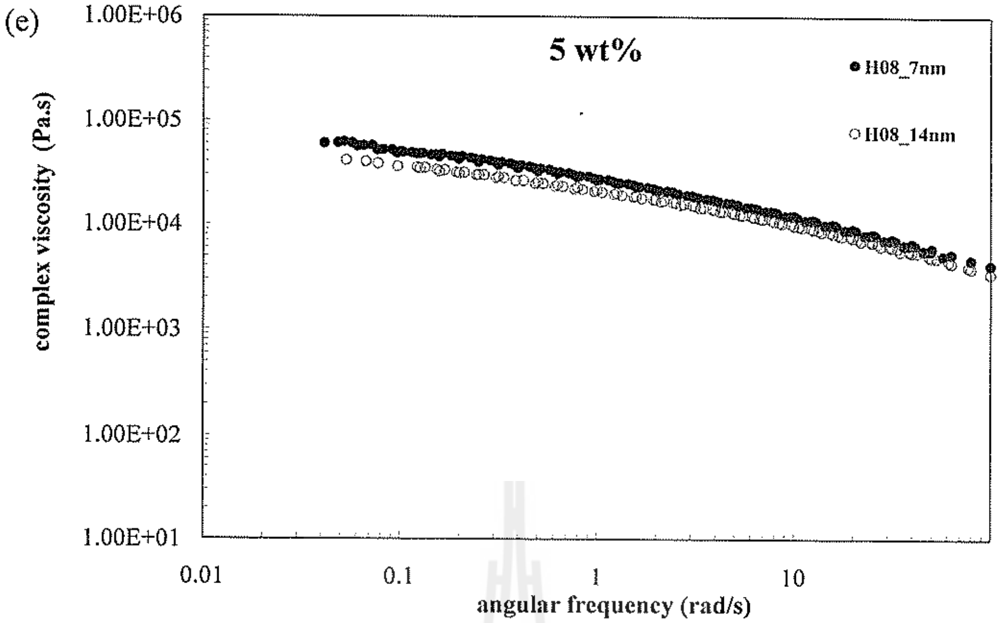


Figure 4.11 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled H08 at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C (continued).



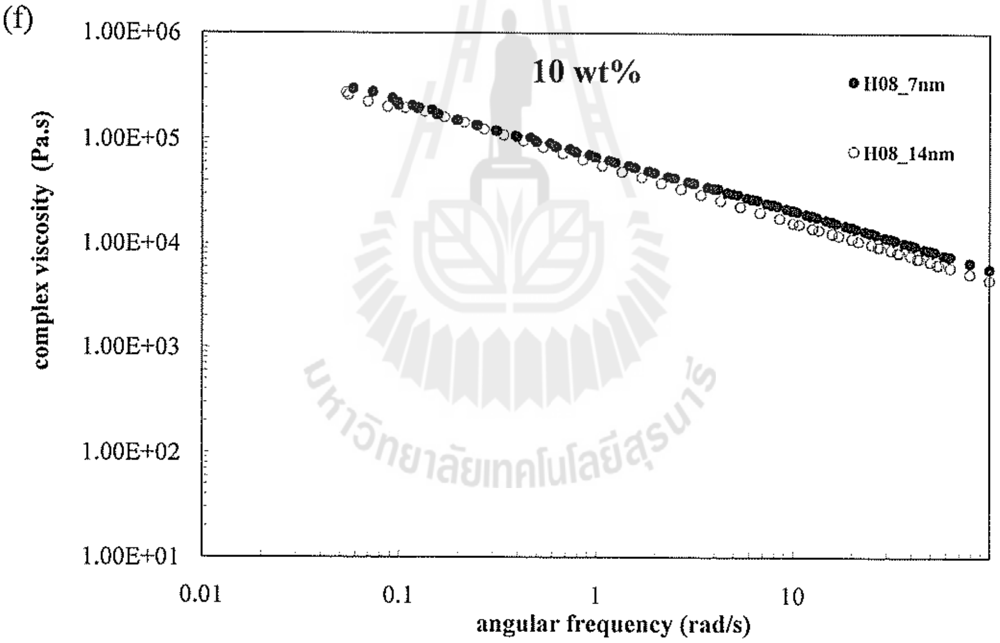


Figure 4.11 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled H08 at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C (continued).

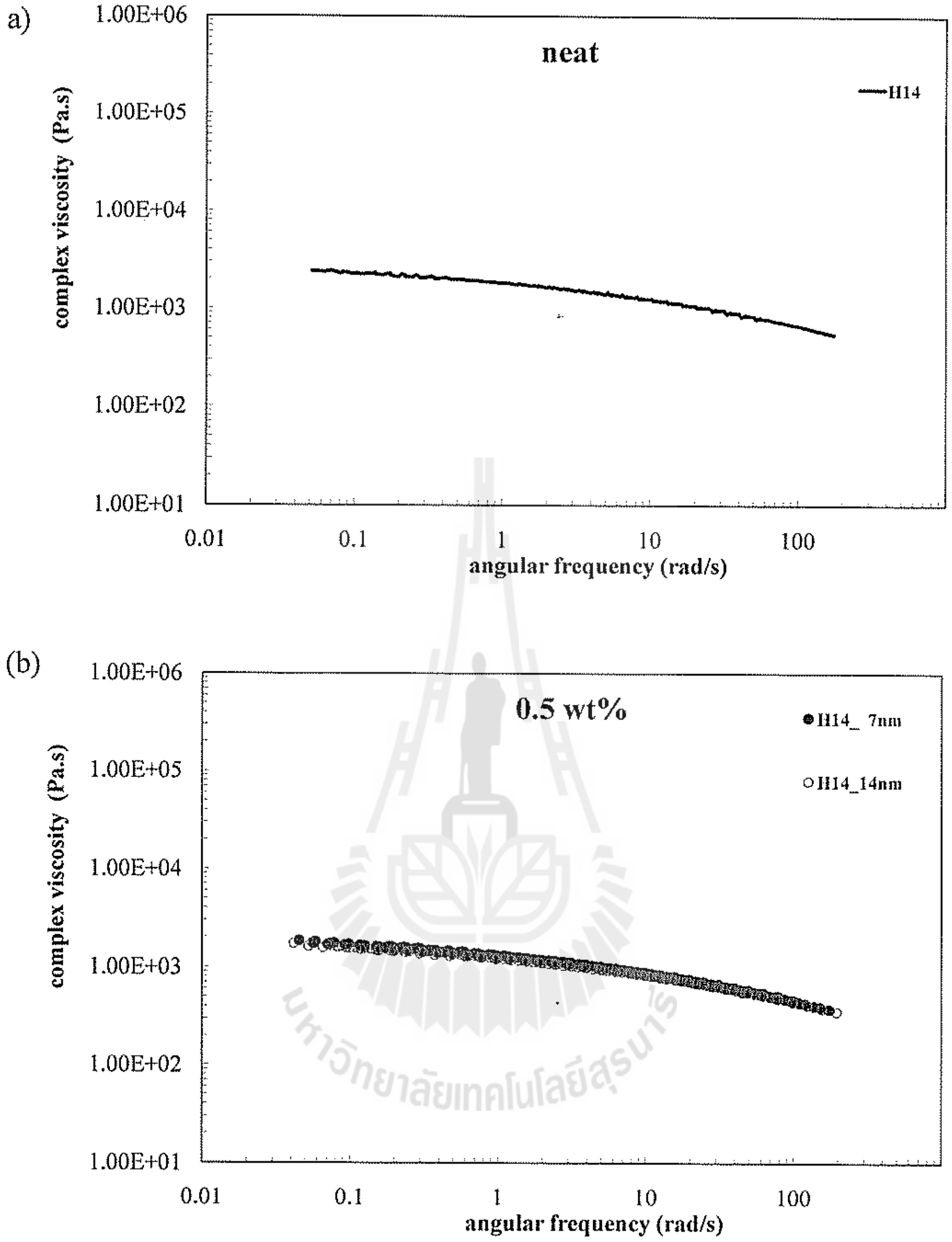


Figure 4.12 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled H14 at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C.

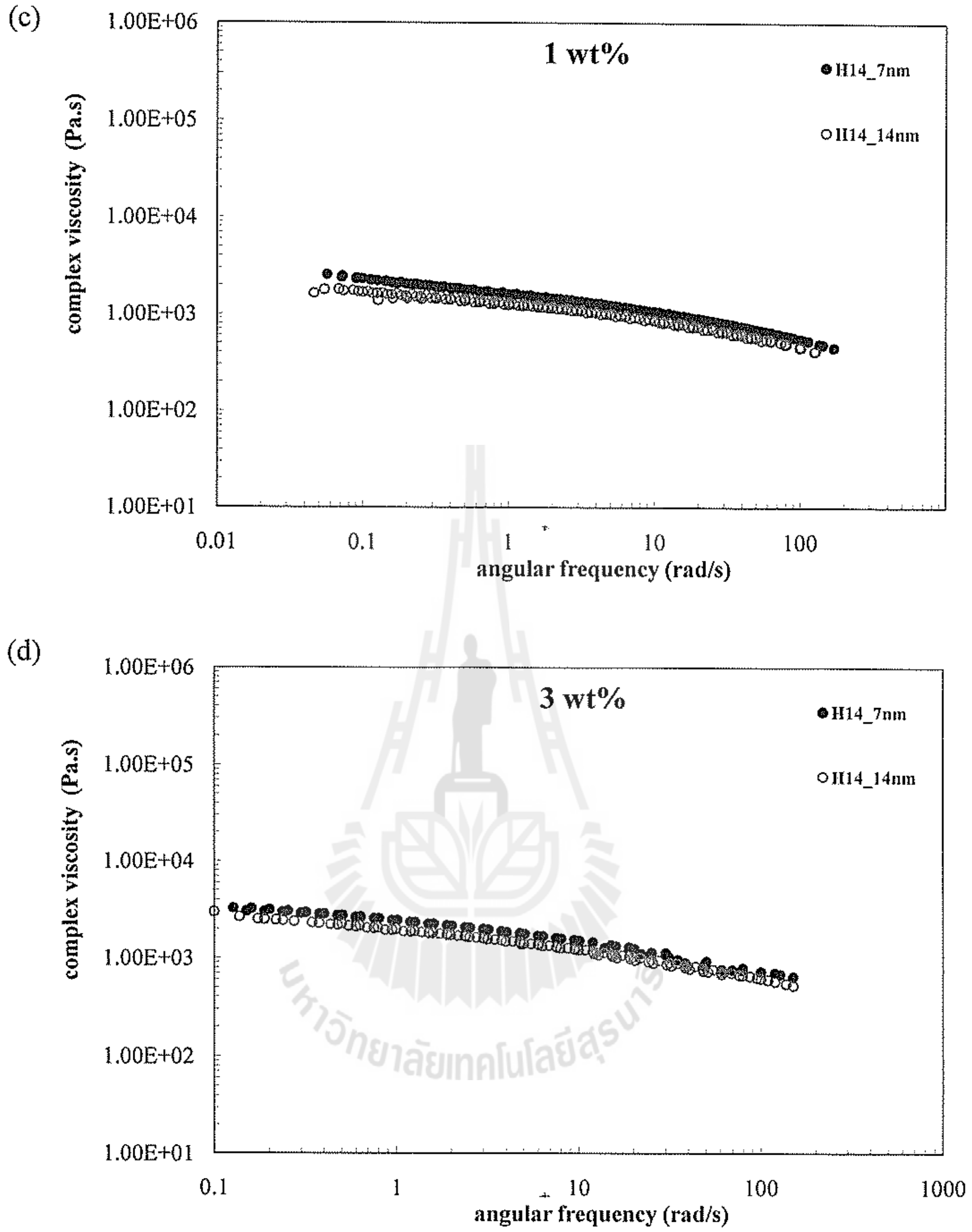


Figure 4.12 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled H14 at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C (continued).

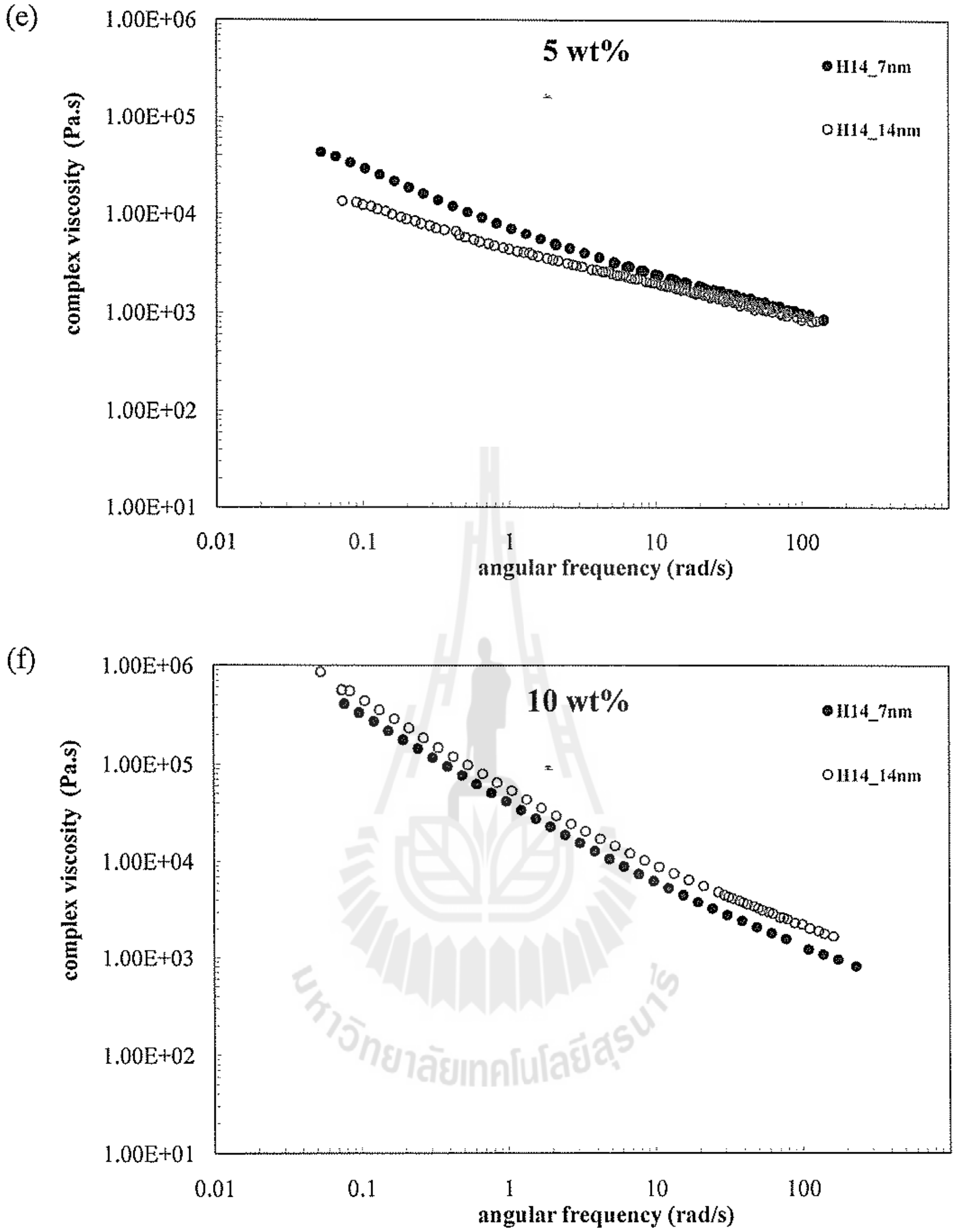


Figure 4.12 Variations of complex viscosity versus frequency for 7 and 14 nm fumed silica filled H14 at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C (continued).

4.3 Rheology of fumed silica filled polyethylene melts by dissolution mixing

Dissolution mixing was prepared for comparison with melt mixing about particles dispersion. To confirm that the melt mixing provides a good distribution as dissolution mixing. The distribution of particles affects the rheological properties. Some specimens from dissolution mixing were prepared. By choosing, linear chain structure (H08) represents for high molecular weight filled with 7 nm hydrophilic fumed silica (smaller diameter size). L30 represents branched chain structure (low molecular weight) filled with 14 nm hydrophilic fumed silica (higher diameter size). It was found that the presence of nanosilica in PE melts by the dissolution mixing on the viscoelastice properties was not differ significantly from the melt mixing. This may due to both melt mixing and dissolution provide a good distribution of nanosilica as an equal. Although, silica nanoparticles are very hard to disperse due to strong attraction forces.

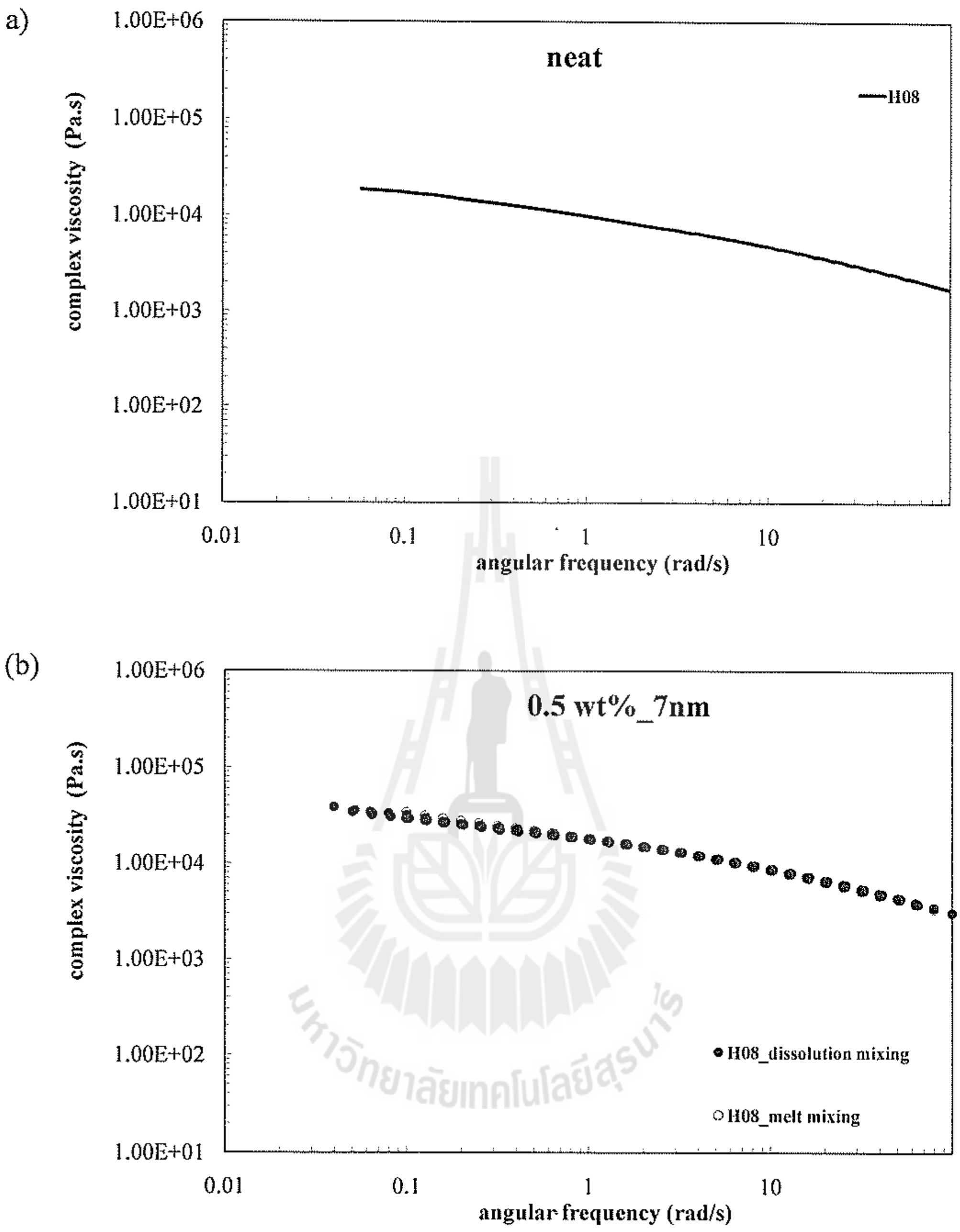


Figure 4.13 Variations of complex viscosity versus frequency for 7 nm fumed silica filled H08 by dissolution mixing (open symbol) and melt mixing (filled symbol) at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C.

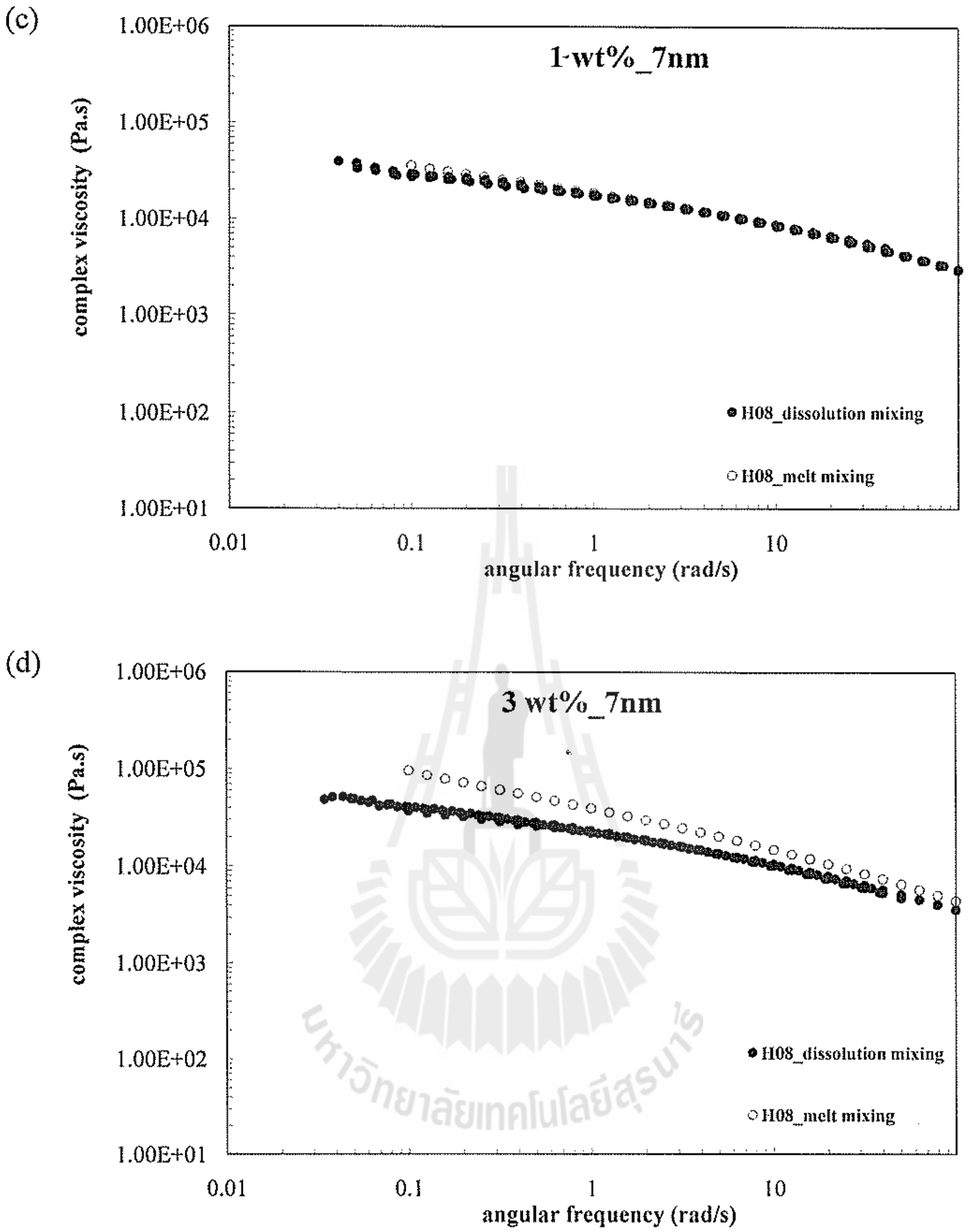
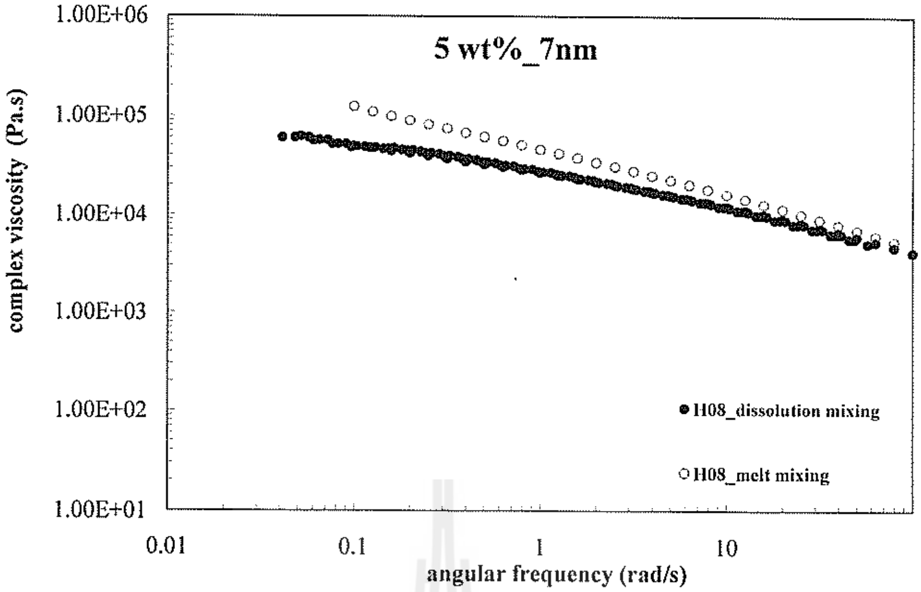


Figure 4.13 Variations of complex viscosity versus frequency for 7 nm fumed silica filled H08 by dissolution mixing (open symbol) and melt mixing (filled symbol) at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C (continued).

(e)



(f)

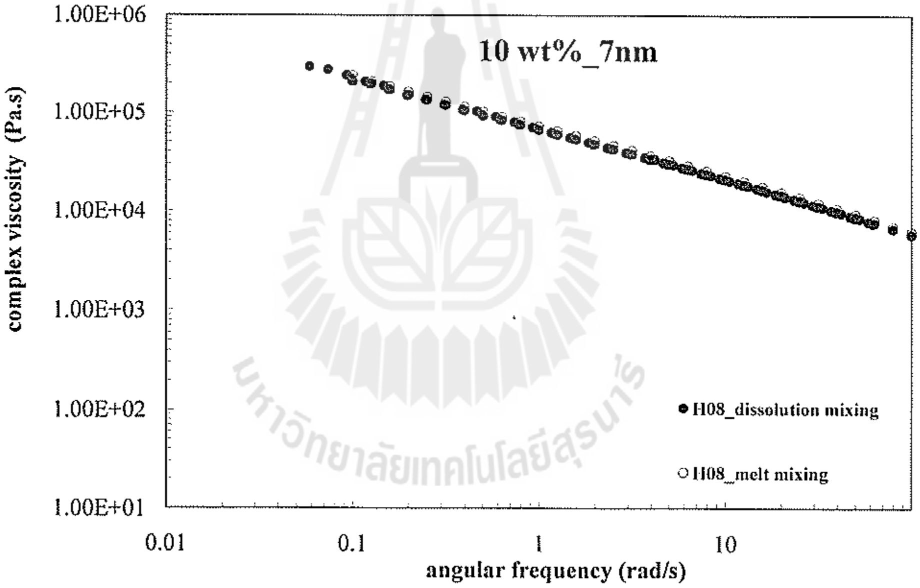


Figure 4.13 Variations of complex viscosity versus frequency for 7 nm fumed silica filled H08 by dissolution mixing (open symbol) and melt mixing (filled symbol) at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C (continued).

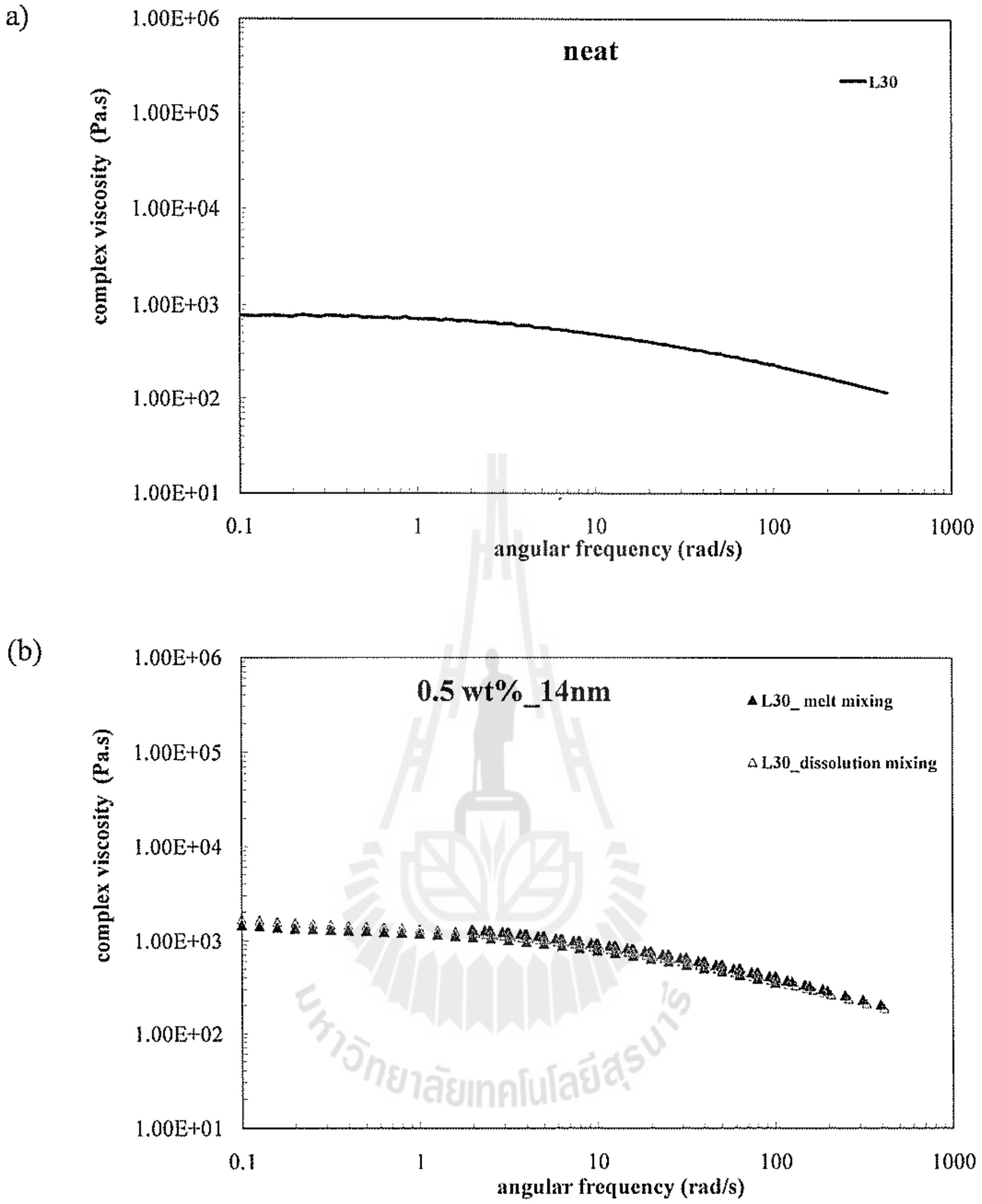
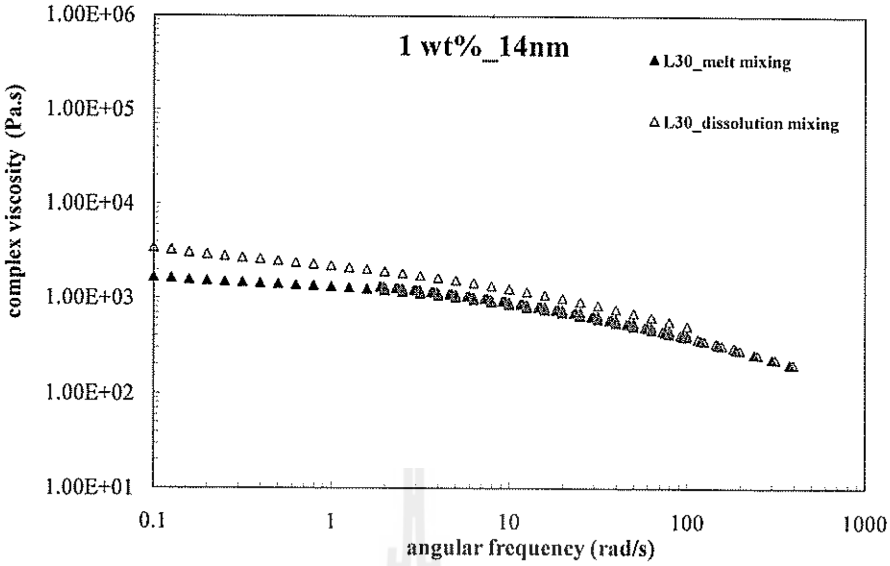


Figure 4.14 Variations of complex viscosity versus frequency for 14 nm fumed silica filled L30 by dissolution mixing (open symbol) and melt mixing (filled symbol) at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C.

(c)



(d)

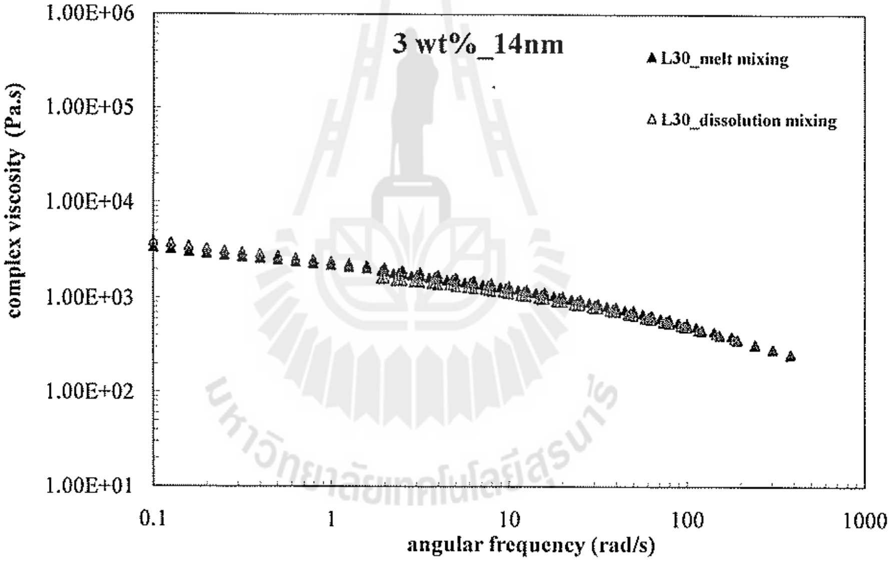
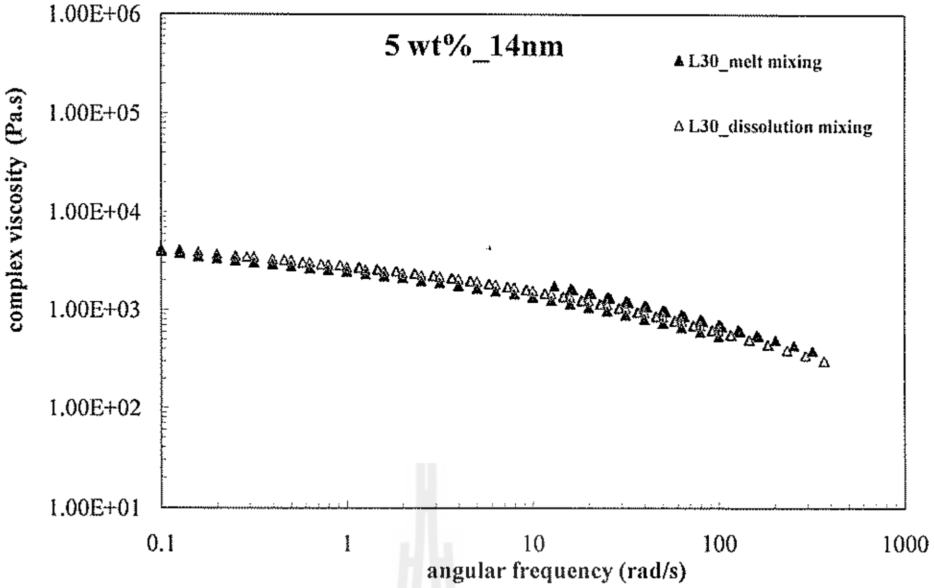


Figure 4.14 Variations of complex viscosity versus frequency for 14 nm fumed silica filled L30 by dissolution mixing (open symbol) and melt mixing (filled symbol) at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C (continued).

(e)



(f)

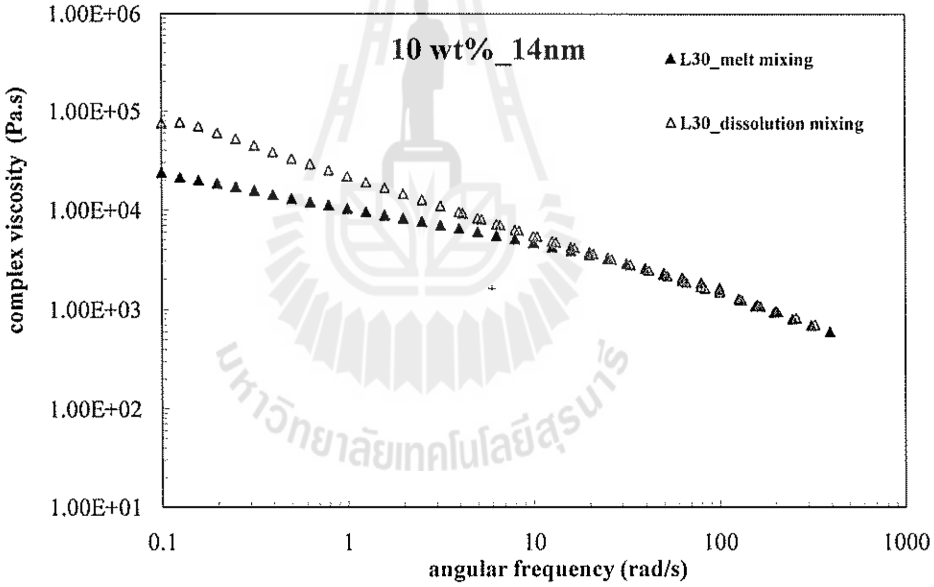


Figure 4.14 Variations of complex viscosity versus frequency for 14 nm fumed silica filled L30 by dissolution mixing (open symbol) and melt mixing (filled symbol) at constant filler loading of (a) neat, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt% and (f) 10 wt% at the reference temperature of 160 °C (continued).

4.4 Morphology of fumed silica filled polyethylene melts

The dispersion of nanosilica particles in polyethylenes was examined using TEM. TEM images of the nanoparticles (as prepared from the dispersion of silica in methanol) are shown in Figure 4.15. It is confirmed that the nanoparticles are spherical with the size of 7 (a) and 14 (b) nm.

(a)

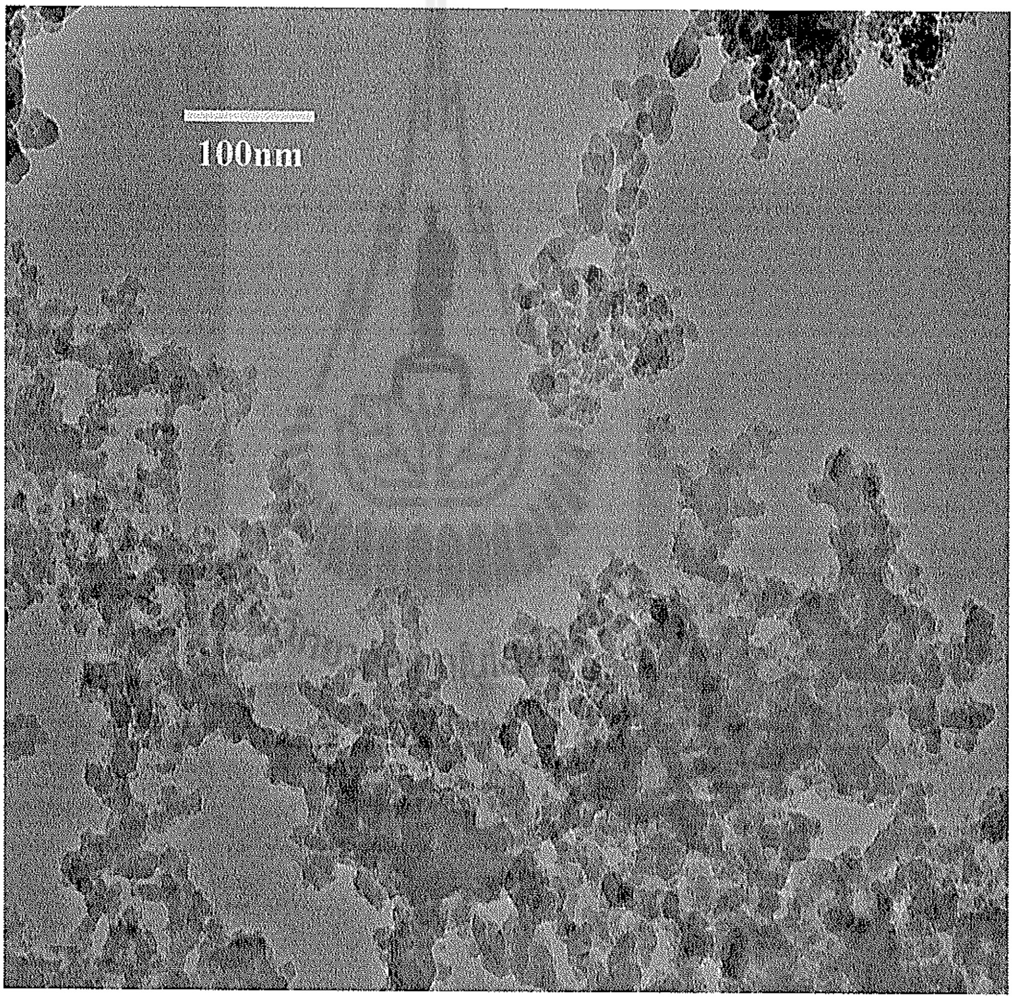


Figure 4.15 TEM images of (a) pure 7 nm, (b) pure 14 nm

(b)

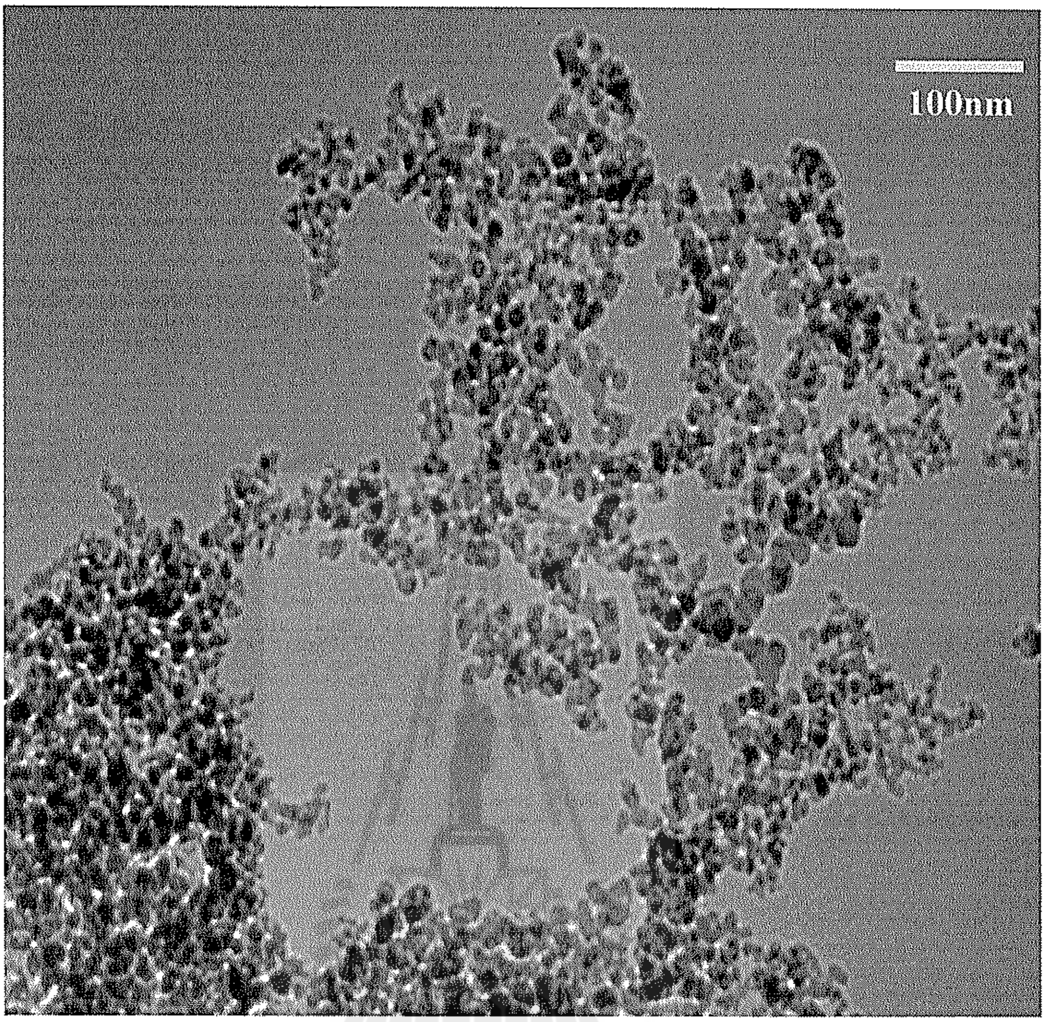


Figure 4.15 TEM images of (a) pure 7 nm, (b) pure 14 nm (continued)

TEM micrographs of 0.5 (7nm) and 1 (14) wt% nanosilica/PE are presented in Figure 4.16 and 4.17 respectively. Relatively good dispersion was observed. It indicates that to some extent, hydrophilic particles could disperse in hydrophobic matrix. As the strong increase of G' was obtained at 5 wt%, it could mean that not only good dispersion but also silica content governs the increase of G'. As both nanosilica sizes displayed the similar results in the rheological properties, it could be that the fumed silica nanoparticles can aggregate to the same cluster size.

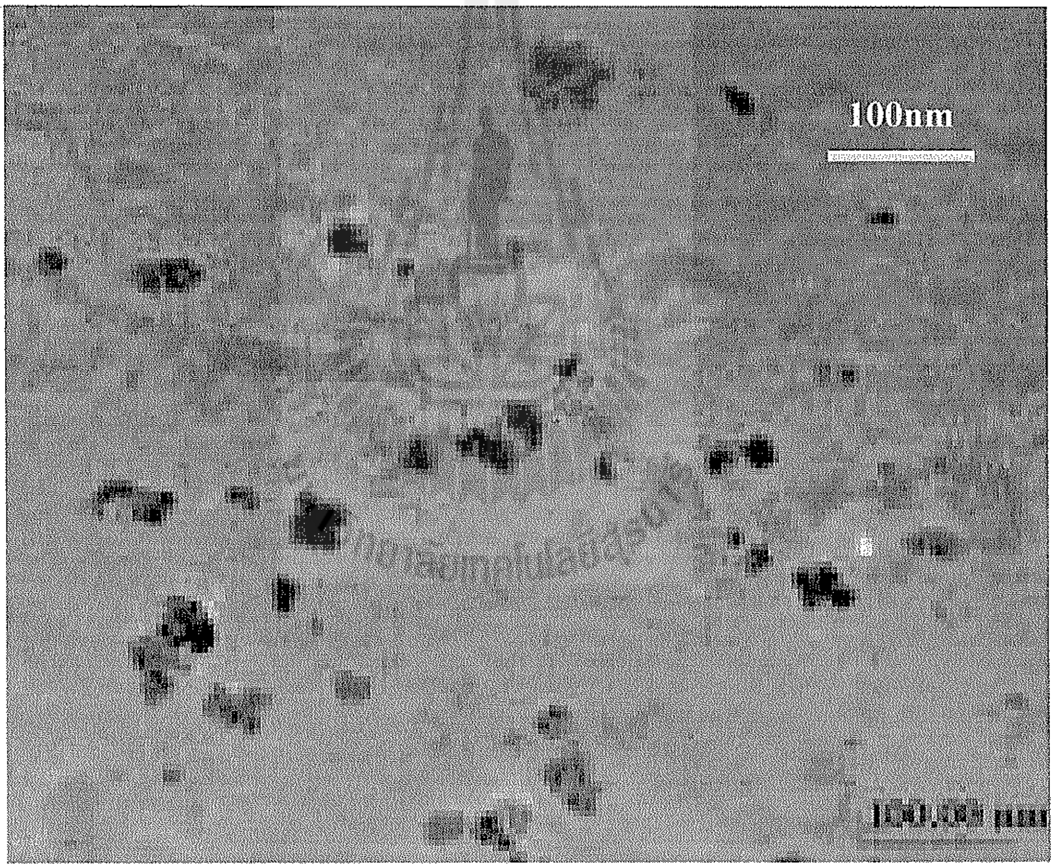


Figure 4.16 TEM images of 0.5 wt% of 7nm fumed silica filled H14

(a)

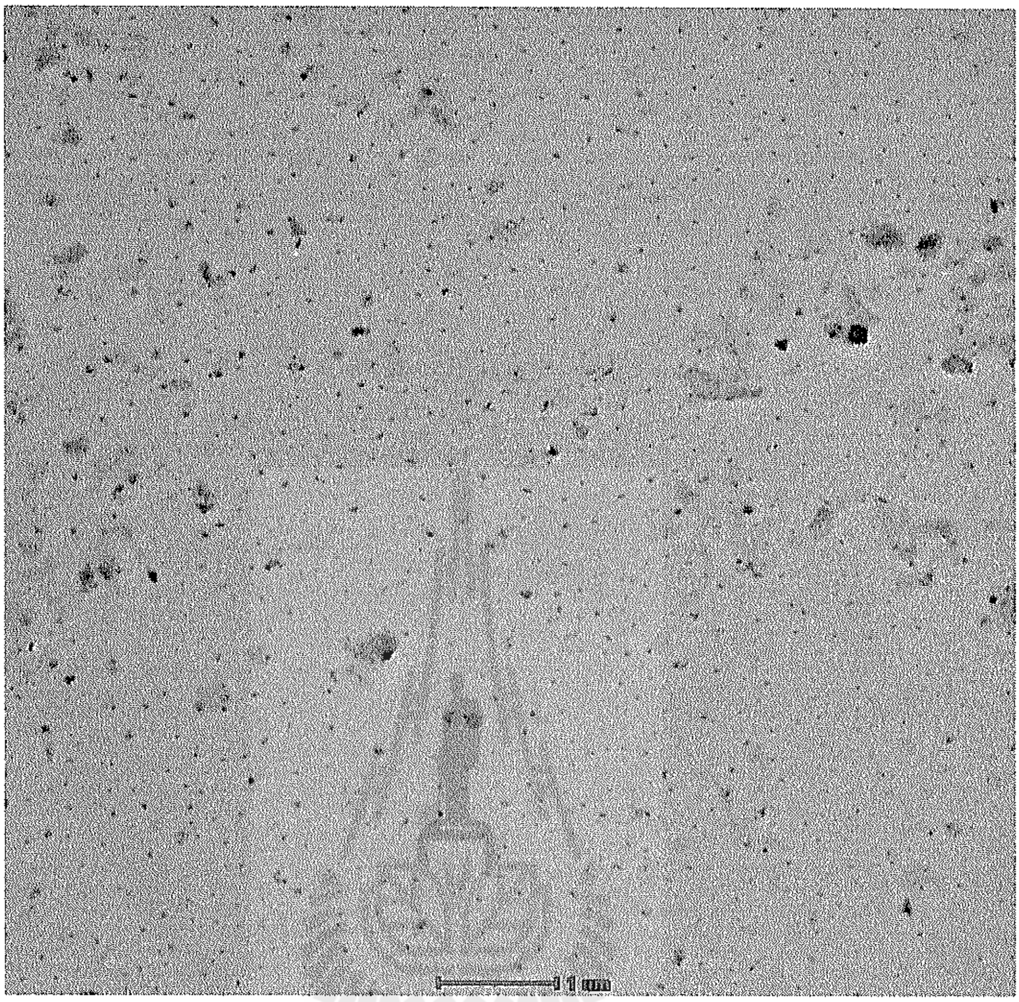


Figure 4.17 TEM images of 1 wt% of 14 nm filled L5 at the scale bar of (a) 1µm (b) 500 nm and (c) 100 nm.

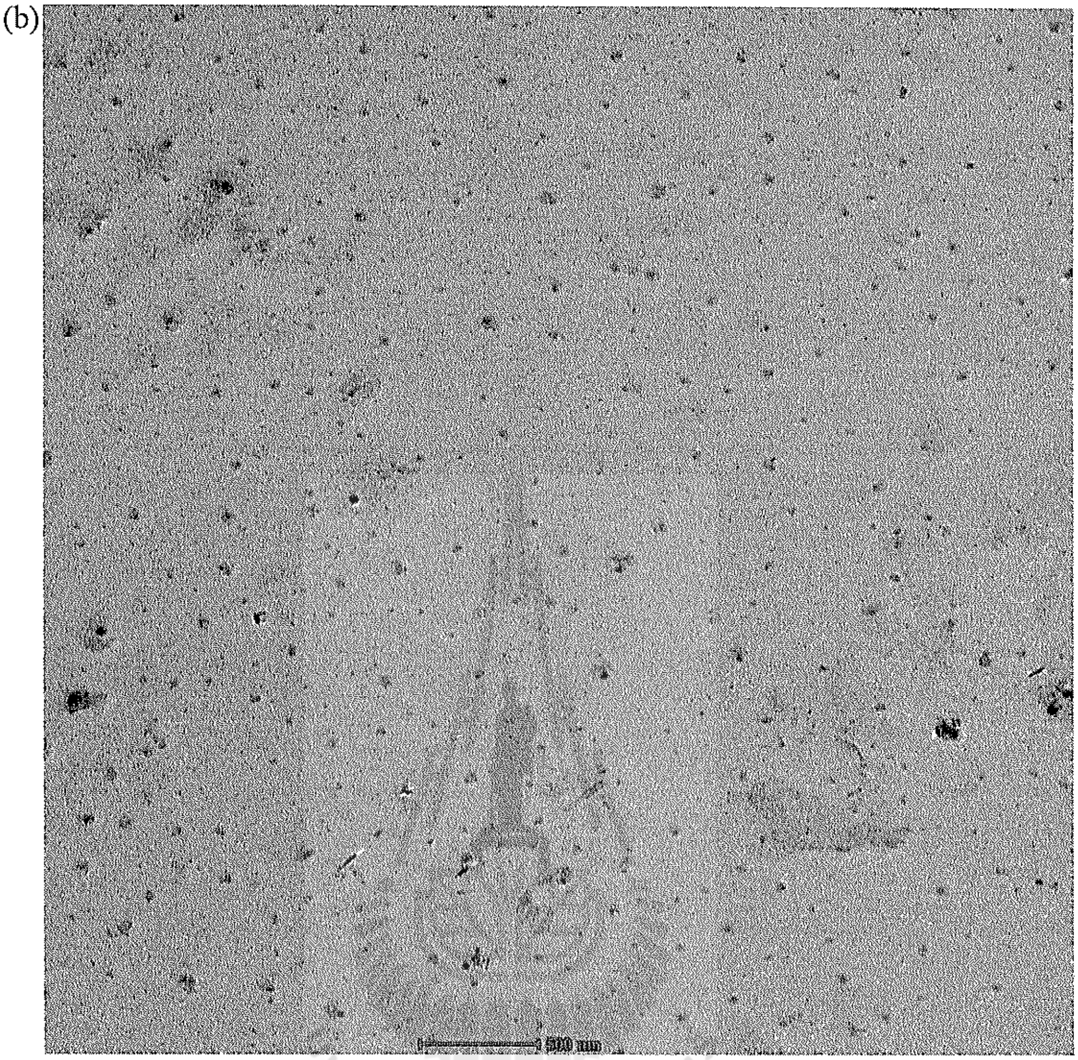


Figure 4.17 TEM images of 1 wt% of 14 nm filled L5 at the scale bar of (a) 1μm (b) 500 nm and (c) 100 nm (continued).

(c)

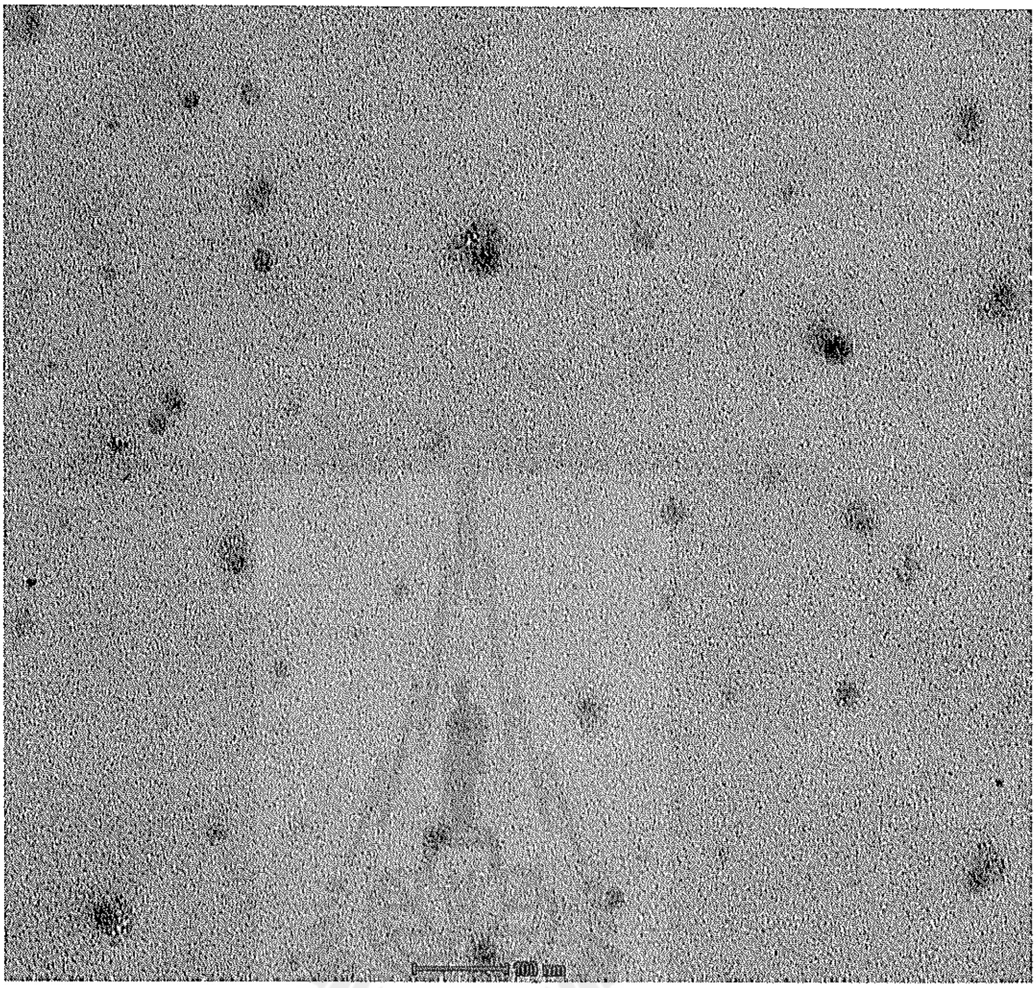


Figure 4.17 TEM images of 1 wt% of 14 nm filled L5 at the scale bar of (a) 1μm (b) 500 nm and (c) 100 nm (continued).

CHAPTER V

CONCLUSIONS

The rheological properties depend on chain structure. The branched chain (LDPE) has restrictions on the movement than linear chain (HDPE) because of branches. Therefore, LDPE has slowly chain mobility or higher relaxation time than HDPE. It reflects on the relationship between the characteristic time scale with the zero shear viscosity at the same zero shear viscosity value. When adding fumed silica nanoparticles, the moduli and complex viscosity in the terminal region are increase with both chain structures. The most increasing rheological properties in filled PE melts is the lowest molecular viscosity (L30> H14> L5> H08 respectively) and it is not depend on chain structure. This is due to low entanglement. It should be have high surface area for adsorption with nanoparticle and with the aid of the adsorption increased in bridging of polymer chains between and along nanosilica surfaces that effectively increased the moduli and complex viscosity.

By adding nanosilica into PE melts affects the rheology especially in the terminal region. It was found that the presence of nanosilica increased the moduli and complex viscosity. At the content $\geq$ 5 wt%, the filled PE melts showed the solid-like behavior. Regardless of the difference in surface area, the viscoelastic results of the two sizes of the nanosilica were comparable. This event may be due to both 7 and 14 nanoparticle sizes aggregates to the same flock size as shown in transmission electron microscopy (TEM).

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APPENDIX A

PROCEDURE TO ESTIMATE THE VOLUME PRACTION OF FUMED SILICA INTO POLYETHYLENE MELTS

Procedure to estimate the volume fraction of fumed silica into polyethylene melts

Weight/ Internal Mixer Batch (g) = 75 wt% Filled *Total Volume Chamber ($315\ cm^3$)*density of PE mass (g/cm^3) (A.1)

Table A.1 Density of polyethylene by ASTM D1505

Polyethylene	Density (g/cm^3)
L5	0.9190
L30	0.9160
H08	0.9540
H14	0.9580

Table A.2 Density of fumed silica

Nanosilica Size	Density (g/cm^3)
7 nm	0.0368
14 nm	0. 0368

Table A.3 Volume fraction and wt% of fumed silica filled L5

Weight per Batch (g)	L5		Fumed Silica				Total Volume (cm^3)	Φ %	wt%
			7 nm		14 nm				
	Weight (g)	Volume (cm^3)	Weight (g)	Volume (cm^3)	Weight (g)	Volume (cm^3)			
217.11	217.11	236.25	0.00	0.00	0.00	0.00	236.25	0.00	0.00
217.11	216.03	235.07	1.09	29.50	1.09	29.50	264.57	11.15	0.50
217.11	214.94	233.89	2.17	59.00	2.17	59.00	292.89	20.14	1.00
217.11	210.60	229.16	6.51	176.99	6.51	176.99	406.16	43.58	3.00
217.11	206.26	224.44	10.86	294.99	10.86	294.99	519.43	56.79	5.00
217.11	195.40	212.63	21.71	589.98	21.71	589.98	802.61	73.51	10.00

Table A.4 Volume fraction and wt% of fumed silica filled L30

Weight per Batch (g)	L30		Fumed Silica				Total Volume (cm^3)	Φ %	wt%
			7 nm		14 nm				
	Weight (g)	Volume (cm^3)	Weight (g)	Volume (cm^3)	Weight (g)	Volume (cm^3)			
216.41	216.41	236.25	0.00	0.00	0.00	0.00	236.25	0.00	0.00
216.41	215.32	235.07	1.08	29.40	1.08	29.40	264.47	11.12	0.50
216.41	214.24	233.89	2.16	58.81	2.16	58.81	292.69	20.09	1.00
216.41	209.91	229.16	6.49	176.42	6.49	176.42	405.58	43.50	3.00
216.41	205.58	224.44	10.82	294.03	10.82	294.03	518.47	56.71	5.00
216.41	194.76	212.63	21.64	588.06	21.64	588.06	800.68	73.44	10.00

Table A.5 Volume fraction and wt% of fumed silica filled H08

Weight per Batch (g)	H08		Fumed Silica				Total Volume (cm^3)	Φ %	wt%
			7 nm		14 nm				
	Weight (g)	Volume (cm^3)	Weight (g)	Volume (cm^3)	Weight (g)	Volume (cm^3)			
225.38	225.38	236.25	0.00	0.00	0.00	0.00	236.25	0.00	0.00
225.38	224.26	235.07	1.13	30.62	1.13	30.62	265.69	11.53	0.50
225.38	223.13	233.89	2.25	61.25	2.25	61.25	295.13	20.75	1.00
225.38	218.62	229.16	6.76	183.74	6.76	183.74	421.90	44.50	3.00
225.38	214.11	224.44	11.27	306.23	11.27	306.23	530.66	57.71	5.00
225.38	202.84	212.63	22.54	612.45	22.54	612.45	825.08	74.23	10.00

Table A.6 Volume fraction and wt% of fumed silica filled H14

Weight per Batch (g)	H14		Fumed Silica				Total Volume (cm^3)	Φ %	wt%
			7 nm		14 nm				
	Weight (g)	Volume (cm^3)	Weight (g)	Volume (cm^3)	Weight (g)	Volume (cm^3)			
226.33	226.33	236.25	0.00	0.00	0.00	0.00	236.25	0.00	0.00
226.33	225.20	235.07	1.13	30.75	1.13	30.75	265.82	11.57	0.50
226.33	224.06	233.89	2.26	61.50	2.26	61.50	295.39	20.82	1.00
226.33	219.54	229.16	6.79	184.51	6.79	184.51	413.67	44.60	3.00
226.33	215.01	224.44	11.32	307.51	11.32	307.51	513.95	57.81	5.00
226.33	203.69	212.63	22.63	615.02	22.63	615.02	827.65	74.31	10.00

APPENDIX B

PUBLICATION

Publication

Thanaman, R., and Deeprasertkul, C. (2012). Effect of molecular characteristics and silica nanoparticle on viscoelastic properties of filled polyethylene melts. In **Proceeding of Pure and Applied Chemistry International Conference** 2012 (pp 1140-1143). Chiangmai, Thailand.

EFFECT OF MOLECULAR CHARACTERISTICS AND SILICA NANOPARTICLES ON VISCOELASTIC PROPERTIES OF FILLED POLYETHYLENE MELTS

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Abstract: Nanosilica filled polyethylenes were prepared by melt processing. Effects of polymer chain structure (linear and branched) and molecular weight as well as nanoparticle size (7 and 14 nm) and content (0-10 wt%) on the viscoelastic properties of the filled melts were investigated. It was found that the presence of nanosilica increased the storage and loss moduli and complex viscosity of the polyethylene melts. At the nanosilica content ≥ 5 wt%, the filled polyethylene melts showed the solid-like behavior in the terminal (low frequecy) region. Regardless of the difference in surface area, the viscoelastic results of the two sizes of the nanosilica were comparable. In addition, both linear and branched chain structures showed no significant difference in the moduli of the filled melts even the branched chains have the slower molecular dynamics. Good dispersion at low nanosilica contents was confirmed by Transmission Electron Microscopy (TEM).

1. Introduction

Polymer nanocomposites has been one of the most widely used materials as it could provide high strength at relatively low filler contents compared to conventional composites. By adding nanofiller to polymers, a direct consequence is the change in the polymer rheology. A rheological study of molten polymer nanocomposites is important to assess their processability. Moreover, viscoelastic properties of nanocomposites in the molten state are generally useful to understand their structure–propertyrelationships. The filler–filler and filler–polymer interactions can strongly influence both linear and nonlinear viscoelastic responses. Melt rheology is thus useful for the investigation of the polymer nanocomposites.

Many previous works have shown that the presence of nanoparticles in polymer melts could either increase or decrease the viscosity [1-2]. The general behavior reported in the literature for oscillatory shear rheological measurements at low frequencies is that the linear rheological properties evolve from a liquid-like behavior to a solid-like behavior as the nanoparticle concentration increases. In the case of viscosity reduction which is not common, one of the proposed criteria is that the size of the particle should be comparable to or smaller than the polymer molecular size[3].

For nanocomposites, the size of the polymer is comparable to or larger than the particle size. With the filler size down to the order of nanometers it can lead to substantial difference in the rheological properties of filled melts as compared to that reinforced with micron sized particles. At similar filler contents, the nanoparticles greatly influence the properties of system more than microparticles because of their higher specific surface areas [4].

Besides nanoparticle content and size, the rheological properties also depend on the polymer matrix. Here the effect of polymer chain structure is focused as well as the effect of nanoparticles. High density (linear chain) and low density (branched chain) polyethylenes with two molecular weights were used. To investigate the effect of nanoparticle size and content, hydrophilic nanosilica (fumed silica) with the size of 7 and 14 nm added at 0-10 wt% were chosen.Linear viscoelastic properties of samples were investigatedbysmall amplitude oscillatory shear measurements.

2. Materials and Methods

2.1 Material

High density (H) and low density (L) polyethylenes were supplied by Thai Polyethylene Co.,Ltd. Their melt flow indices are listed in Table 1. Hydrophilic fumed silica (SiO_2) nanoparticles with an average size of 7 and 14 nm were used. Both were purchased from Aldrich.

2.2 Sample Preparation

An internal mixer (Haake Rheomix 600p) was employed to mix PE and silica using a rotor speed of 50 rpm at 160°C. Before mixing, nanosilica was dried in an oven at 70°C for 8 hours. Contents of fumed silica in the range of 0.5-10% by weight were used. The disk-like samples with a diameter of 25 mm for oscillatory shear measurement were prepared by compression molding (Lab tech engineering Co.,Ltd. model LP20-B).

2.3 Rheological Testing

Oscillatory shear measurements were performed using an AR-G2 rheometer. Measurements were carried out using parallel plate geometry at a temperature range of 120-200°C under nitrogen atmosphere. Frequency sweep with an angular frequency in range of 0.1-100 rad/sec at low strain of 2% was applied.

Table 1: Melt flow index (MFI), complex viscosity and characteristic time of polyethylenes used

PE	**MFI**(g/10min)	η_0^* (Pa.s)	τ_cx10^3 (s)
H08	0.8	27.32 x10^3	16.0
H14	14	2.62 x10^3	3.2[a]
L5	5	5.0 x10^3	25.0
L30	30	0.9x10^3	1.3

[a]: extrapolated data

2.4 TEM Sample Preparation and Testing

Transmission electron microscopy (TEM) was used to examine the filler dispersion. The samples were microtomed to thin sections (~ 130–150 nm) using the Ultramicrotome with a diamond knife at -80 °C. Sections were placed flat on a copper grid coated with carbon. The samples were then brought up to room temperature. TEM was performed on the *FEI Tecnai G^{2}20* (FEI Co., Eindhoven, Netherlands) with an accelerating voltage of 200 kV.

3. Resultsand Discussion

3.1 Rheology of polyethylene melts

The linear viscoelastic (LVE) results at various temperatures were shifted to 160°C by the WLF equation. Figure 1 shows a typical LVE behavior in the terminal region i.e. the moduli scale with angular frequency (ω) where G' ~ ω^2 and G" ~ ω^1. The angular frequency at which G' crosses over G", so-called thecrossover frequency (ω_c) is determined.

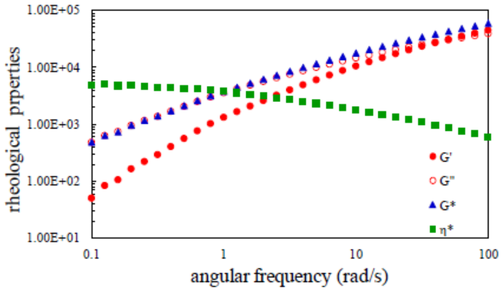

Figure 1. Typical LVE behavior in the terminal region of polymer melts (here is neat L5 at temperature of 160°C).

The characteristic time (τ_c) is then calculated from the inverse of ω_c, $\tau_c = 1/\omega_c$. This $\tau_c$can relate to the longest relaxation time of the polymer chain. In this work, the frequency range below and beyond $\omega_c$was considered the terminal region and rubbery region, respectively.

The master curve of storage and loss moduli as a function of frequency of these polyethylenes is presented in Figure 2. Only low density polyethylene melts could show the terminal behavior. The crossover frequency (ω_c) of these polyethylenes except H14 was obtained. Experimentally, H14 was solidified at low temperature before the crossover frequencycould be reached. The ω_c was thus extrapolated. The characteristic time (τ_c) was then calculated and also listed in Table 1. For the same chain structure the polyethylenes with the higher zero viscosity (i.e. higher molecular weight) showed longer τ_c. It means that H08 takes longer time to relax than H14, and L5 longer than L30.

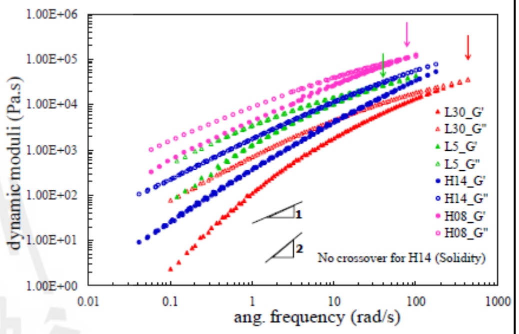

Figure 2.Master curve of dynamic moduli versus frequency of long-chain branched (L30 and L5) and linear (H14 and H08) polyethylenes at 160°C.

3.2 Rheology of fumed silica filled polyethylene melts

Figure 3 presents G' and G"moduli of the filled L5 melts. At low loadings, both moduli increased with increasing ω and in the low frequency region G" is larger than G', displaying the viscous nature.With increasing the filler loading, the moduli increased over the whole frequency range by which the increase was more pronounced in the low frequency region and in G' more than in G".It was also noticed that the crossover frequency (ω_c) was shifted to lower values, indicating an increase in the longest relaxation time. It could mean that the presence of fumed silica contributes to the elasticity of the polyethylene melts. At 10 wt% loading for L5, both G' and G" became almost frequency independent (log–log plot). Similar results were also obtained for H-08, H-14, and L-30 (not presented here).Generally, frequency-independent moduli are characteristic for solids and indicate that the polymer chain relaxation is slowed down and the chain reptation is stronglyrestrained [4].

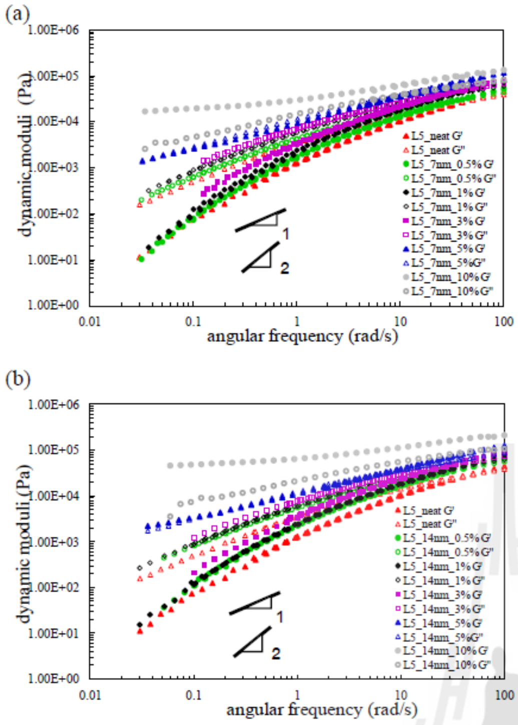

Figure 3.Storage and loss moduli of the fumed silica (a) 7 and (b) 14 nm filled L5 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160°C.

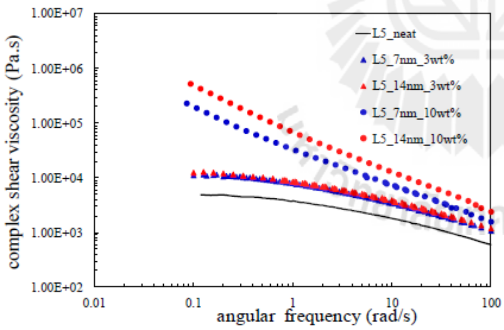

Figure 4.Complex viscosity versus frequency for 7 and 14 nm fumed silica filled L5 at 0, 3, and 10wt%

Besides the viscoelastic moduli, the complex viscosity of the neat and the filled L5 is plotted. Figure 4 displays the complex viscosity versus frequency at 3 and 10 wt% loadings.As shown, at low filler loading the samples show a frequency-independent behavior in the low frequency region, whereas at high loading the viscosity diverges. This diverge corresponds to the solid-like behavior observed in the storage modulus. Similar results were also obtained for L-30, H-08and H-14 (not presented here). In terms of the silica particle size, with the larger surface area smaller size should have more effect on the viscosity. However, the results were inconclusive that the viscosity was higher in the presence of 7-nm silica particles.

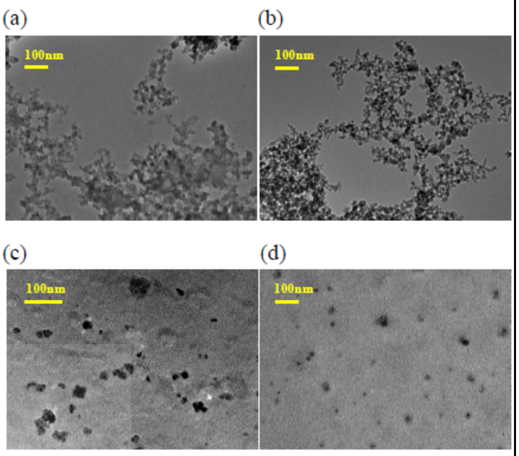

Figure 5. TEM images of (a) pure 7 nm, (b) pure 14 nm, (c) 0.5 wt% of 7nm filled H14, and (d) 1 wt% of 14 nm filled L5 at the scale bar of 100 nm.

Preliminary study on the dispersion of silica nanoparticles in polyethylenes was examined. TEM images of the fumed nanosilica 7 and 14nm (as obtained from evaporating the silica dispersion) and their filled L5 (0.5 wt%) and H14 (1 wt%) are shown in Figure 5. Relatively good dispersion was observed at the low loadings.

4. Conclusions

Typical linear viscoelastic behavior at low frequency was generally obtained for both linear and branched polyethylene melts. The branched structure though showed stronger viscosity-characteristic time relation as due to the additional mode of molecular relaxation. The addition of fumed silica to polyethylene increased bothstorage and loss moduli as well as complex viscosity especially at low-frequency. It suggests that silica nanoparticles influence the relaxation dynamics more than the plateau elastic modulus. The change from liquid-like behavior to solid-like behavior (independent of frequency) was observed at high loading (≥ 5 wt%). It indicates that in the presence of nanofillers at particular loading some reinforcing network must be formed. The 7 nm and 14 nm showed relatively the same behavior, implying that the filled melts may not differentiate these two sizes.

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BIOGRAPHY

Ms. Ratchanok Thanaman was born on September 2, 1981 in Khon Kaen, Thailand. She finished high school from Chumphae Suksa School in 2000. She attended Khonkaen University and graduated in 2004 with a Bachelor’s degree in Fodd Technology. She then continued her Master’s degree in Polymer Engineering at School of Polymer Engineering, Institute of Engineering, Suranaree University of Technology. During her graduate study, she got a research assistant scholarship from Suranaree University of Technology and Center of Excellence for Petroleum, Petrochemical, and Advanced Materials, Chulalongkorn University, Thailand. Her research was about fumed silica nanoparticle filled polyethylene melts. In the period of her study, she presented one poster presentation entitle: **“Effect of molecular characteristics and silica nanoparticles on viscoelastic properties of filled polyethylene melts”** at Pure and Applied Chemistry International Conference 2012 (PACCON 2012) in Chiang Mai, Thailand.