

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**INVESTIGATION OF FILM FORMING, OPTICAL AND ELECTRICAL
PROPERTIES OF AgNPs DOPED PS/AgNPs COMPOSITES**



M.Sc. THESIS

Can AKAOĞLU

Department of Physics Engineering

Physics Programme

JULY 2017

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Thesis Advisor: Assoc. Prof. Dr. Şaziye UĞUR

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**AgNPs KATKILI PS/AgNPs KOMPOZİTLERİNİN FİLM OLUŞTURMA,
OPTİKSEL VE ELEKTRİKSEL ÖZELLİKLERİNİN ARAŞTIRILMASI**

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To CÖYM group,



FOREWORD

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Can Akaoğlu
Physicist



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ABBREVIATIONS

P	: Pyrene
PS	: Polystyrene
Ag	: Silver
AgNPs	: Silver nanoparticles
PS/AgNPs	: Polystyrene/Silver nanoparticles
SSF	: Steady state fluorescence
UVV	: Photon transmission
FTRF	: Fast transient fluorescence
SEM	: Scanning electron microscope
PR	: Plasmon resonance
SPR	: Surface plasmon resonance
KPS	: Potassium persulfate
SDS	: Sodium dodecyl sulfate
GPC	: Gel permeation chromatography
DSC	: Differential scanning calorimeter
PVP	: Poly (vinyl pyrrolidone)
MEF	: Metal enhanced fluorescence



SYMBOLS

T_g	: Glass transition temperature
k_f	: Radiative transition constant
k_{nr}	: Nonradiative transition constant
I_0	: Uninfluenced light intensity
I	: Influenced light intensity
F	: Representation of a fluorescent molecule
F^*	: Excited state of fluorescent molecule
δ	: Delta Function
t	: Time
A_0	: Amplitude constant
τ_0	: Initial lifetime
k_q	: Quencher constant
$[Q]$	: Quencher concentration
D	: Diffusion coefficient
Δx	: Distance
π	: Pi number
N_A	: Avagadro's number
R	: Radius
r_0	: Initial radii of void
R_0	: Initial radii of particle
k_S	: Complex formation constant
k_m	: Quenching effect of metal
k_{fm}	: Enhancing effect of metal
ϕ_m	: Quantum yield near metallic surface
τ_m	: Lifetime value near metallic surface
η	: Viscosity
$\rho(r)$	: Relative density
ΔG	: Gibbs' free energy
h	: Planck's constant
V	: Molar volume
k	: Boltzmann's constant
ΔE	: Backbone activation energy
ΔH	: Viscos flow activation energy
T	: Temperature
ΔS	: Entropy
A	: Amplitude
T_r	: Tube renewal time
ν	: Frequency
$\sigma(t)$	: Total crossing density
$\sigma_1(t)$	: First contribution to crossing density
$\sigma_2(t)$	: Second contribution to crossing density
M_w	: Molecular weight

ρ_{Ag}	: Density of silver
ρ_{PVP}	: Density of poly (vinyl pyrrolodine)
ρ_{PS}	: Density of polystyrene
λ_{ex}	: Excitation wavelength
λ_{em}	: Emission wavelength
I_p	: Fluorescence intensity of pyrene
I_{tr}	: Transmittance intensity
$(I_{tr})_{\infty}$	: Transmitted light intensity at infinity
$(I_{tr})_m$	: Maximum transmitted light intensity
R_s	: Surface resistivity
σ	: Surface conductivity
T_0	: Minimum film formation temperature
T_h	: Healing temperature
T_e	: Fluorescence enhancement temperature
$I(t)$	: Time dependent light intensity
$\langle \tau \rangle$	: Mean lifetime
I_{enc}	: Enhanced fluorescence intensity
R	: Reptation frequency produced by photon transmission measurements
B	: Reptation frequency produced by lifetime measurements
n_{PS}	: Refractive indice of polystyrene
n_{PVP}	: Refractive indice of poly (vinyl pyrrolodine)
n_{Ag}	: Refractive indice of silver
n_{AgNPs}	: Refractive indice of silver nanoparticles
$^{\circ}C$	: Celcius degree
K	: Kelvin
m	: Meter
nm	: Nanometer
ml	: Mililiter
S	: Siemens
$kcal$	: Kilocalorie
R^2	: Coefficient of determination
V	: Volume
s	: Second
g	: Gram
γ	: Surface energy

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INVESTIGATION OF FILM FORMING, OPTICAL AND ELECTRICAL PROPERTIES OF AgNPs DOPED PS/AgNPs COMPOSITES

SUMMARY

In this study, film formation behavior of pyrene (P) labeled polystyrene (PS) based and silver nanoparticles (AgNPs) doped composite films were investigated by using two different film formation methods such as thermal annealing and exposing to solvent vapor. In order to understand the effects of mass fraction of AgNPs on film formation, nine different powder films were prepared by using drop casting method and each film contains different amount of AgNPs in the range of 0-50 wt%. All powder films were prepared at the room temperature.

In the first experiment, all of powder films were annealed at various temperatures between 100 °C and 250 °C with 10 °C temperature increment separately. After each annealing step, steady state fluorescence (SSF) technique, fast transient fluorescence (FTRF) technique and photon transmission (UVV) technique were used in order to monitor film formation process. The classical latex film formation is observed in the range of 0-30 wt% of AgNPs content. In this range, film transparencies are found between 40-85%. Above this range, instead of continuous films, partially film formation is seen and transparency of films decreased drastically with increasing AgNPs content. Fluorescence enhancement and reduced lifetime were also observed with increasing AgNPs content in the range of 3-20 wt% due to the interactions between the pyrenes and the electron plasma in nearby silver nanoparticles. Scanning electron microscope (SEM) images were also taken to compare optical data with film morphology. The SEM results is shown as compatible with the optical observations. Electrical conductivity of the films were also measured by using two probe method which is used to measure surface resistivities (R_s) of the films. The surface resistivity was converted into surface conductivity (σ) using the relation $\sigma(S)=1/R_s$ (Ω). It is seen that increasing AgNPs content did not alter so much the conductivities of the films. All films were determined as dielectric materials.

In the second experiment, seven different powder films including 0, 1, 5, 10, 20, 30, 50 wt% of AgNPs content were used in order to obtain continuous films by using chemical vapor deposition method. The film formation process were monitored by using FTRF and UVV techniques. It is seen that solvent vapor acts as a fluorescence quencher and successfully induce the latex film formation process. In the range of 0-20 wt% of AgNPs content, films were found transparent (above 85% transparency). Above this range, translucent films were obtained. It is observed that lifetime of P also decreased with increasing vapor exposure time. Thus, the quenching effect of organic solvent is verified due to FTRF data. Also reptation frequencies from UVV and FTRF data were calculated by using de Gennes' reptation model. For both techniques, reptation frequencies first decrease up to 10 wt% of AgNPS, then starts to increase. In order to support our optical data, a comparison were made between these results and the SEM images of the films. It is shown that the solvent vapor not only affects the film formation of the films, but also controls the morphology of the films. Above 10

wt% of AgNPs content, aggregations are seen on the film morphology. So that, instead of continuous film, partially film formation is observed above this ratio. This results were found consistent with the optical data according to behavior of reptation frequencies. Electrical conductivity of the films were also measured. Although the conductivity of composites were showed an increase of 3 orders of magnitude with increasing AgNPs content, the obtained films were found still as dielectric materials.

To sum up, the properties of composite films were compared according to their film formation methods. As it is clearly seen from experimental results, vapor exposed films were found more transparent than annealed films. Although the electrical conductivity of vapor exposed films were higher, all films were found as dielectric materials. According to SEM images, classical latex formation process is occurred for both experiments. The findings of first experiment potentially provide a new approach for studying the film formation process of metal doped polymer composites. In this respect, this work presents a simple and efficient method for modulating the emission intensities of luminescent plastics and for the next generation of smart fluorescent polymers. Second experiment also supported the effects of AgNPs on transparency, conductivity and morphology of the films. Both methods are cheap and easy to apply. It can be said that, these methods are also appropriate for industrial applications.

AgNPs KATKILI PS/AgNPs KOMPOZİTLERİNİN FİLM OLUŞTURMA, OPTİKSEL VE ELEKTRİKSEL ÖZELLİKLERİNİN ARAŞTIRILMASI

ÖZET

Bu çalışmada, piren (P) etiketli lateks polistiren (PS) bazlı, gümüş nanoparçacık (AgNPs) katkılı (PS/AgNPs) kompozitlerinden damlatma metoduyla oluşturulmuş filmlerin morfolojileri, elektriksel iletkenlikleri ve film oluşum süreçleri spektroskopik analizle incelendi. Film oluşum işlemi, termal tavlama ve organik çözücü buharı olmak üzere, iki farklı metot kullanılarak takip edildi. Ayrıca bu iki farklı metot ile elde edilmiş filmlerin karşılaştırması yapıldı.

Her iki deney için de öncelikle, emülsiyon polimerizasyonu ile hazırlanmış piren etiketli PS latekslerin, distile su (dH_2O) ile seyreltilerek stok çözelti içindeki dispersiyonu sağlandı. Daha sonra, stok çözelti kullanılarak, çeşitli oranlarda AgNPs eklendi. AgNPs'nın dışında bir kabuk olarak kaplı poly (vinil prolidon) (PVP) sayesinde, gümüş atomları da birbiri ile etkileşime girmeden sulu çözelti içinde kolayca dağılabilen bir formdaydı. Bu yüzden AgNPs'nın homojen dağılabilmesi için ekstradan bir yüzey aktif maddeye ihtiyaç kalmadan, sadece mekanik karıştırma ile stok çözelti içine dispersiyonu sağlandı. Farklı oranlarda elde edilen PS/AgNPs kompozit çözeltileri, damlatma metodu olarak bilinen ve basitçe, damlatılan yüzeyi özdeş çözelti damlalarıyla kaplamayı sağlayan yöntem ile cam plakalar üzerine damlatıldı. Cam plaka üzerindeki kompozit çözelti içindeki suyun buharlaşması için 1 gün beklendi. Su buharlaştıktan sonra lateks parçacıkların doğasından kaynaklı olarak toz filmler elde edildi. Her bir film için ayrı ayrı inceleme yapıldı.

İlk deneyde tavlama ile oluşturulmuş filmler elde edildi. Her bir film farklı oranlarda AgNPs katkısı içerecek şekilde, %0, %1, %3, %5, %10, %20, %30, %40 ve %50 AgNPs oranına sahip 9 farklı film hazırlandı. Kullanılan PS polimerinin camsı geçiş sıcaklığı (T_g) olan $105\text{ }^\circ\text{C}$ 'nin altındaki bir sıcaklıktan başlayarak ve sıcaklığı 10°ar 10°ar arttırarak $100\text{ }^\circ\text{C}$ 'den $280\text{ }^\circ\text{C}$ 'ye kadar kompozit filmler tavlandı. Her bir sıcaklık değeri için bu filmlerin, floresans ışık şiddeti, transparanlık ve floresans yaşamömrü ölçümleri alındı. Floresans ölçümleri için kararlı durum floresans (SSF), transparanlık ölçümleri için foton geçirkenlik (UVV) ve floresans yaşamömrü ölçümleri için hızlı zaman ayrışmalı floresans (FTRF) teknikleri kullanıldı. Bu ölçümler, $100\text{-}280\text{ }^\circ\text{C}$ aralığındaki her bir sıcaklık değeri için ayrı ayrı alındı ve minimum film oluşturma sıcaklığı (T_0), filmin kaynaşma sıcaklığı (T_h) ve floresans artış sıcaklığı (T_e) gibi parametreler her kompozit film için ayrı ayrı belirlendi. Metal yüzeylerin floresans şiddeti üzerine olası etkilerinden biri olan floresans artışı etkisi özellikle %3-20 aralığında AgNPs içerikli kompozit filmler için gözlemlendi. Floresans şiddeti (I_p) - sıcaklık grafiklerinde gümüş oranı arttıkça, floresans şiddetlerindeki Gaussiyenimsi davranışın yerini daha keskin piklerin aldığı gözlemlendi. Bir başka deyişle, bu grafiklerdeki pik noktalarına denk gelen sıcaklık noktasına (T_h) daha ani sıçramalar olduğu saptandı. Gümüş oranı arttıkça, I_p - sıcaklık grafikleri, saf PS film ile kıyaslandığında daralmaya başlamaktadır ve daha keskin pikler görülmektedir. Floresans artışı daha iyi gözlemleyebilmek için, floresans artışı (I_{enc}) - konsantrasyon

grafığı çizildi. Floresans artışı, gümüş katkılı filmlerin saf PS'den elde edilen filmlere göre floresans şiddetinin oranlanması ile elde edildi ($I_p/(I_p)_{\text{pure}}$). Özellikle filmlerin T_h değerlerine yakın olan 230 °C'de, %3-20 AgNPs katkılı filmlerin floresans şiddetlerinin, saf PS filme göre 2.5 ile 4 kat daha yüksek olduğu belirlendi. Her bir film ve her tavlama sıcaklığı için ayrı ayrı transparanlık ölçümleri alındı. Beklendiği gibi AgNPs katkısı arttıkça, film transparanlıklarında azalma gözlemlendi. Buna rağmen %0-10 AgNPs katkısı aralığındaki filmlerin transparanlık değerleri %50'nin üzerinde bulundu. Floresans yaşamömrü ölçümleri de yine her tavlama sıcaklığı için ayrı ayrı hesaplandı. Yaşamömrü değerlerinin belirli bir sıcaklığa kadar sabit kaldığı ve yüksek sıcaklıklarda düşüşe geçtiği gözlemlendi. Yaşamömrünün düşüşe geçmeye başladığı sıcaklığın (T_e), aynı zamanda floresans şiddetindeki artışın başladığı sıcaklığa denk geldiği saptandı. Bu durumda, metalik bir yüzey olan AgNPs'nin floresans artışına yol açtığı FTRF tekniği kullanılarak da desteklendi. Film oluşumuna teorik yaklaşım olarak boşluk kapanma (Void closure) ile kaynaşma ve interdifüzyon (Healing and interdiffusion) modelleri kullanıldı. Bu iki modelin teorik altyapısına uygun olacak şekilde deneysel sonuçlar değerlendirildi ve teoriyle ilişkili olan grafikler çizilerek yeni veriler elde edildi. Elde edilen verilerden, omurga (backbone) aktivasyon enerjisi ve viskoz akış aktivasyon enerjisi de her bir film için belirlendi. Özellikle %3-20 AgNPs katkılı filmlerin omurga aktivasyon enerjileri (ΔE) değerlerinin, floresans artışında 230°C'de gözlenen davranışın aynısını sergilediği görüldü. %3-10 arasında bu enerji değerleri yükselirken, %10'dan %20 ye geçerken yeniden azaldığı; fakat saf PS'ten elde edilmiş filme göre daha yüksek aktivasyon enerjisine sahip olduğu gözlemlendi. Ayrıca iki prop metodu kullanılarak her filmin elektriksel iletkenlikleri de ölçüldü. Kompozit filmlerin tümü, yükselen AgNPs içeriğine göre yaklaşık 4 kat artmasına rağmen, dielektrik malzeme olarak belirlendi. Taramalı elektron mikroskobu (SEM) görüntüleri alınarak, filmlerin morfolojileri de ayrı ayrı incelendi. Tavlanmamış, 200 °C'de tavlanmış ve 280 °C'de tavlanmış filmlerin görüntüleri kıyas yapılarak incelendi. Lateks polimerden elde edilmiş filmler, tavlanmamışken küresel parçacık olarak görünürken, 200 °C'de bu küresel formu kaybettiği ve 280 °C'de ise parçacık arası boşlukların tamamen kapandığı gözlemlendi. Özellikle %0-20 aralığı için düzgün ve sürekli film oluştuğu gözlemlendi. %20 AgNPs oranının üstündeki filmlerin morfolojilerinde yer yer AgNPs topaklanmaları gözlemlendi.

İkinci deneyde, film oluşturma metodu olarak çözücü buharı kullanıldı. Bu kez %0, %1, %5, %10, %20, %30 ve %50 olmak üzere 7 farklı AgNPs katkılı film hazırlandı. Hazırlanmış olan filmler bir kuartz küvetin içine dik bir şekilde tutturulup sabitlenerek ve küvete ayrıca PS için kuvvetli bir çözücü olan kloroform ve zayıf bir çözücü olan heptan organik çözümleri eşit oranlarda eklenerek deney düzeneği hazırlandı. Kimyasalların direkt olarak filme temas etmeden, sadece aynı küvetin içinde bulunarak, salınan kimyasal buharın film üzerine oluşturduğu etkiler incelendi. Eklenen kimyasalların buharlarının etkisiyle çözünen kompozitlerin film oluşum süreçleri foton geçirgenlik (UVV) ve floresans yaşamömrü (FTRF) ölçümleriyle takip edildi. UVV test sonuçlarına bağlı olarak, %0-20 AgNPs katkılı kompozit filmler %85'in üzerinde ışık geçirgenliğine sahip olarak transparan olarak belirlendi. %20'nin üzerindeki filmler ise %55 üzerinde bir ışık geçirgenliğine sahip olup, yarısaydam olarak belirlendi. Filmlerdeki AgNPs katkısı arttıkça, çözücü buharının da daha kısa sürede filmin içine difüz edip, filmlerin transparanlığındaki satürasyon değerine daha kısa sürede ulaşmasını sağladığı gözlemlendi. Yani, AgNPs oranı arttıkça, film oluşum hızında da artışlar görüldü. %1 AgNPs katkılı filmin transparanlığının satürasyon değerine yaklaşık 8 dakika ulaştığı gözlemlenirken, %50 AgNPs katkılı filmin sadece 2 dakikada bu değere ulaştığı gözlemlendi. Floresans yaşamömrü ölçümlerinde ise,

buhara maruz kalma süresi arttıkça ışık şiddetinde azalma görüldü. Bir başka deyişle, organik buhar filmin içine difuz ettikçe, floresans şiddetinde çok keskin bir düşüş yaşandı. Işık şiddetinin yanısıra, her bir filmde bulunan pirenin yaşamömrünün de düştüğü gözlemlendi. Dolayısıyla, çözücü kimyasalların hem yaşamömrünü hem de floresans şiddetini düşürerek, bir floresans sönmüleyici olarak davrandığı saptandı. Öte yandan optik geçirgenlik ve yaşamömrü deneylerinden elde edilen verilerle, de Gennes'in sürünge (reptation) modeline uygun olarak sürünme frekansları belirlendi. Yaşamömrü ölçümlerinin floresans sönmüleme teorik altyapısına uyarlanmasıyla B sürünme frekansları, optik geçirgenlik testlerinin sürünge modelinin teorik altyapısına uyarlanması ile R sürünme frekansları elde edildi. Bu frekans değerlerinin her iki deneyde de aynı davranışı göstererek %10' a kadar düşüş yaşadığı ve bu değerden sonra tekrar artmaya başladığı gözlemlendi. Artan frekans değerleri, %10'un üzerindeki değerler için AgNPs toplanmaları olduğunu göstermektedir. Buhara maruz kalmış her bir film için yine elektriksel iletkenlik ölçümü iki prop metoduyla alındı. Film oluşumu tamamlandıktan sonra alınan ölçümlere göre, filmlerin elektriksel iletkenlikleri 10^3 kat artmış olarak gözlemlendi. Buna rağmen, filmler yine de dielektrik malzeme olarak belirlendi. Film morfolojilerini incelemek için yine SEM görüntüleri analiz edildi. Yine bu metotta da, klasik lateks film oluşumunun başarıyla gerçekleştiği gözlemlendi. Sürünme frekanslarını destekleyici sonuç olarak, bu görüntülerde de %10'a kadar düzgün ve sürekli film görünürken, bu orandan sonrası için yer yer AgNPs toplanmaları gözlemlendi. AgNPs oranı arttıkça toplanmaların da ayrıca arttığı gözlemlendi. Bu toplanmalar, morfolojiye negatif bir etki yaratsa da, AgNPs'nin birbirine yaklaşması sonucu elektriksel iletkenliğin 10^3 mertebesinde artmasını açıklamaktadır.

Sonuç olarak, iki farklı deneysel çalışma ile elde edilmiş kompozit filmlerin, film oluşum süreçleri incelendi. Deneylerin birinde metalik yüzey etkisi ile floresans artışı gözlemlenirken, diğerinde buhar etkisiyle floresans sönmüleme gözlemlendi. Kimyasal buhar ile elde edilmiş filmlerin, tavlama ile elde edilmiş filmlere göre açıkça daha transparan olduğu görüldü. Buhar etkisi ile elde edilen filmlerde, %0-20 arası AgNPs katkısı aralığında transparenlik %105-92 arasında değişirken, yine aynı aralıkta tavlama ile elde edilen filmlerde transparenlik %44-85 arasında saptandı. Elektriksel iletkenlik olarak da yine kimyasal buhara maruz kalmış filmlerin daha iletken olduğu gözlemlense de, her iki deney ile elde edilmiş filmlerin dielektrik malzemeler oldukları belirlendi. Elektriksel iletkenlik artışının çok fazla olmamasının sonucunu AgNPs'nin çevresindeki PVP kabuğuna bağlamak mümkündür. Gümüş atomlarını küresel formda tutabilmek için kullanılan ve bir kabuk gibi gümüş çekirdeği çevreleyen PVP, gümüş atomlarının çevresinde bir yalıtkan gibi davranarak elektriksel iletkenliğin dielektrik sınırından çıkmasına engel olmuştur. Bunu desteklemek için saf gümüşten (%100 AgNPs) elde edilen filmin iletkenliği de ayrıca ölçülmüş olup, yine dielektrik malzeme olarak belirlenmiştir. Dolayısıyla, yalıtkan PVP polimeri ile kaplanan AgNPs'nin düşük iletkenlik değerleri büyük ölçüde PVP polimerinden kaynaklanmaktadır. Film morfolojileri için yapılan SEM analizlerine göre, iki yöntemde de klasik lateks film oluşumu gözlemlendi. Morfolojideki toplanmalar çözücü buharıyla elde edilmiş filmler için %10'luk AgNPs katkısından sonra başlarken, tavlama ile elde edilen filmlerde %20'den itibaren başladığı görüldü. Kullanılan ilk metodun, metal katkılı kompozit filmler için yeni bir bakış açısı niteliğinde olduğunu düşünmekteyiz. Emisyon şiddetine metal etkisi gözlemlendiğinden, gelecek jenerasyonlar için akıllı floresan (fluorescent) polimerler ve ışıldayan (luminescent) plastikler için, tavlama metodunun basit ve etkili bir metot olduğu sonucuna varıldı. İkinci deney sonuçlarından da, kimyasal buharın bir floresans sönmüleyici olarak davrandığı, ayrıca film oluşumunu

ve film morfolojisini doğrudan etkilendiđi gözlemlendi. İlk deneyi de destekleyici bir sonuç olarak, kompozitlerdeki AgNPs oranının, elektriksel iletkenliđi, film transparanlığını ve film morfolojisini etkilediđi açıkça görüldü. Her iki yöntemin de ucuz ve zahmetsiz olması, sanayide de kullanılabilir olduklarını gösterdi.



1. INTRODUCTION

Polymers are the complex structures which consist of numerous covalent bonded atoms or molecules. The first steps of polymer processing are started in 19th century with the discovery of polystyrene (PS) [1] and nowadays, polymers are widely used in various fields such as biotechnology, solar energy systems, automotive, packaging [2], drug delivery systems [3] and marine environment [4]. Polymers can be classified according to their derivation types into two groups: natural polymers and synthetic polymers. While natural polymer types famously include DNA, proteins, gelatin, cellulose and so on, synthetic polymer types include polyethylene, polypropylene, nylon etc. Due to their mechanical, physical or thermal properties, polymers can be stated in different forms such as tough, soft, rigid, flexible, rubbery or glassy in order to use in various fields. Also, these properties can be adjusted either after production or during the production of polymers by using additives or modifiers. On the other hand, these are not only the known methods which can either reinforce or adjust the properties of polymers.

Composites, which are consist of at least two different type of materials, also can be used in order to enhance the properties of materials. These different types of materials' physical or chemical characteristics should significantly differ [5] and also an interface occurs between two phases as a bonding surface [6]. These phases are called as reinforcing phase and matrix phase respectively [7]. Matrix phase can consist of polymers, metals, ceramics; furthermore reinforcing agents could be in the form of fibers, sheets or particles and they separately entrenched into matrix phase in order to obtain appropriate materials for various purposes. Reinforcing agents can improve mechanical properties such as strength [8] and stiffness, electrical conductivity [9], thermal stability and magnetic properties [10] of a composite. Polymer matrix which is the one type of three matrix elements of a composite is generally preferred to use due to its low weight, cheap cost, chemical resistance and ease of production [11,12]. Also, polymer matrix composites (PMC) can be manufactured with various methods such as hand lay-up, resin molding, compression molding, thermoplastic processing.

All methods have different advantages or disadvantages due to their fields of application in industry. Apart from micro-scaled structures, reinforcing agents could be in nanoscale and they are called as nano-composites.

Nanocomposites are defined as composite materials, but at least one dimension of composite should be in the range from 0.1 to 100 nm [13]. Usage of nanoparticles instead of macro particles is altered the physical properties of a composite. The most important dissimilarity between macrostructured and nanostructured materials is surface (interface) area per unit volume and nanostructured materials have larger area [14]. If the same composition is considered, nanocomposites which are lower-dimensional materials may have significantly different properties than larger-dimensional materials; because most of the chemical and physical interactions are carried out by surfaces and surface properties [15].

In the presence of all these information which are mentioned above, latex polymers are excellent materials considering their spherical shape and they are widely used in various fields such as paints, inks, coatings and drug delivery systems. Latexes can be defined as colloidal polymer particles which are dispersed in water [16]. They can be obtained by using emulsion polymerization which is a kind of radical polymerization and this polymerization generally starts with an emulsion incorporating water, monomer, and surfactant [17]. Evaporation of water causes to get the particles closer to each other. Thus, polymers in the form of latex are superior materials for thin film studies since they can be self-formed films after the evaporation of water at the room temperature. Latexes can be divided into two categories as hard and soft latexes depending on their glass transition temperature (T_g). T_g can be described as the minimum temperature value which mobilizes the polymer chains. While hard latexes have high T_g values, the T_g values of soft latexes are lower. The applications of latex polymers still keep their popularity particularly for adhesives and thin film studies.

In order to obtain more efficient materials, metal nanoparticles can be used as a reinforcing agent in composites due to its unique properties depending on their size, shape, and composition [18]. As a metal, silver nanoparticles (AgNPs) are used for various research areas such as photonics, microelectronics, biosensors and antimicrobial applications [19]. Apart from these properties, the effect of metals to the luminescence is still up to date research field due to collective response of electrons in metal nanoparticles to optical fields which is called as surface plasmon resonance

(SPR) [20]. Metal surfaces can be altered the fluorescence intensity of a fluorescent molecule due to photon induced oscillation of electron charge density [21]. This behavior of plasmonic nanoparticles still have unrevealed parts in literature and should be investigated further.

In this study, pyrene (P) doped polystyrene (PS) latexes were used as a polymer matrix and silver nanoparticles (AgNPs) was used as a reinforcing agent in order to obtain polystyrene/silver nanoparticles (PS/AgNPs) composites. By using drop casting method, powder films were obtained by these composites after evaporation of water at the room temperature. Obtained films were investigated by using two different film formation methods such as thermal annealing and exposing films to the organic solvent. In order to monitor film formation behavior of composites, spectroscopic methods such as steady state fluorescence (SSF) technique, fast transient fluorescence (FTRF) technique and photon transmission (UVV) measurements technique were used. Two different fluorescence alterations were observed. Fluorescence intensity enhancement was observed at annealing experiments due to SPR effect and fluorescence quenching was observed at organic solvent experiments due to quenching effect of solvent vapor. Electrical conductivity, transparency, and morphology of the films were investigated for both film formation methods. Advantages and disadvantages of the methods were discussed by making a comparison between two different experimental data.



2. BASIC CONCEPTS

2.1 Luminescence

Luminescence can be defined as the emission of light from any matter and it is occurred by exciting an atom electronically [22]. Luminescence can be divided into two categories: fluorescence and phosphorescence. These categories take their names off to the nature of excited states. According to quantum mechanics, when an atom is considered, the energy of an atom is quantized and every energy level has its own permitted energy value. Thus, if an electron transfer from higher energy level to lower energy level, a light which has the equal energy value between these two energy levels is emitted. Basically, if this transition is made from singlet excited state, it is called as fluorescence and if it is made from triplet excited state, it is called as phosphorescence. The main difference between these excited states is the spin orientation. In the case of fluorescence, spin orientation of paired electrons is opposite. However, this orientation is the same for phosphorescence. This also explains that in singlet state total spin is equal to zero and in triplet state total spin is equal to one.

In excited singlet states, electron which is existed in the excited orbital is paired to the second electron which is existed in the ground state orbital. A standard lifetime of fluorescence is about 10 nanoseconds. The fluorophore can be defined as a fluorescent molecule and that means it can re-emit the light after an excitation. Therefore, the lifetime of a standard fluorophore can be described as the average time between its excitation and its return to the ground state. Considering these short lifetimes, it can be concluded that studying time-resolved spectroscopy is more complicated since it needs more qualified optics and electronics. However, time-resolved emission gives more information about the molecules when it is compared with steady-state or stationary measurements.

In the case of phosphorescence, because of the same spin orientation that mentioned above, the transition is more complicated. According to Pauli exclusion principle, the electrons which have same spin orientation cannot be located in the same orbital. Thus,

the transitions are forbidden to ground state according to quantum mechanics. However, electron changes its spin to opposite sign in order to make this transition. Since the transitions are forbidden, the lifetime of phosphorescence is slower and in the range of a millisecond and a second.

Apart from these radiative transitions, nonradiative transitions between two electronic states could be occurred by the conversion of electronic energy to the vibrational energy. When a fluorophore is excited to the higher singlet level, generally it rapidly turns back to its first excited singlet state. These type of transitions are called as "internal conversions". The lifetimes of internal conversions are 10 picoseconds or less. Transitions could also be occurred between first excited singlet and lowest excited triplet states. This types of transitions are called as "intersystem crossing". Even if the fluorophore excited to higher energy levels (i.e third excited state), first of all, it will make an internal conversion to the first excited state. Fluorescence and intersystem crossing can merely start from first excited singlet state. Schematic representation of these transitions can be described well with Jablonski diagram (see Fig. 2.1).

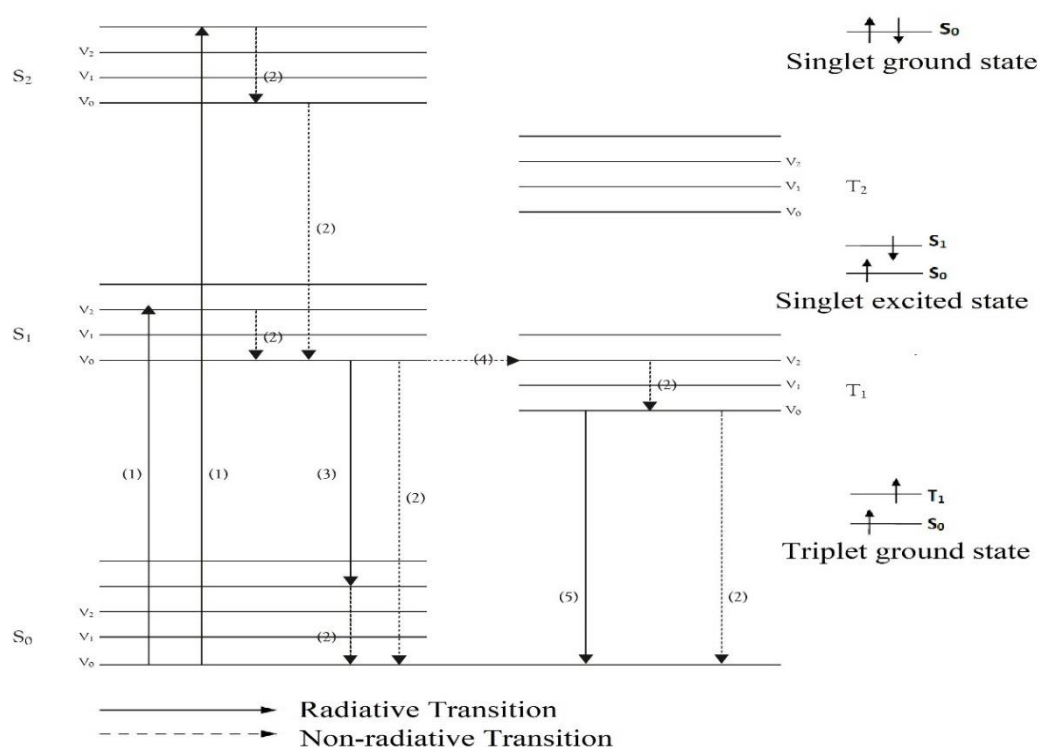
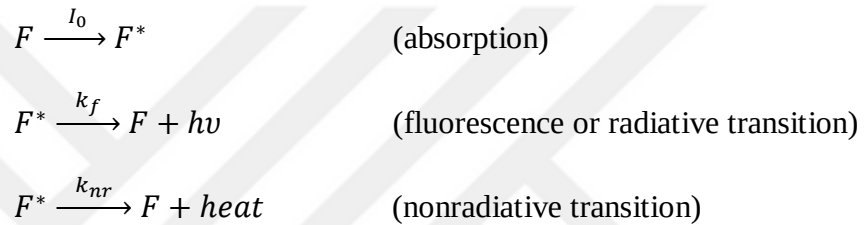


Figure 2.1 : Schematic representation of (1) absorption, (2) interval conversation , (3) fluorescence, (4) intersystem crossing, (5) phosphorescence transitions according to the Jablonski Diagram. (0,1,2,3...) subscripts represent the energy level of the state.

To sum up, if a transition occurs between the same degeneration level (i.e. from singlet to singlet), it is an internal conversion and if a transition occurs between two different degeneration type (i.e. from singlet to triplet), it is an intersystem crossing.

2.2 Steady State and Fast Transient Fluorescence Techniques

As it is defined in Luminescence section, the radiative transition of a fluorophore from singlet excited state to ground state is defined as the emission of fluorescence [22]. In order to obtain more stronger fluorescence, fluorophore should be excited at the peak wavelength of its absorption spectrum. When a fluorescent molecule is excited by the incident light intensity, I_0 , possible transitions can be shown as:



Here, F and F^* represent the fluorescent molecule and the form of its excited state, k_f and k_{nr} are constants which belong to the radiative and nonradiative transitions respectively. Thus, rate law can be written as:

$$\frac{d[F^*]}{dt} = I_0 - (k_f + k_{nr})[F^*] \quad (2.1)$$

In fluorescence experiments, the light is given to sample continuously by using generally a xenon lamp. Thus, we can conclude that the time change of F^* should be equal to zero since it is not time-dependent. Therefore, $I_0 = [F^*](k_f + k_{nr})$ is obtained. If we put this relation into fluorescence intensity (I_f), the following expression is obtained:

$$I_F = k_f[F^*] = I_0 \frac{k_f}{(k_f + k_{nr})} \quad (2.2)$$

Quantum yield which is the ratio of released photons per one excited molecule through fluorescence can be defined as:

$$\Phi_m = k_f / (k_f + k_{nr})$$

Apart from these conditions, if the light is given transient instead of continuously, the transient behavior of molecule can be observed. This type of excitation can be created by using a pulsed laser or a nanosecond flash lamp. The rate equation again can be used in order to define the transient condition by considering I_0 as a delta (δ) function since the incident light is discontinuous and instantaneous. If we express the rate equation as a function of time (t):

$$[F^*](t) = F_0 \exp[-(k_f + k_{nr})t] \quad (2.3)$$

Here, F_0 represents the concentration of F^* at $t=0$. Now, time dependent fluorescence intensity, $I_f(t)$ can be written as:

$$I_F(t) = k_f F_0 \exp[-(k_f + k_{nr})t] = A_0 \exp[-(k_f + k_{nr})t] \quad (2.4)$$

Where A_0 is constant. Generally, normal fluorescence decays obey to a single exponential function. Inverse of $(k_f + k_{nr})$ is defined as fluorescence lifetime τ_F and independent of incident and emitted light:

$$I_F(t) = A_0 \exp[-t/\tau_0] \quad (2.5)$$

Fluorescence behavior of a molecule changes depending on a solvent because of the alteration of polarity, viscosity, or both, of the microenvironment. Also, this behavior can be affected by the various variations such as temperature, pH, and concentration.

For example, certain fluorescent probes, such as pyrene [23,24], exhibit a dependence of their spectral characteristics upon the polarity of the medium in which they are dispersed. Both the steady state and transient fluorescence measurements of pyrene are given Fig. 2.2. Fig. 2.2 (a) shows the steady-state fluorescence spectrum of pyrene (P) excited at 345 nm. A microenvironmental change can induce a shift in the peak wavelength, a change in intensities of some vibronic peaks and a change in their ratios. The pyrene intensity ratio of peaks changes with an increase in polarity of the solvent. Thus, this ratio can be an effective tool as a probe to determine the polarity around a pyrene molecule. Figure 1b shows the time profile of pyrene fluorescence. The fluorescence at 395 nm is fitted to a single exponential function (see eq. 2.5) with a time constant of 200 ns. The lifetime of the excited state of a fluorescent probe is also sensitive both to the nature of the medium in which it is located and to the viscosity of

its local environment. In air-saturated dispersions, this dependence is accentuated since the viscosity of the microenvironment occupied by the fluor affects both the "intrinsic" radiationless deactivation processes of the excited singlet state and the diffusion rate of oxygen and other adventitious quenchers, present in the system. As described in the following section, the lifetime is shortened if other deactivation processes additionally take place from the excited state.

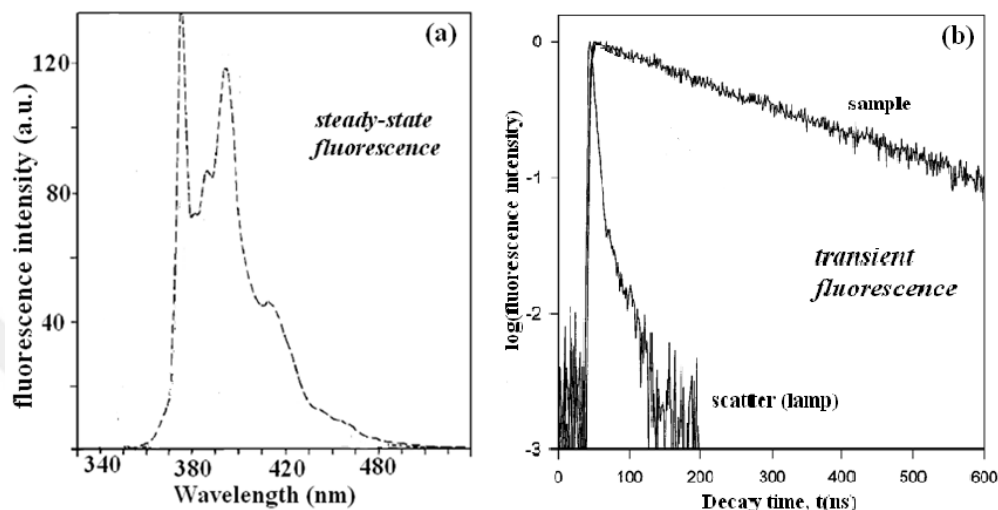
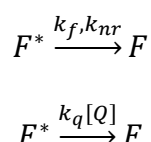


Figure 2.2 : (a) Fluorescence spectrum of pyrene (excitation wavelength: 345 nm). (b) Fluorescence decay curve of pyrene measured using Strobe Master Technique (SMS). The sharp peak represents the lamp of SMS.

2.3 Fluorescence Quenching

Fluorescence quenching can be expressed as the decrease of the fluorescence intensity of a sample because of the molecular interactions between the fluorophore and quencher [22]. These interactions could be excited-state reactions, molecular arrangement, energy transfer, ground-state complex formation and collisional (dynamic) quenching. Quenching can be shown as schematically:



Here F and F^* represent the fluorescent molecule and its excited form, k_f , k_{nr} , and k_q represent the fluorescence (radiative), nonradiative and quenching rate constants respectively and Q is the quencher. Although optical properties of the sample can be caused to quenching, this type of quenching is trivial and gives a little molecular information. If it is not be considered, there are two types of quenching: dynamic and

static quenching. Static quenching is generally a complex procedure and in case, diffusion does not occur (which is not our interest). However, it gives a significant information about binding between fluorescent molecule and quencher. Thus, it is also beneficial to give a brief information about the theory of static quenching. In spite of static quenching, in the case of dynamic quenching, diffusion occurs the whole time of the lifetime of the excited state and during this diffusion, the photochemical reaction such as emission of the photon is not observed. Oxygen is the most known quencher and many types of quenchers such as halogens, ethers, Iodide, Chloride have existed.

2.3.1 Dynamic quenching

Dynamic quenching is observed more frequently in the form of the liquid since the eye or quencher is able to move within the solution [22]. By considering this information, it can be said that the results of quenching are directly related to the volume and distance within the solution. The distance which is taken by quencher molecule during the lifetime of the fluorophore in the excited state is given by $\Delta x = \sqrt{(2D\tau)}$ where D is the diffusion coefficient.

If we write the quenching rate in terms of a single rate coefficient k_q , and the lifetime of F without quenching as τ_0 into the Stern-Volmer equation, the equation takes the form:

$$\tau^{-1} = \tau_0^{-1} + k_q[Q] \quad (2.6)$$

Where $[Q]$ represents the quencher concentration and k_q is given by:

$$k_q = 4\pi N_A D R x 10^{-3}$$

Here, D is sum of the diffusion coefficient that mentioned above, R represents the sum of their interaction radii and N_A is Avogadro's number. If we rewrite the eq. (2.6) with an another form:

$$\frac{\tau_0}{\tau} = 1 + k_q\tau_0[Q] \quad (2.7)$$

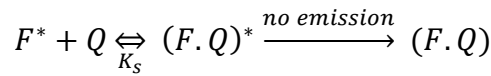
is obtained. If we use the useful relation between the light intensities and lifetimes, eq. 2.7 becomes:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_q\tau_0[Q] \quad (2.8)$$

where I_0 and I are the uninfluenced and influenced fluorescence intensities by the quencher, respectively.

2.3.2 Static quenching

Although static quenching is not applied in our experiments, it is valuable to be known as theoretically. Static quenching is a result of a nonfluorescent complex between the fluorophore and quencher. This mentioned complex absorbs the photon and instantly returns to its ground state without emission of this photon again. A static quenching can be shown as schemetically:



Again here F and F^* represent to the fluorescent molecule and its excited form and Q represents to quencher. K_s is the constant for complex formation and mathematically can be defined as:

$$K_s = \frac{[F - Q]}{[F][Q]} \quad (2.9)$$

where $[F-Q]$ is the concentration of the complex. Therefore, if we substitute total concentration of fluorophore as $[F_0] = [F] + [F - Q]$ and fluorescence intensities into equation (2.9)

$$\frac{I_0}{I} = 1 + K_s[Q] \quad (2.10)$$

is obtained. This expression is similar to Stern-Volmer equation. In order to distinguish static and dynamic quenching, temperature and fluorescence lifetimes play a crucial role. In the presence of increasing temperature, k_q values also increase. However, k_s values decrease as inversely proportional to the temperature. In addition to temperature behavior, fluorescence lifetime proportion of static quenching is equal to one ($\tau/\tau_0=1$) and constant. However, dynamic quenching is time-dependent process and changes by the fluorescence intensity ($\tau/\tau_0=I/I_0$).

2.4 Effects of Metal Surfaces on Fluorescence

When nanocomposites with noble metal nanoclusters are exposed to light, they exhibit a strong absorption maximum at a particular wavelength due to photon induced

oscillation of the electron charge density [21]. This collective response of electrons in metal nanoparticles to optical fields is called plasmon resonance (PR) or surface plasmon resonance (SPR) in the case of thin films [20]. The emission spectral properties of fluorescent species (fluorophores) can be dramatically altered by the presence of nearby metallic surfaces [25]. Three distinct observations can therefore be made for fluorophores in close proximity to metallic surfaces (or plasmonic nanoparticles) [26]:

- (1) quenching at short distances; when the fluorophores are close to the metallic surface ($<50 \text{ \AA}$), due to the reduced quantum yield the emission intensity of fluorophores will be decreased near the surface due to quenching [27]. The quenching results in increased photostability because the molecules spend less time in the excited state and thus have a fewer reactions. Since the lifetime of the fluorophores will be decreased, quenching by the surface is expected to result in increased stability and an increase in the number of excitation-deexcitation cycles prior to photodecomposition.
- (2) an increase in the excitation field; an increase in the excitation field will result in an increased emission intensity when compared to the sample with no metal, both observed for the same incident intensity [28]. The lifetimes will remain the same.
- (3) an increase in the radiative decay rate; the metal-induced increase in the radiative rate (or quantum yield) [29] will result in an increase in the fluorescence emission intensity and a reduction in the fluorescence lifetime. The spectral properties of the fluorophores are maintained.

The concept of modifying the radiative decay rate is unfamiliar to fluorescence spectroscopy. It is informative to consider the novel spectral effects expected by increasing the radiative rate [26]. Assume the presence of a nearby metal (m) surface increases the radiative rate by addition of a new rate k_{fm} (Fig. 2.3, bottom). For the present discussion we will not consider the quenching effects of the metal (k_m).

In this case the quantum yield and lifetime of the fluorophore near the metal surface are given by

$$\phi_m = (k_f + k_{fm}) / (k_f + k_{fm} + k_{nr}) \quad (2.11)$$

$$\tau_m = 1 / (k_f + k_{fm} + k_{nr}) \quad (2.12)$$

These equations result in unusual predictions for a fluorophore near a metal surface. As the value of k_{fm} increases, the quantum yield increases while the lifetime decreases. The effects of the rate k_{fm} are dramatically different from the effects of the rate-collisional quenching $k_q [Q]$. In the case of collisional quenching both the lifetimes and quantum yields decrease. The effects of metallic colloids which increase k_{fm} are dramatically different. In this case the lifetimes decrease but the quantum yields increase.

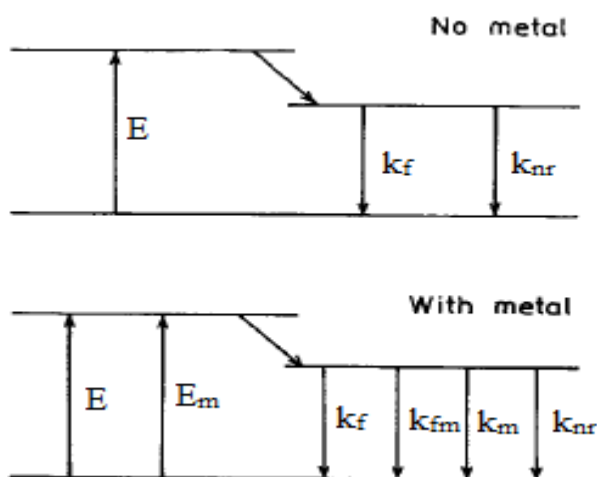


Figure 2.3 : Jablonski diagram without (top) and with (bottom) the effects of near metal surfaces. For distances over 50 Å the effect of quenching by the metal (k_m) is expected to be minimal [26].



3. THEORY

3.1 Film Formation Models

3.1.1 Void closure model

In the viscous form of polymers, dry converging of two particles which are in contact with each other were declared by Dillon et. al [30] for the first time. Shear stress which is occurred by surface tension of polymer is given rise to particle deformation and void closure between particles (i.e. polymer-air interfacial tension). Kinetics of void closure can be used in order to determine the elapsed time for optical clearness (transparency) and film formation [31]. The relation between the viscosity of nearby medium η and shrinkage of spherical voids of radius r can be given as [32]:

$$\frac{dr}{dt} = \frac{\gamma}{2\eta} \left(\frac{1}{\rho(r)} \right) \quad (3.1)$$

Here, γ is the surface energy, t is time and $\rho(r)$ is the relative density. According to eq. (3.1) it is clearly seen that the surface energy gives rise to decrement in void size. Also, $\rho(r)$ depends on the microstructural characteristics of the material including the number of voids, the initial size and packing. $\rho(r)$ can be defined as the proportion of voids to the total volume ratio of polymeric material. Whereas r comes close to zero, $\rho(r)$ increases too (never goes to infinity) and for larger r values $\rho(r)$ decreases. eq. (3.1) can be found almost identical to the equation which is used to define the time dependence of the lowest temperature to initiate the film formation during latex film formation process [33,34]. If we consider that viscosity is time-independent, then integration of eq. (3.1) gives the relation as:

$$t = \frac{2\eta}{\gamma} \int_{r_0}^r \rho(r) dr \quad (3.2)$$

Where r_0 is the initial void radius at the time $t=0$. The temperature dependence of the viscosity of polymer melt is influenced by the overcoming forces of macromolecular interaction. These forces give rise to the segments of polymer chain in order to jump

over from equilibrium position one to another. This process is occurred when the temperature is reached to the sufficient value in order to create adequate free volume largeness and is related with the overcoming of potential barrier. The height of this barrier represents the free energy of activation, ΔG , in the case of viscos flow. Activation energy can also be defined as the minimum amount of energy that can activate the atoms or molecules in order to initiate chemical transformation or physical transportation and it is one of the fundamentals of viscosity behavior. For temperature-dependent viscosity behavior, Frenkel-Eyring theory explains the following relation [35]:

$$\eta = \frac{N_0 h}{V} e^{\frac{\Delta G}{kT}} \quad (3.3)$$

Where N_0 is Avagadro's number, h is Planck's constant, V is molar volume and k is Boltzmann's constant. If we substitute Gibbs free energy ($\Delta G = \Delta H - (T \Delta S)$) which is the free energy amount of pure polymer-solvent mixture into eq. (3.3):

$$\eta = A e^{\frac{\Delta H}{kT}} \quad (3.4)$$

where ΔH is the activation energy of viscos flow, ΔS is the entropy of activation of viscos flow and T is temperature. Here, A is constant and it is also independent of temperature. If we combine this viscosity equation with eq. (3.2), following useful relation can be obtained:

$$t = -\frac{2A}{\gamma} e^{\frac{\Delta H}{kT}} \int_{r_0}^r \rho(r) dr \quad (3.5)$$

eq. (3.5) is generally used to understand the fluorescence and optical transmission data in order to explain void closure mechanism.

3.1.2 Healing and interdiffusion model

Reptation model [36] is generally used to explain the behavior of a polymer chain which is confined to a tube. The chain makes back-and-forth Brownian motion which can be explained as a random motion of particles in the gas or liquid. After they leave tube, ending points of the chain gains mobility to move in any direction. So that the initial tube position of the polymer chain is lost slowly. Besides, the Gaussian chain which is escaped from the initial tube is named as minor chain [37,38]. While the minor chain enlarges, the spherical envelope also grows as it is shown in Fig. 3.1 (a). The

completely escape time of the chain represents to $t = T_r$ and T_r is named as tube renewal time.

If we consider that the polymer chains are located in the latex particles, they have the interface that separates two particles by each other at $t=0$. In time, this particle-particle interface which is the boundary of these particles becomes narrower and then disappears. Because, the length of each minor chain increases and these chains go across the interface. This process is named as healing (see Fig. 3.1 (b)) and it can be divided into two stages. Firstly, the chains get broader and fill all the free volume between the particles because of the growth of minor chains. At this stage, the boundaries which is located at $t=0$ is vanished, the chains of different particles is not completely merged and particle-particle interfaces can still be distinguished. At second stage, interdiffusion of chains between adjacent particles cover all the particle-particle interface and this interface is no longer distinguishable.

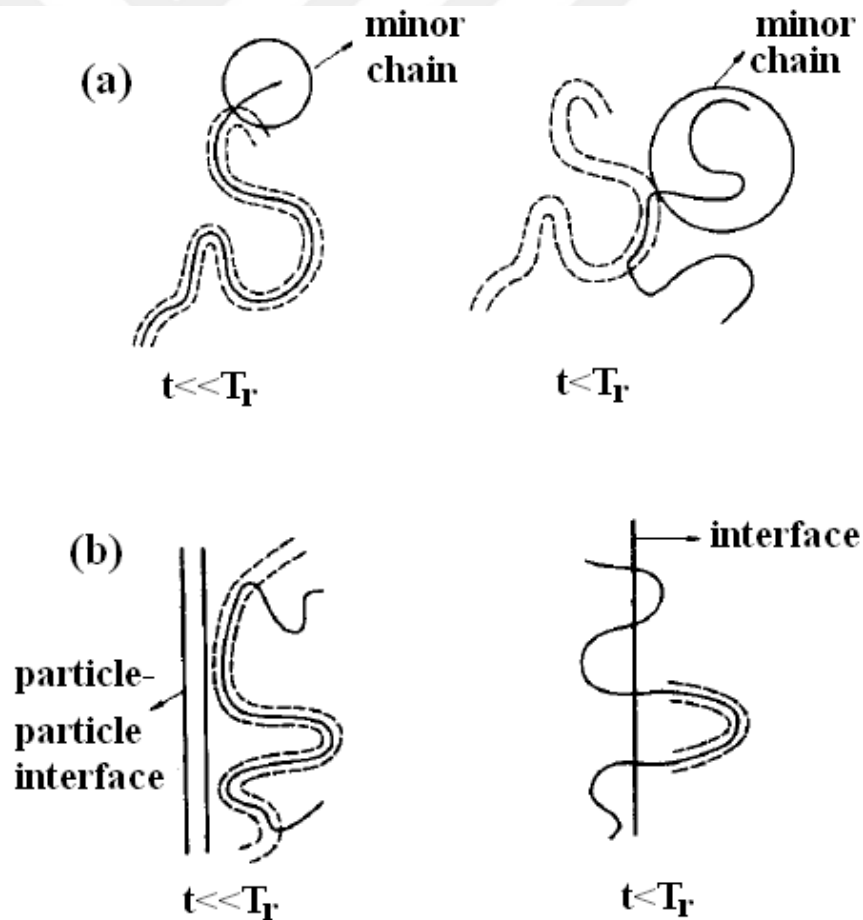


Figure 3.1 : Disengagement of a Gaussian chain from its initial tube in reptation model. (a) The emergence and growth of minor chains. (b) Healing at particle-particle junction due to growing of minor chains.

In Figure 3.1, T_r is the tube renewal time and dotted lines represent the tube created by the topological constraints imposed by the neighboring chains. Note that the particle-particle interface is initially rendered as a double line, to emphasize the existence of space between the particles. The interface, rendered as a single straight line, is now threaded by a number of minor chains from either side, but not yet completely healed.

Prager-Tirrell (PT) [39] used de Gennes's "reptation" model [36] to explain configurational relaxation at the polymer-polymer junction where each polymer chain is considered to be confined to a tube in which executes a random back and forth motion. A homopolymer chain with N freely jointed segments of length L was considered by PT, which moves back and forth by one segment with a frequency ν . In time the chain displaces down the tube by a number of segments, m . Here, $\nu/2$ is called the 'diffusion coefficient' of m in one dimensional motion. PT calculated the probability of the net displacement with m during the time t in the range of $m-\Delta$ to $m+(\Delta+d\Delta)$ segments. A Gaussian probability density was obtained for small times and large N . The total "crossing density" $\sigma(t)$ (chains per unit area) at junction surface then was calculated from the contributions $\sigma_1(t)$ due to chains still retaining some portion of their initial tubes, plus a remainder σ_2 i.e. contribution comes from chains which have relaxed at least once. σ_1 and σ_2 contributions to σ are presented in Fig. 3.1 at the interface. In terms of reduced time $\tau = 2\nu t / N^2$ the total crossing density can be written as:

$$\frac{\sigma(\tau)}{\sigma(\infty)} = 2\pi^{-1/2} \left[\tau^{1/2} + 2 \sum_{k=0}^{\infty} (-1)^k \left[\tau^{1/2} \exp\left(-\frac{k^2}{\tau}\right) - \pi^{-\frac{1}{2}} \text{erfc}(k/\tau^{1/2}) \right] \right] \quad (3.6)$$

where ν and N are the diffusion coefficient and number of freely jointed segment of polymer chain, n and k are the running indexes of the series. For small τ values the summation term of the above equation is very small and can be neglected, which then results in [37,39]:

$$\frac{\sigma(\tau)}{\sigma(\infty)} = 2\pi^{-1/2} \tau^{1/2} \quad (3.7)$$

This was predicted by de Gennes on the basis of scaling arguments.

4. EXPERIMENTAL

4.1 Materials

4.1.1 PS latex particles

Fluorescent polystyrene (PS) latexes were produced via an emulsion polymerization process [40]. The polymerization was performed batchwise using a thermostated reactor equipped with a condenser, thermocouple, mechanical stirring paddle, and nitrogen inlet. Water (50 ml), styrene monomer (3 g; 99 % pure from Janssen), and 0.014 g of fluorescent 1-pyrenylmethyl methacrylate (PolyFluor® 394) were first mixed in the polymerization reactor, where the temperature was kept constant (at 70 °C). The water-soluble radical initiator potassium persulfate (KPS) (1.6 % wt/wt over styrene) dissolved in a small amount of water (2 ml) was then introduced in order to induce styrene polymerization. The surfactant sodium dodecyl sulfate (SDS) (0.025 % wt/vol) were added to the polymerization recipe. The polymerization was conducted under agitation at 400 rpm for 12 h under a nitrogen atmosphere at 70 °C. The particle size was measured using a Malvern Instruments (Malvern, UK) Nano ZS and the mean diameter of these particles was found to be 349 nm. Fig. 4.1 (a) shows SEM image of PS latex produced for this study. The weight-average molecular weights (M_w) of individual PS chains were measured by gel permeation chromatography (GPC) and found to 2.66×10^5 g/mol. The glass transition temperatures (T_g) of the PS latexes were determined using a differential scanning calorimeter (DSC) and found to be around 105 °C.

4.1.2 Silver nanoparticles

Poly(vinyl pyrrolidone) (PVP) covered core-shell silver nanoparticles (AgNPs) of 95% purity (metal basis) were purchased from the SkySpring Nanomaterials, Inc. (Westhollow Dr, Houston, USA), in the powder form. These particles are composed of 25 wt% of Ag in the core and 75 wt% of PVP polymer in the shell and the average diameter of AgNPs is 15 nm. Fig. 4.1 (b) shows the SEM image of AgNPs used in this study.

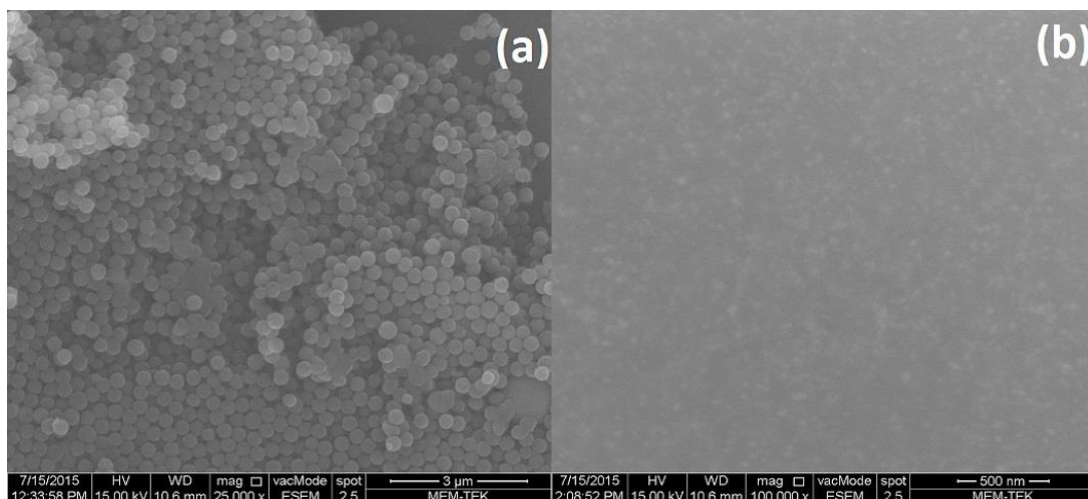


Figure 4.1 : SEM images of (a) PS latex and (b) AgNPs used in this study.

4.1.3 Preparation of PS/AgNPs composite films

Composite film preparation was carried out in the following manner: A stock solution of PS particles was prepared by diluting PS dispersion with DI water (10.1g/L) under mechanical stirring. The seven different PS latex/AgNPs dispersions were prepared by adding different amount of powder of AgNPs to PS latex dispersion. Further, these dispersions were magnetically stirred at least for 1h. Glass substrates which are 1 mm thick and $0.8 \times 2.5 \text{ cm}^2$ in size were washed in acetone and deionized water, then dried in oven. Each PS/AgNPs dispersion was subsequently coated onto the surface of the glass substrates by drop casting method and dried at the room temperature. After drying process, seven different PS/AgNPs powder films with 0, 1, 5, 10, 20, 30 and 50 wt% of AgNPs content were obtained. Film samples were weighted before and after the film casting to determine the film thickness. The thickness of the films was determined from the weight and the density of samples ($\rho_{\text{Ag}}=10.49 \text{ g.cm}^{-3}$, $\rho_{\text{PVP}}=1.2 \text{ g.cm}^{-3}$ and $\rho_{\text{PS}}=1.05 \text{ g.cm}^{-3}$) [41,42] and found to increase with increasing AgNPs content. Film thicknesses are given in the results and discussion section.

4.2 Measurements

4.2.1 Steady state fluorescence measurements

In order to obtain the data of fluorescence which belongs to the thermal annealing experiments, Perkin Elmer LS50 fluorescence spectrometer is used in this study and schematic representation of a typical fluorescence spectrometer is shown in Fig. 4.2. The spectrometer's detector is placed perpendicular to the arrival direction of the

excitation beam. As a excitation light, xenon lamp which can emit the light in the wide range of wavelength is used. In order to adjust the wavelength parameter of the emitted light, a excitation monochromator is located into the spectrometer. Another monochromator is located in front of the dedector to categorize the scattered light by the fluorescent sample with respect to its wavelengths. Fluorescence emission measurements are taken by keeping the excitation wavelength (λ_{ex}) constant. In this case, emission monochromator scans the emission intensities of corresponding wavelength of the light and the results are plotted by computer with respect to the wavelengths (x-axis) and intensities (y-axis). In addition, fluorescence excitation measurements are taken by keeping the exact emission wavelength (λ_{em}) of the emission dedector constant. This time, excitation monochromator scans the excitation values of the corresponding wavelengths.

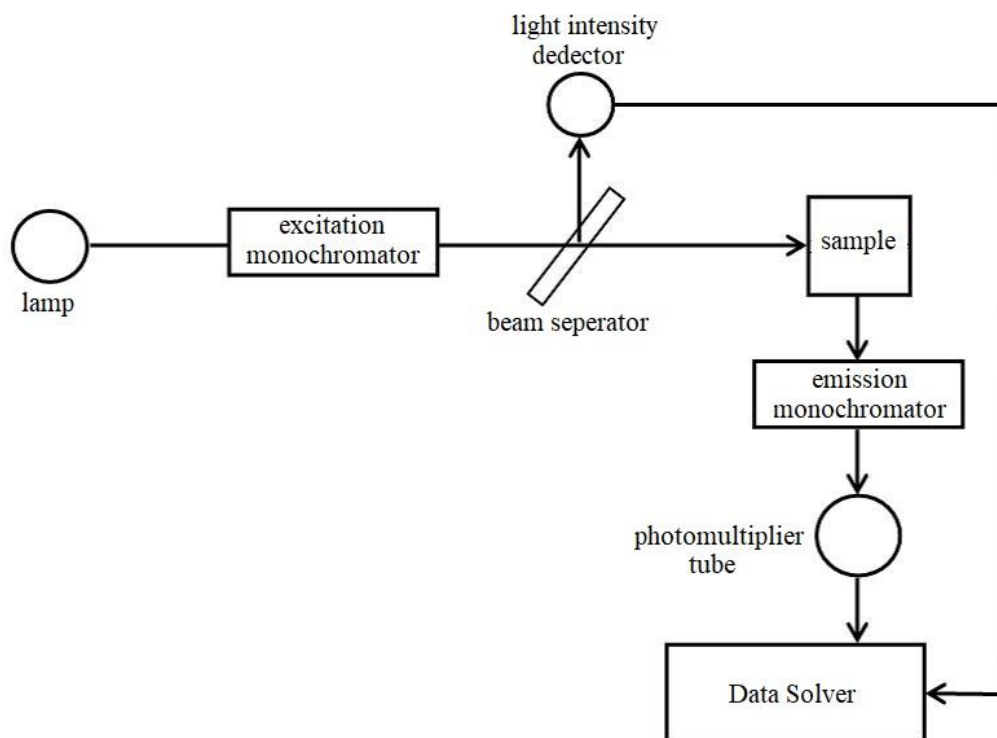


Figure 4.2 : Schematic representation of a typical fluorescence spectrometer.

Here, we performed two different experiments. In the first experiment, we studied film formation of PS/AgNPs composite films by thermal annealing. The powder films prepared in section 4.1.3 were annealed at various temperatures between 100°C-280°C for 10 min. After annealing, each sample was placed in the solid surface accessory of a Perkin-Elmer Model LS-50 fluorescence spectrometer. Pyrene (P) was excited at 345 nm and fluorescence emission were detected between 350–500 nm. Fluorescence

spectra were taken at 90° with respect to excitation light at room temperature. Slit widths were kept to provide the resolution of 5 nm during all SSF measurements. The sample position, incident (I_0), and emission (I_p) light intensities are shown in Fig. 4.3 (a). As it is mentioned in the section 5.1, Fig. 5.1 shows emission spectrum of pyrene excited with 345 nm excitation light (solid line). Excitation at 345 nm produces two emission maximum at 375nm and 395nm, respectively.

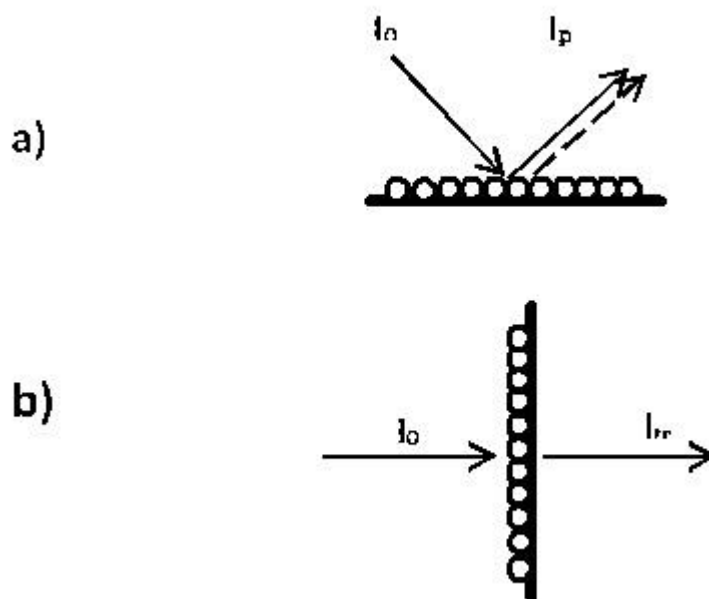


Figure 4.3 : Schematic illustration of sample position and (a) incident light (I_0), and P emission (I_p) intensities; (b) transmitted light intensity (I_{tr}).

4.2.2 Photon transmission (UVV) measurements

In order to measure optical transmission of PS/AgNPs composite films “Carry 100 Bio UV-Visible Spectrometer” is used and working principle of this spectrometer is shown in Fig. 4.4. In spectrometer, two different compartment which are used to place sample and reference composite films is found to obtain the transmission data. Incident light (I_0) which is arised from light source passes through the sample and reference and arrives to photodiode. Transmitted light (I_{tr}) can be monitored as a function of time or wavelength and the results are transferred to the computer which is connected to UV-VIS spectrometer.

Deuterium or halogen lamp can be used as lightsource and UV-VIS spectrometer can be used in the range of 190-1100 nm. In this case, Deuterium lamp is used for UV light region (190-326 nm) and halogen lamp is used for visible light region (326-1100 nm).

Plane mirror (P1) is used to block or unblock the light which is came from Deuterium lamp (DL). When P1 is activated, the light that comes from DL is blocked and give rise to reflect the light that comes from halogen lamp (HL) to toroidal mirror (T1). The light which is came from the light source is reflected by T2 and arrives to the monochromator by passing through the enterance slit (ES1). Monochromator reflects the light to the spherical mirror (S3). The reflected light beam from S3 comes to beam seperator (BS) and it is divided by BS into two equal beam parts. One half of the light beam reaches to P4 and another half reaches to P5. Here, P4 and P5 are both plane mirrors. These two mirrors reflect the light to the photodiodes and the data is transferred to computer.

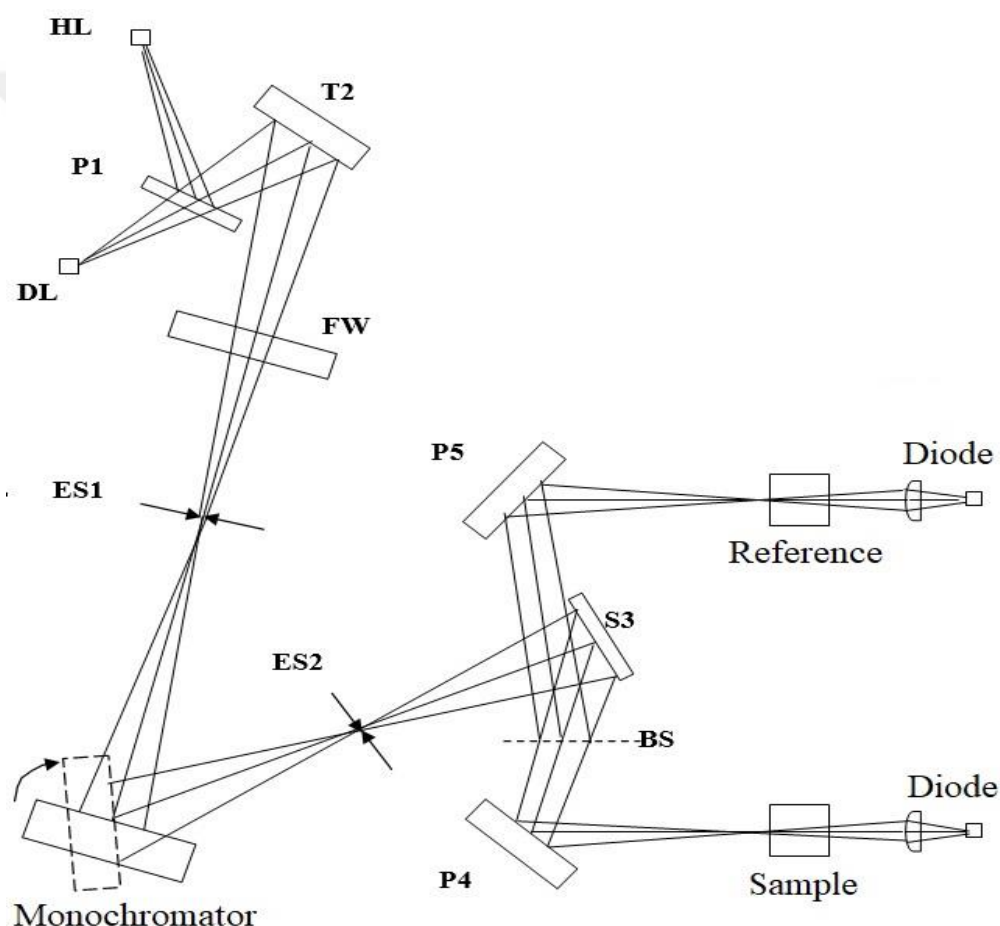


Figure 4.4 : Schematic representation of UV-VIS spectrometer used in this study.

Total transmittance data of sample is obtained from computer and it is calculated from difference of transmitted light intensities between sample and reference. In our experiments, glass plate is used as a layer which holds PS/AgNPs composite films in the powder form. So that, empty glass is taken as a reference during experiments and

as a result, the effects of glass plate on the transmitted light intensity data is eliminated by computer.

For all samples of thermal annealing experiments, the transmittances of the films were detected at 550 nm. A glass plate was used as a standard for all UVV experiments, and measurements were carried out at room temperature after each annealing processes together with fluorescence measurements, simultaneously. The sample position and the transmitted light intensity, I_{tr} , are presented in Fig. 4.3 (b). The absorption spectrum of AgNPs particles was also taken with UV-VIS spectrometer.

In the second experiment, this time the film formation of PS/AgNPs films, as prepared in section 4.1.3, was studied exposing the films to organic solvent vapor. For all samples of the chemical vapor deposition experiments, the transmittances of the films were detected at 600 nm. The sample position and the transmitted light intensity, I_{tr} , are presented in the section 5.2 (position 2). All measurements were done at the room temperature.

4.2.3 Fluorescence lifetime measurements

In this study, lifetime measurements are taken by using PTI Strobe Master Fluorescence Spectrometer (see Fig. 4.5). For this type of fluorescence spectrometer, nanoseconds

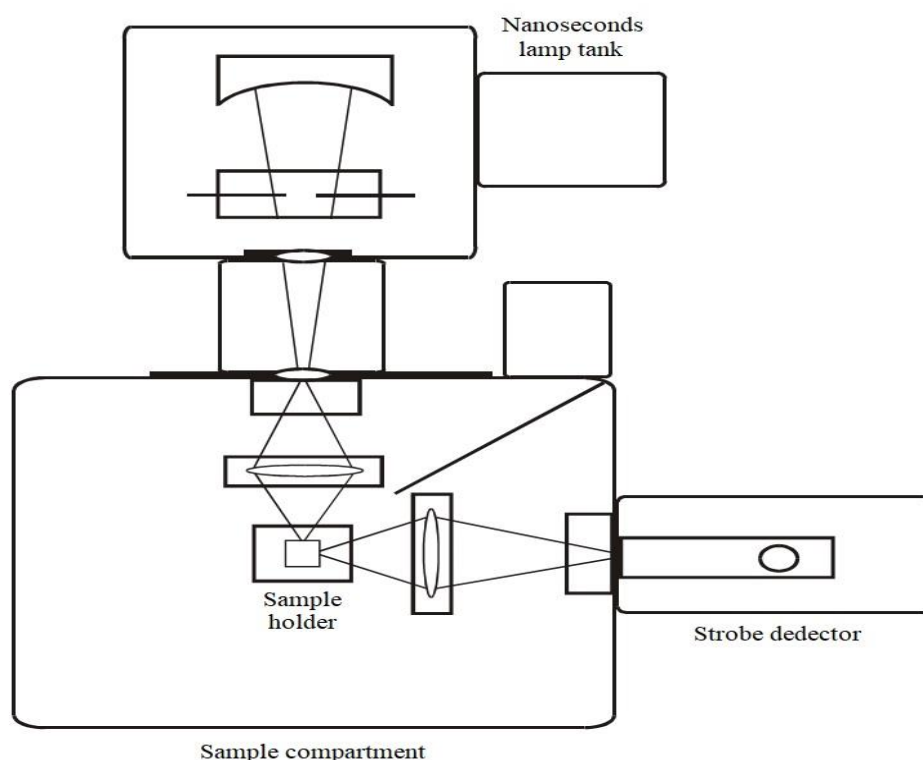
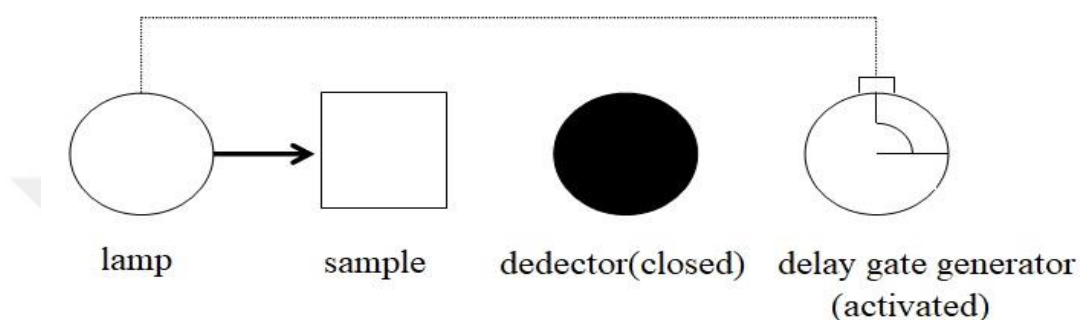
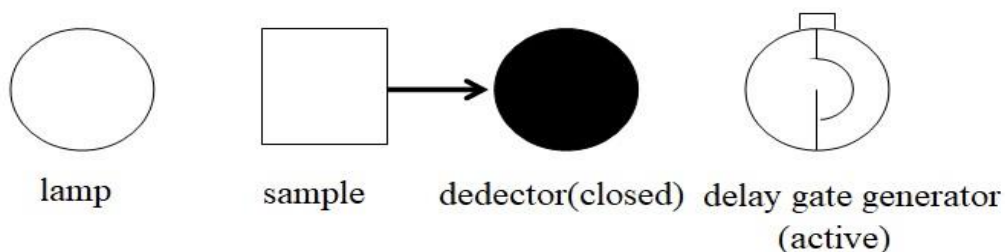


Figure 4.5 : Schematic representation of the FTRF spectrometer.

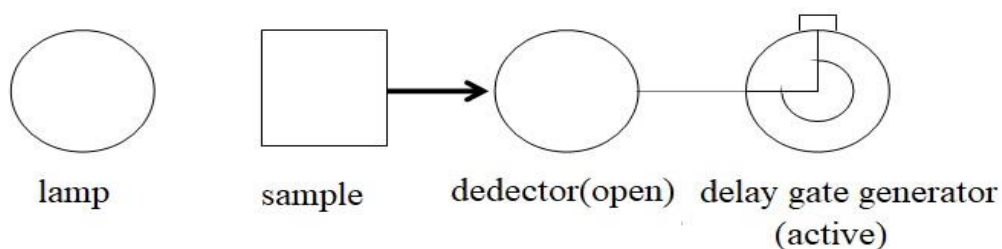
lamp is used in order to obtain excitation pulse. Excitation pulse is activated just for a very little time whereafter it is released. The detector is lost its fluorescence density merely when excitation pulse is activated. Activation time (or window of time) is controlled by a delay gate generator. The standard delay time which is used for our experiment system is 100 pikoseconds. Delay is increased with every pulse signal and by using this method, decay curves are obtained. Working mechanism of the fluorescence spectrometer can be divided into three stages which are shown in Fig. 4.6.



1. Lamp give rise to activate the delay gate generator.



2. Excited sample begins to emission and delay gate generator is still activated.



3. Delay gate generator activates the dedector and emmission intensity is obtained.

Figure 4.6 : Schematic demonstration of working princple of the FTRF spectrometer.

This procedure is in the loop and it is repeated constantly during the lifetime measurements. In every loop, delay gate generator increase the total time with 100

pikoseconds (0.1 ns) increment. Every pulse represent a data which gives the decay curve at the end of the measurements (see Fig. 4.7).

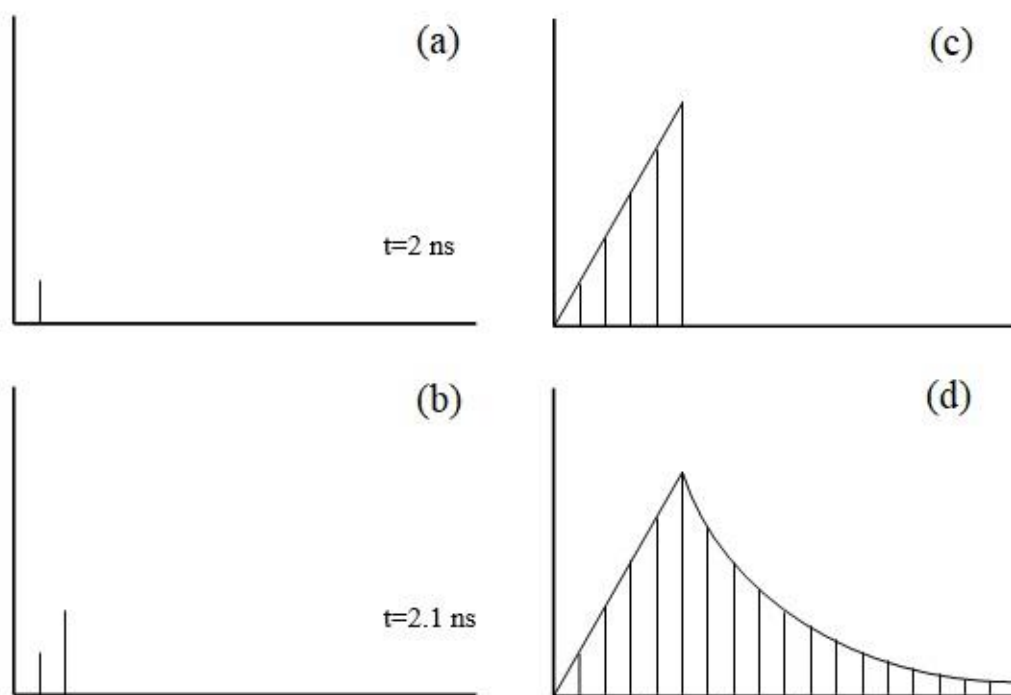


Figure 4.7 : Data view of the decay curves (a) after first pulse data is taken, (b) after second pulse data is taken, (c) after 10 pulse data is taken and (d) after all pulse data is taken by the computer.

For thermal annealing experiments, all the decay measurements were made at 90° position and slit widths were kept at 15 nm. Experiments were performed using a sample holder as given in Fig 4.3(a), which was placed in the SMS.

In vapor exposure experiment, samples were placed in a quartz cell which will be given in the next section with a solvent mixture composed of chloroform (as a good solvent for PS) and heptane (as a poor solvent for PS) at the bottom. In both experiments, film samples illuminated with 345 nm excitation light; pyrene fluorescence emission was detected at 375 nm. The fluorescence decay was collected over three decades of decay.

4.2.4 SEM measurements

Scanning electron micrographs (SEM) of the PS/AgNPs films were taken at 10–20 kV in a FEI QUANTA FEG 250 microscope in MEMTEK-ITU. A thin film of gold (10 nm) was sputtered onto the surface of samples using a Hummer-600 sputtering system to help image the PS/AgNPs films against the glass background.

4.2.5 Electrical conductivity measurements

Electrical conductivity was measured by a two-probe method using a Keithley Model 6517a Electrometer with an ultra high resistance meter. For the surface resistance measurements, the samples were coated onto thin rectangular glass slabs with typical dimensions of 2.5x2.5 cm². The electrical contact was made using a silver paste. Electrical resistivities of the composite films were measured by alternating polarity technique with electrometer and a test fixture. The composite films were placed in the test fixture, which has disk shaped electrodes, then their surface resistivities, R_s (Ω), were measured for 15 s under 100 V alternating potential. All the resistivities of the composite films were determined for four different orientations and measurements were repeated many times to lower the error level. The surface resistivity was converted into surface conductivity (σ) using the relation $\sigma(S)=1/R_s$ (Ω).



5. RESULTS AND DISCUSSIONS

5.1 Film Formation Process of PS/AgNPs Composites by Thermal Annealing

In our thermal annealing experiments, 9 different composite films including 0, 1, 3, 5, 10, 20, 30, 40 and 50 wt% of AgNPs content were prepared. All films are annealed from 100 °C to 280 °C with 10 °C temperature increment. As the methods of measurements are mentioned in the previous sections, fluorescence intensities, mean lifetimes and transparencies of films were determined for 19 different temperature values. Minimum film formation temperature (T_0), healing temperature (T_h), fluorescence enhancement temperature (T_e) of composites films were concluded. Viscos flow and backbone activation energies of composite films were also calculated from experimental data.

Metallic particles and colloids display characteristic absorption spectra due to electron oscillation induced by the incident light, which is called the surface plasmon resonance (SPR). The dispersions of silver nanoparticles display intense colors due to the plasmon resonance absorption. The surface of a metal is like plasma, having free electrons in the conduction band and positively charged nuclei. Surface plasmon resonance is a collective excitation of the electrons in the conduction band near the surface of the nanoparticles. Electrons are limited to specific vibrations modes by the particle's size and shape. Therefore, metallic nanoparticles have characteristic optical absorption spectra in the UV-Vis region [43]. The absorption spectrum of the AgNPs nanoparticles used in this study is shown in Fig. 5.1 (dashed line). The surface plasmon resonance wavelength value determined by the wavelength corresponding to the absorption maximum was 435 nm.

Fluorescence emission spectra of 0, 20 and 30 wt% of AgNPs content composite films annealed for 10 min at various temperatures are shown in Fig. 5.2, respectively. It is seen that the emission maximum is almost unchanged, the position and profile of the emission spectra do not vary indicating that no conformational changes of pyrene molecules occur under annealing and/or increasing AgNPs content. As the annealing

temperature is increased, fluorescence intensity, I_p from all film samples first increased and then decreased with increasing annealing temperatures. Here, it was interesting to notice that the emission spectra of pyrene become narrower when the AgNPs content was increased. The normalized emission and absorption spectra of both pure PS (solid line) and AgNPs (dashed line) films is given in Fig. 5.1.

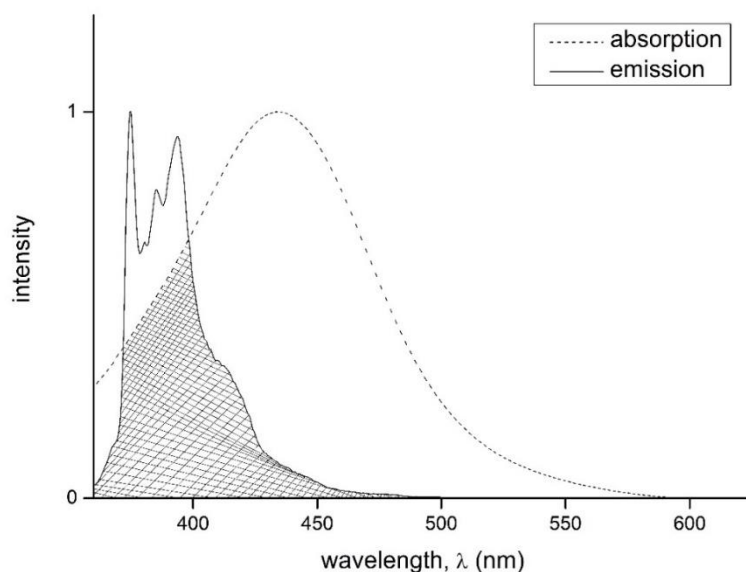


Figure 5.1 : Emission spectrum of pyrene (—) for 345 nm excitation light and absorption spectrum of AgNPs particles (....) used in this study.

It can be seen that pure PS film displays the characteristic emission spectrum of pyrene monomer appearing at 375nm and 395nm when excited at the excitation light of 345nm. Whereas, AgNPs film (no fluorescence is observed) shows a broad absorption band peaked at 435nm. From this figure, it is obvious that the emission spectrum of pyrene overlaps with the absorption band of AgNPs (see the shaded area in figure) meaning that the emission light of pyrene is absorbed by AgNPs, which is critical for resonant energy transfer. It is well known that resonant energy transfer can occur only where there is a spectral overlap between the emission spectrum of the donor (pyrene) and the absorption spectrum of the acceptor (AgNPs) and the relative orientations of the transition dipole moments are similar [44]. Since no spectral shifts in the fluorescence spectrum of the pyrene were observed with increasing AgNPs content, the film formation of PS/AgNPs composites were studied by measuring the fluorescence intensity of pyrene, I_p at 375 nm as a function of the annealing temperature.

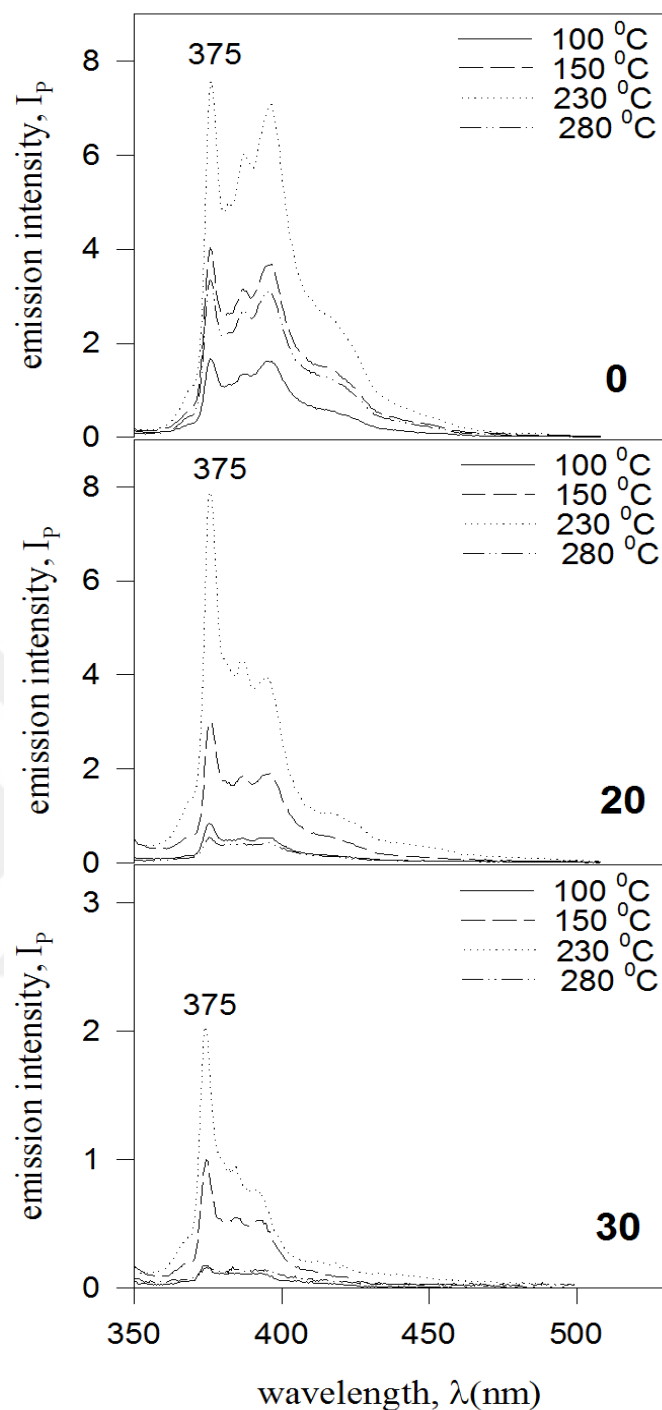


Figure 5.2 : Fluorescence emission spectra from PS/AgNPs composite films for 0, 20 and 30 wt% of AgNPs content after being annealed at various temperatures for 10 min. Numbers on each curve represent annealing temperatures.

Figures 5.3 and 5.4 illustrate the transmitted (I_{tr}) and fluorescence (I_p) light intensities versus annealing temperatures, T for 0, 1, 3, 5, 10, 20, 30, 40 and 50 wt% of AgNPs content films. I_{tr} and I_p data shown in this study were obtained from at least three independent data sets indicating that all experimental datas are identical and reproducible. For all film samples, upon annealing the transmitted light intensity I_{tr}

started to increase above a certain onset temperature which is known as the minimum film formation temperature, T_0 . It then reaches a plateau for all film samples (see Fig. 5.3).

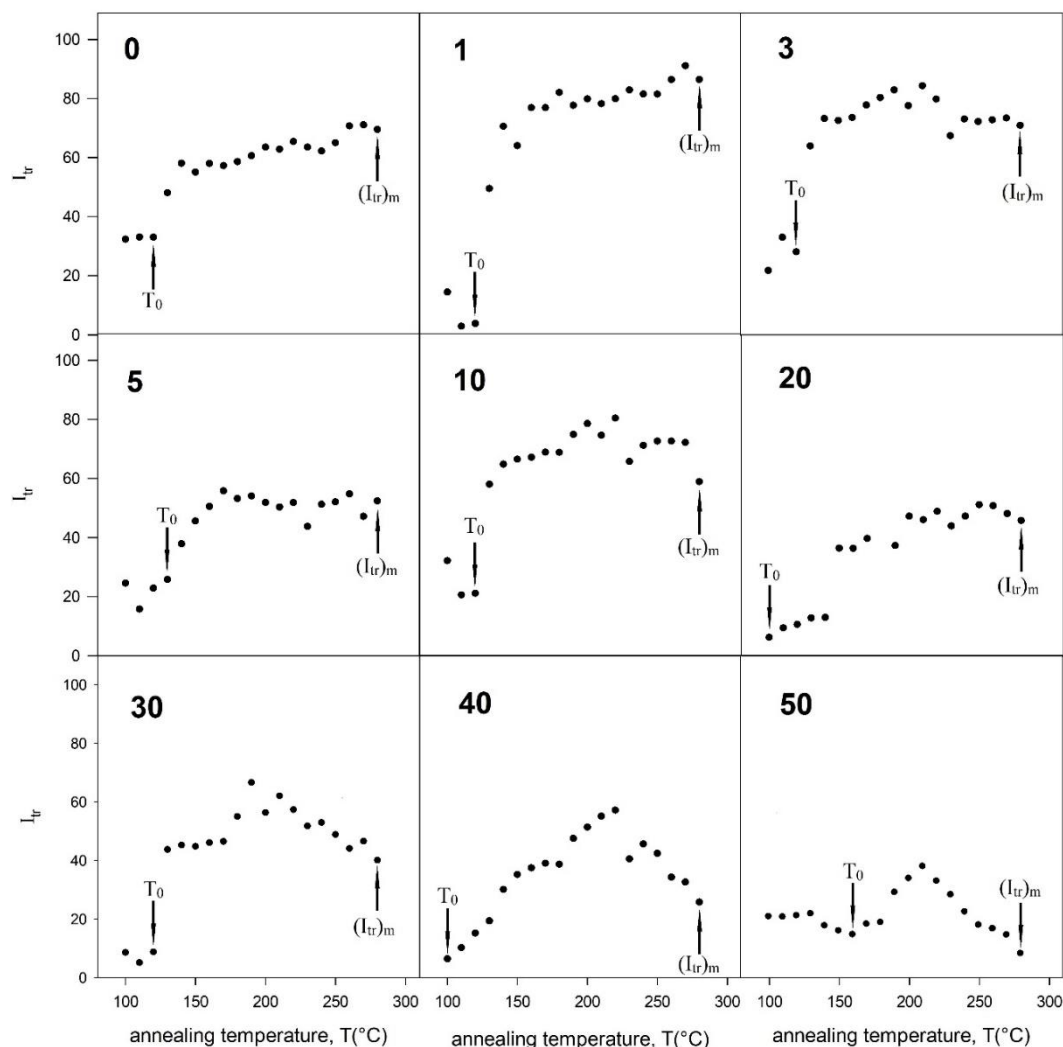


Figure 5.3 : Plots of I_{tr} versus annealing temperature for various AgNPs content films. Numbers on each curve represent AgNPs content in the film. Here, T_0 is the minimum film formation temperature.

As seen in Fig. 5.4, the fluorescence intensity, I_p , from composites with 0-40 wt% of AgNPs content first increased, reached a maximum, and then decreased as the annealing temperature increased [45-48]. The temperature at which I_p reached the maximum is the healing temperature, T_h . The increase in I_{tr} above T_0 can be explained through an evaluation of the transparency of the composite films upon annealing. Since we measured the transmittances of the films at 550 nm (above the absorption wavelength of both pyrene and AgNPs), the absorption of the films is negligible at this wavelength. Most probably, an increase in the I_{tr} in the visible region corresponds to

the void closure process [45]. Namely, the polystyrene starts to flow upon annealing process, and the voids between PS particles are then be filled due to the viscous flow. Further annealing at higher temperatures caused healing and interdiffusion processes [45-48], resulting in a more transparent film.

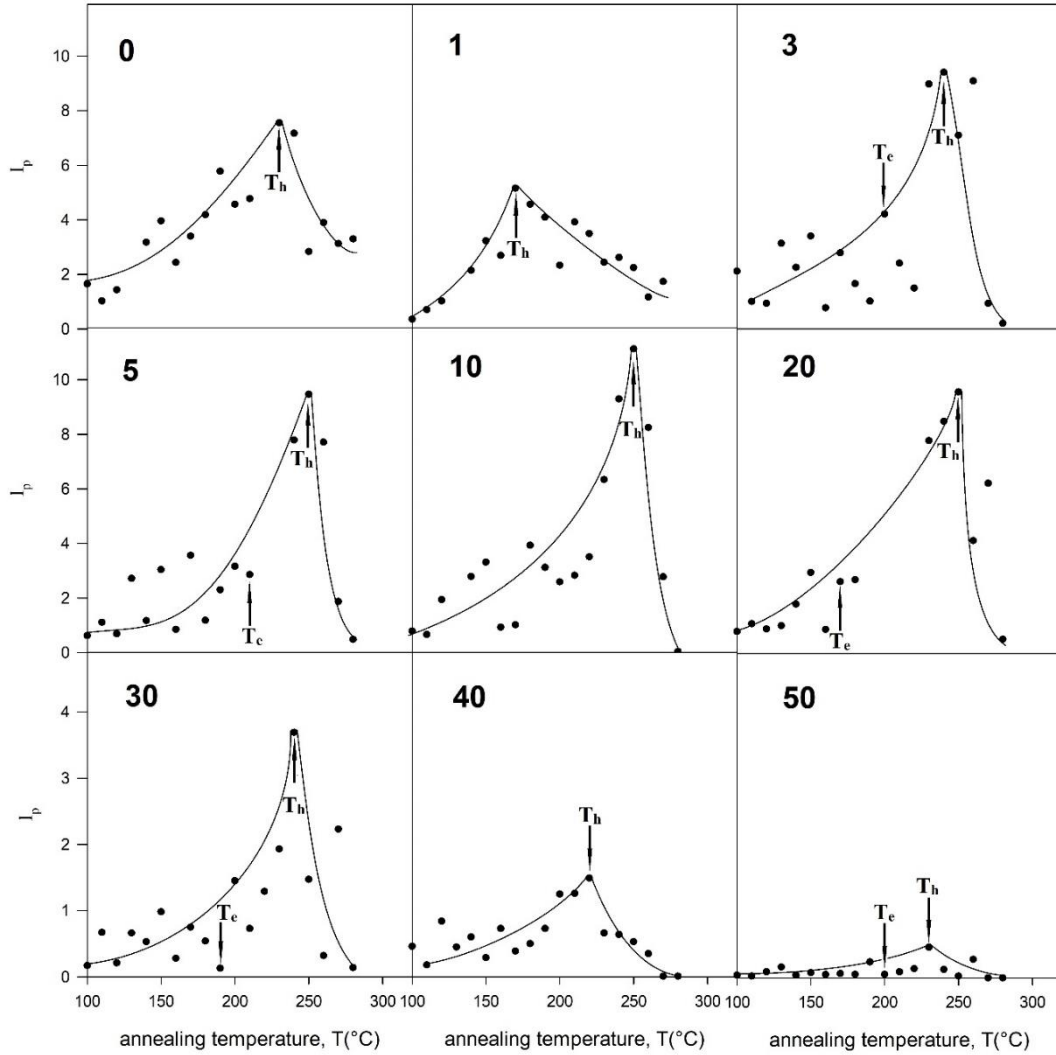


Figure 5.4 : Plots of I_P versus annealing temperature for various AgNPs content films. Numbers on each curve represent AgNPs content in the film. Here, T_h is the healing temperature.

On the other hand, the increase in I_P presumably corresponds to the void closure process up to the T_h point where the healing process takes place. The decrease in I_P above T_h can be understood as interdiffusion processes between the polymer chains [49]. However, I_P intensity from composite which has 50 wt% of AgNPs behave quite differently. In other words, I_P intensities from this composite is very weak and almost remain unchanged during annealing. This could be mainly attributed to the fluorescence quenching of pyrene by AgNPs and surface scattering of the films.

Because, as can be seen from Fig. 5.1, the emission of pyrene should be easily absorbed by AgNPs leading to fluorescence quenching at high AgNPs contents and also strong scattering from the AgNPs aggregations as can be seen from SEM images in the next section.

It was noted that both the emission spectrum and I_P curves of composite films became narrower relative to the pure PS film (see Figs. 5.2 and 5.4) when the AgNPs content was increased. Here we believe in that the narrowed emission may be due to coupling of the emission light from pyrenes (labeled to PS chain) with the metal plasmon from the silver (Ag) core of AgNPs [26,50,51]. As seen in Fig. 5.4, for 1 wt% of AgNPs content film, the coupling is weak so the narrowness is not obvious while this effect is more pronounced for 3-30 wt% of AgNPs content films. Moreover, from Fig. 5.4., the fluorescence emission intensity is seen to enhance with an increase of AgNPs content in the range of 3-20 wt%. Lifetime measurements in the next section support the coupling mechanism between the pyrene and AgNPs metal core and the enhancement in I_P . The lifetime of pyrene became shorter with an increase of AgNPs, supporting our prediction that the fluorescence enhancement occurs through an increase of the intrinsic decay rate for the pyrene near the metal surface (see Fig. 5.8). Therefore, the considerable narrowing of the emission spectra can be understood as a consequence of the resonance character of the lifetime reduction in dependence on emission wavelength [26,50,51].

On the other hand, to see the effect of AgNPs content on the optical transmission of the composite films, I_{tr} values of composites at 280 °C, $(I_{tr})_m$, (see Fig. 5.3) were plotted versus AgNPs content in Fig 5.5. As seen in Fig 5.5, $(I_{tr})_m$ first decreases exponentially up to 30 wt% of AgNPs content, then decreases linearly with increasing AgNPs content. The decrease of $(I_{tr})_m$ indicates that AgNPs increases the interface scattering, which results in a significant decrease of transmission at the visible region for AgNPs content above 30 wt%. Based on this, we can conclude that the inclusion of AgNPs has significant effect on the optical transmission of composite films.

In the light of these results, the behavior of I_P for composite films with AgNPs content above 40 wt% can be explained with the schematic picture in Fig 5.6. In Fig. 5.6 (a), at the early stage of film formation the powder film possesses many voids which results in short mean free (λ) and optical (s) paths of a photon. At this stage most of the light is scattered (I_{sc}) from the surface of the film, which yields low I_P . Since pyrene

molecules are isolated and far from the AgNPs, their photophysical properties are similar to pyrenes in the absence of AgNPs. Thus, the emission occurs only from pyrene molecules far from the AgNPs with constant fluorescence lifetime.

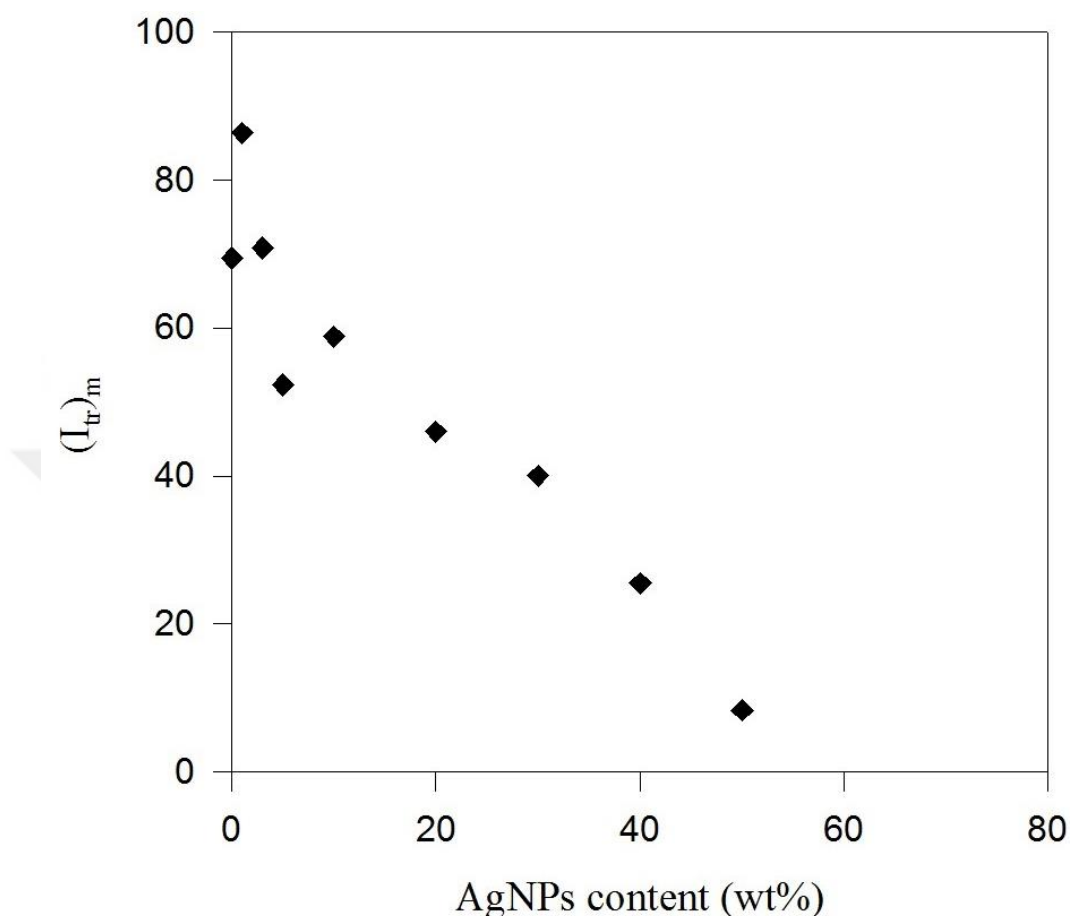


Figure 5.5 : Plot of the maxima of transmitted light intensities, $(I_{tr})_m$ versus AgNPs content.

Figure 5.6 (b) presents a film in which, interparticle voids are disappeared due to annealing and pyrene emission started to increase, which give rise to a long mean free $\langle a \rangle$ and long optical (s) paths. As soon as the voids are filled, the healing process takes place and $\langle a \rangle$ and s become longer than before. Pyrenes become closer to the surface of AgNPs due to annealing which is very important for surface-enhanced fluorescence [52]. As a result, an enhanced absorption and coupling to plasmons facilitates metal-enhanced pyrene fluorescence as well as a greater photostability and a shorter lifetime. Thus, pyrenes both far from the AgNPs and near to AgNPs contribute to the fluorescence intensity and I_p reaches its maximum value where scattered light, I_{sc} substantially decreases. Then because of further annealing, interdiffusion process takes place (see Figure 5.6 (c)) and AgNPs particles are fully mixed with pyrenes and remain imbedded in the polymer film. As a result, distance

between pyrenes and AgNPs particles decreases which leads to the quenching of pyrenes with shorter lifetimes, therefore I_P intensity decreases further with annealing. Finally, film becomes a fully transparent film with longest $\langle a \rangle$ but shorter s values. This film has low I_P and I_{sc} intensities. This picture can not be observed for the film with 50 wt% of AgNPs content. Because, in addition to the quenching of pyrenes by AgNPs content, the high opacity of the film blocks the journey of the photon in the film and prevents fluorescence emission. Thus, the fluorescence method cannot be applied to study film formation process above 50 wt% of AgNPs content.

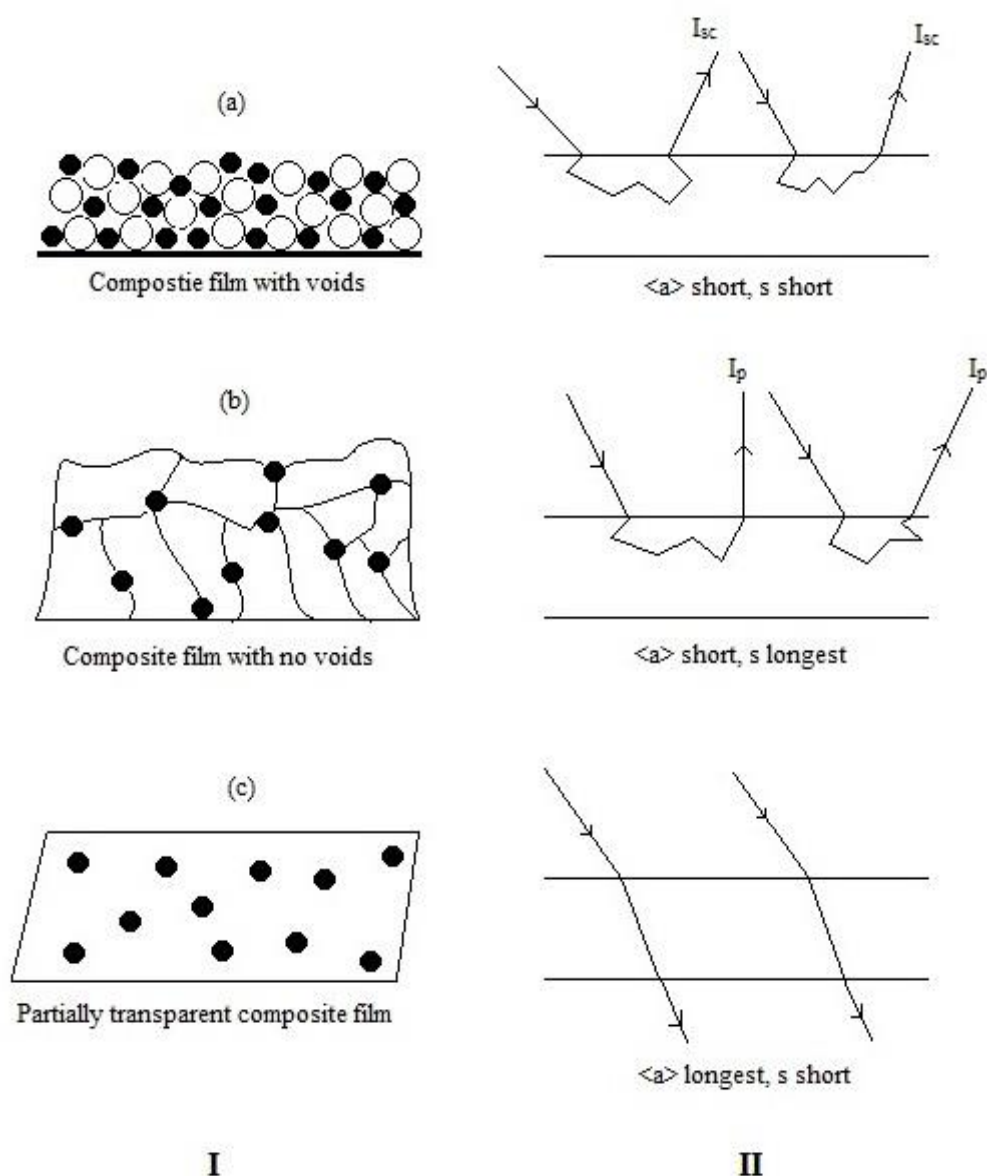


Figure 5.6 : Cartoon representation of PS/AgNPs composite films at several annealing steps. (a) Film possesses many voids that results in very low I_P and I_{tr} , (b) interparticle voids disappear due to annealing, I_P reaches its maximum value, and (c) transparent film with no voids but some AgNPs background and has low I_P but high I_{tr} .

5.1.1 Void closure

In order to quantify the behavior of I_{tr} above T_0 and I_p below T_h in Figs. 5.3 and 5.4, we can apply the phenomenological void closure model given in the section 3.1.1. Equation 3.5 can be employed by assuming that the interparticle voids are equal in size and the number of voids stays constant during film formation (i.e. $\rho(r) \approx r^{-3}$). Then integration of equation 3.5 gives the relation:

$$t = \frac{2AC}{\gamma} \exp\left(\frac{\Delta H}{kT}\right) \left(\frac{1}{r^2} - \frac{1}{r_0^2}\right) \quad (5.1)$$

Where C is a constant related to relative density $\rho(r)$. As stated before, a decrease in void size (r) causes an increase in I_p . If the assumption is made that I_p is inversely proportional to the 6th power of void radius, r , then equation 5.1 can be written as:

$$t = \frac{2AC}{\gamma} \exp\left(\frac{\Delta H}{kT}\right) \left(I^{\frac{1}{3}}\right) \quad (5.2)$$

Here, r_0^{-2} is omitted from the relation since it is very small compared to the r^{-2} values after the void closure processes is started. eq. 5.2 can be solved for I_p and I_{tr} ($=I$) to interpret the results in Figs 5.3 and 5.4 as:

$$I_{tr}(T) = S(t) \exp\left(-\frac{3\Delta H}{kT}\right) \quad (5.3)$$

where $S(t) = (\gamma t / 2AC)^3$. For a given time the logarithmic form of eq 3.5 can be written as follows:

$$\ln(I_{tr}(T)) = \ln(S(t)) - \left(\frac{3\Delta H}{kT}\right) \quad (5.4)$$

As indicated above, the increase in both I_{tr} and I_p originates due to the void closure process, and so eq. 5.4 was applied to I_{tr} above T_0 and to I_p below T_h for all film samples. The related figures with eq. 5.4 will be given in the section 5.1.3. The measured ΔH_{tr} and ΔH_p activation energies are listed in Table 5.1. The ΔH values seems almost not to change with increasing AgNPs content, showing that the viscous flow process is not affected by AgNPs content. Since AgNPs particles are significantly smaller (15nm) than the latex particles (345nm), they cannot effect the viscous flow of polymer chains. Therefore, due to this reason we have not observed any major change in viscous flow activation energy for all film samples in this study.

Table 5.1 : Experimentally produced activation energy values

AgNPs(wt%)	T ₀ (°C)	T _h (°C)	ΔH ^p (kcal.mol ⁻¹)	ΔE(kcal.mol ⁻¹)	ΔH ^{tr} (kcal.mol ⁻¹)
0	120	230	1,831±0,260	20,247±0,296	1,557 ±0,139
1	120	170	3,821±0,221	10,075±0,175	5,988±1,291
3	120	240	3,660±0,637	108,626±0,926	3,142±0,239
5	130	250	4,143±0,195	119,327±0,484	1,813±0,205
10	120	250	2,459±0,3	214,672±1,599	2,438±0,453
20	100	250	2,198±0,229	95,698±0,897	5,542±0,633
30	120	240	0,077±0,225	101,215±1,03	5.54±0,401
40	100	220	3,411±0,361	106,440±1,460	3,615±0,075
50	130	230	2,361±0,5	85,569±1,889	2.77±0,352

(ΔH: viscous flow activation energy ; ΔE: backbone activation energy)

5.1.2 Healing and interdiffusion

The decrease in I_p above T_h in Fig. 5.4 was already explained in previous section, by interdiffusion of polymer chains. As the annealing temperature is increased above T_h , some parts of the polymer chains may cross the junction surface and particle boundaries may disappear, and as a result I_p decreases due to the transparency of the film.

In order to compare our results with the crossing density of the PT model given in the section 3.1.2, the temperature dependence of $\sigma(\tau)/\sigma(\infty)$ can be modeled by taking into account the following Arrhenius relation for the linear diffusion coefficient:

$$v = v_0 \exp\left(-\frac{\Delta E}{kT}\right) \quad (5.5)$$

Here ΔE is defined as the activation energy for backbone motion depending on the temperature interval. Combining eq. 3.7 and eq. 5.5, a useful relation is obtained as

$$\frac{\sigma(\tau)}{\sigma(\infty)} = A_0 \exp\left(-\frac{\Delta E}{2kT}\right) \quad (5.6)$$

where $R_0 = (8v_0 t / \pi N^2)^{1/2}$ is a temperature independent coefficient. The decrease in I_p in Fig. 5.4 above T_h is already related to the disappearance of particle-particle interface. As annealing temperature increased, more chains relaxed across the junction surface and as a result the crossing density increased. Now, it can be assumed that I_p is inversely proportional to the crossing density $\sigma(\tau)$ and then the phenomenological equation can be written as:

$$I_p(\infty) = R_0^{-1} \exp\left(\frac{\Delta E}{2kT}\right) \quad (5.7)$$

The activation energy of backbone motion, ΔE , is produced by least-squares fitting the data in Fig. 5.11 (the left hand side) to eq. 13, and these are listed in Table 5.1. These results show that AgNPs nanoparticles have little effect on the diffusion of PS chains across the particle-particle interface at low AgNPs content (0 and 1 wt%). However, a much greater effect is obviously seen at higher AgNPs content films. Namely, about 10 fold increase is seen in ΔE values of AgNPs content films in the range of 3-40 wt%. Since, nanoparticles can sit at the interface between latex particles and thereby reduce the total area of contact between latex particles in the films. Therefore AgNPs will present a physical barrier to interdiffusion at the interfaces between latex particles. As a result of the restricted mobility along particle interfaces, PS chains require higher thermal energy to overcome these restrictions.

On the other hand, ΔE values are found much larger than the void closure activation energies. This result is understandable because a single chain needs more energy to execute diffusion across the polymer-polymer interface than if it were accomplished by the viscous flow process which involves the collective motion of polymer chains.

5.1.3 Fluorescence lifetime and fluorescence enhancement

The origin of the narrowness in emission spectra and enhancement in fluorescence intensity, I_p can be further elucidated by fluorescence lifetime measurements. The proximity of fluorophores to metallic particles enables the modification of radiative decay rates [26]. In order to determine the radiative rate enhancement experimentally, the fluorescence decay curves of composite films were taken after each annealing step. Fig. 5.7 (a) presents the fluorescence decay profiles of pyrene (P) from the composite film with 20 wt% of AgNPs content annealed at 130 °C. In order to probe the film formation process and also to prove our assumption related with the fluorescence enhancement during annealing, the fluorescence decay curves were measured and fitted to the sum of two exponentials for all film samples:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (5.8)$$

Here, t represents the decay time, τ_1 and τ_2 are the long and short components of pyrene lifetimes, and A_1 and A_2 are the corresponding amplitudes of the decay curves. A typical decay curve and its fit to eq. (5.8) is shown in Fig. 5.7 (a) and (b) for 20 wt% of AgNPs content film. The goodness of fit of the decay was judged by the distribution of residuals and associated chi square (χ^2) values. The amplitudes (A_1 , A_2) and lifetimes (τ_1 , τ_2) values were produced at each annealing step using the non-linear least squares analysis. It was shown that all χ^2 values ranged between 0.85 and 1.3, indicating that the double-exponential function fit well. Not surprisingly, the decays are nonexponential since they represent averaging over molecules with a large distribution of enhancement and quenching.

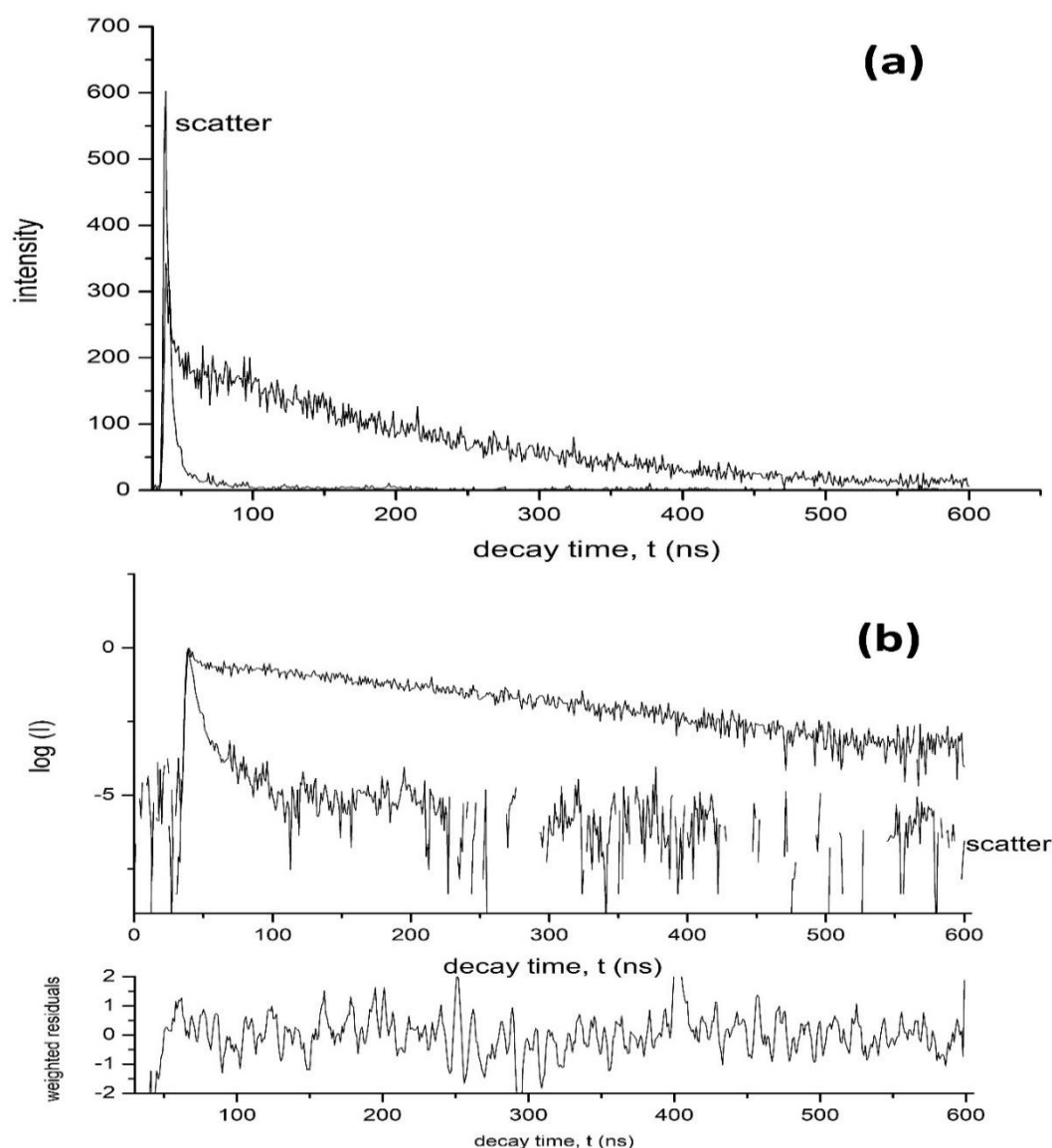


Figure 5.7 : (a) Fluorescence decay profile of excited pyrene and (b) its fit to eq. (5.8) annealed at (130 °C) temperature for 20 wt% of AgNPs content films. The sharp peaked curve is the lamp profile.

Emission enhancement near metal surfaces is believed to occur through an increase of the intrinsic decay rate for the fluorophore near the metal surface. As a result, lifetime is an important parameter through which to evaluate this mechanism. Mean lifetimes of pyrene ($\langle\tau\rangle$) were calculated from the relation:

$$\langle\tau\rangle = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (5.9)$$

In order to see the effect of annealing and AgNPs content on film formation of PS latex, $\langle\tau\rangle$ values were measured using (A_1 , A_2) and (τ_1 , τ_2) values for all film samples (not shown). The measured $\langle\tau\rangle$ values as a function of temperature are shown in Fig. 5.8 for 0, 3, 5, 20, 30 and 50 wt% of AgNPs content.

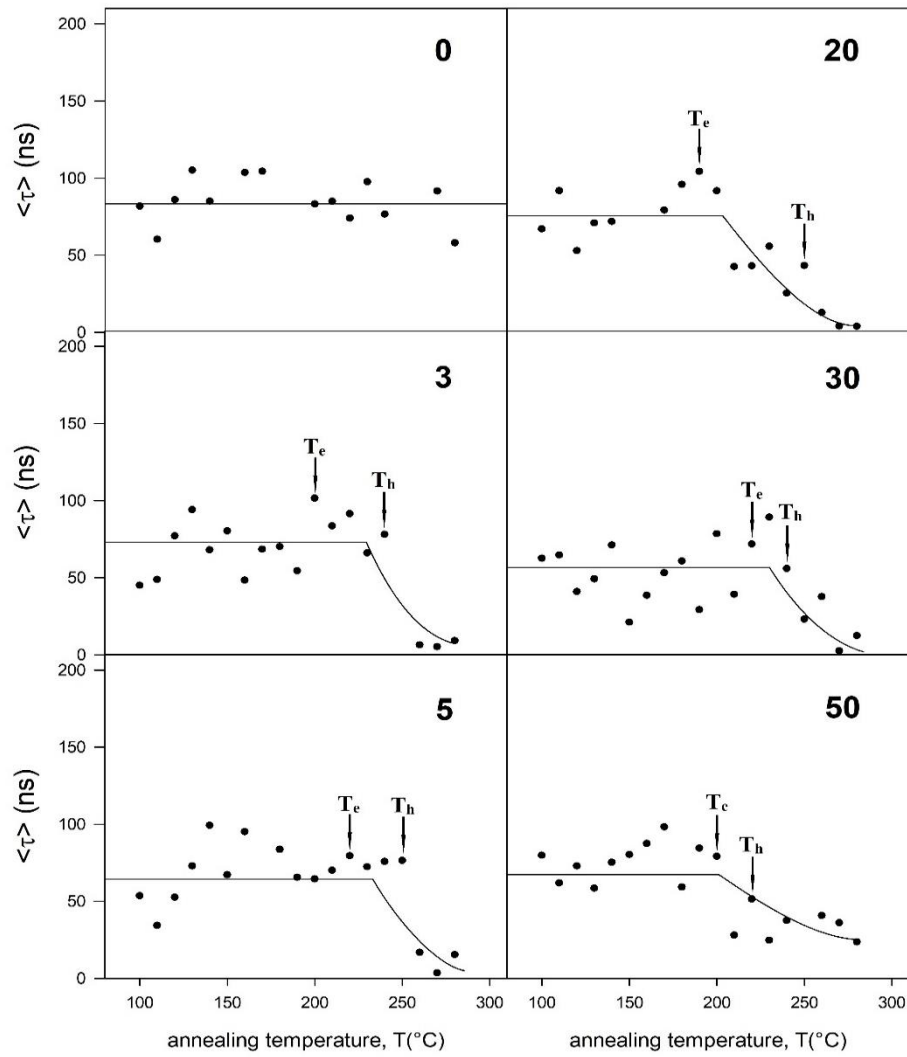


Figure 5.8 : Plot of the $\langle\tau\rangle$ values versus annealing temperature for 0, 3, 5, 20, 30 and 50 wt% of AgNPs content films.

It is seen that the average lifetime of pyrene in the pure PS (0 wt% of AgNPs content) film was around 100 ns and almost does not change with increasing annealing temperature. It is not surprising because there is no any quencher in the pure PS film and there should be no change in the fluorescence lifetime, $\langle\tau\rangle$ during film formation. However, for 3-30 wt% of AgNPs content films, $\langle\tau\rangle$ values first remains almost constant around 100ns up to a certain temperature T_e and then decreased progressively with further annealing at temperatures above T_e . Here, it is worthy to note that this temperature is coincide with the temperature at which the I_p start to increase for AgNPs content films (see Fig 5.4). As seen in Fig 5.4, for the temperature range between T_e and T_h , I_p increases substantially while the average lifetime $\langle\tau\rangle$ is decreasing. Thus, the decrease in $\langle\tau\rangle$ values in this temperature range can be explained by the coupling of excited states of pyrene with plasmons of the AgNPs and the subsequent nonradiative energy transfer from pyrene to AgNPs particles [53]. Then, AgNPs itself radiates the coupled quanta, with the very short plasmon lifetime decreasing the excited-state lifetime of the pyrene. This leads to the enhancement of the radiative rate and subsequent increase in fluorescence intensity I_p in (T_e - T_h) temperature range. This finding is also consistent with the schematic picture in Fig. 5.6 in the previous section. In order to further understand the effect of AgNPs content on I_p values with annealing, we have also plotted the enhancement rate (I_{enc}) versus AgNPs content for 100°C and 250°C annealing temperatures in Fig 5.9. I_{enc} is defined as the ratio of fluorescence intensity observed from AgNPs content films divided by that from the pure PS film having no AgNPs for each annealing temperature.

For the films annealed at 100°C, it seems that the presence of AgNPs has almost no effect on fluorescence intensity indicating that no coupling occurs between pyrene and silver nanoparticles at this annealing temperature. However, for 250°C annealing temperature, the enhancement effect is particularly evident for AgNPs content films above 1 wt% , where nearly a 4 fold enhancement is observed for 10 wt% of AgNPs content. In addition, enhancement effect seems to disappeared above 20 wt% of AgNPs content indicating that fluorescence quenching occurred once pyrenes immediate contact with the AgNPs particles due to interdiffusion of polymer chains. For higher AgNPs concentrations above 20 wt%, during the interdiffusion process, AgNPs particles are fully mixed with the PS phase and burried in it. Since the pyrenes are covalently attached to the PS chains, they become closer to AgNPs resulting in

nonradiative energy transfer between them [27], so that quenching becomes significant in that case. This is the first time that such metal enhanced fluorescence (MEF) and quenching observed during the film formation of (core-shell) metal particles doped polymer latex composites with annealing.

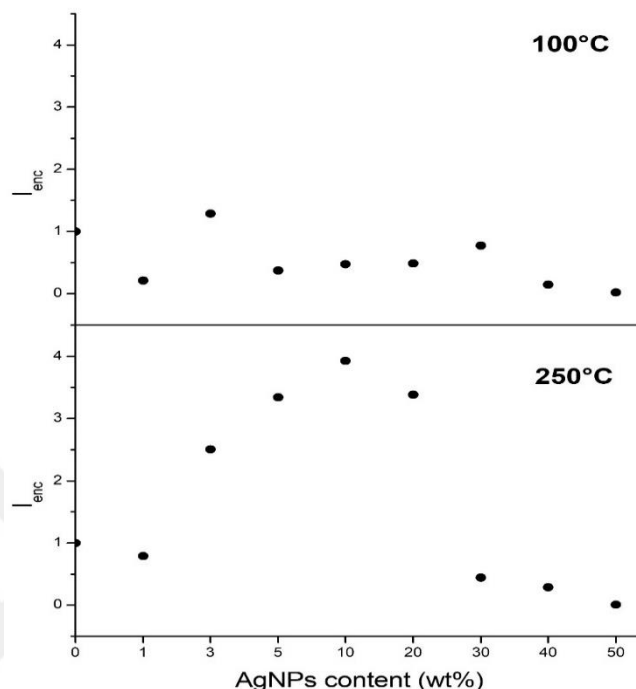


Figure 5.9 : Fluorescence enhancement rate (I_{enc}) versus AgNPs content at 100 °C and 250 °C annealing temperatures, respectively.

These findings are helpful for understanding the photophysics of pyrene-metal interactions and also for the numerous practical applications for the next generation of fluorescent polymers. Our approach to increase the emission intensity in metal particles doped polymers only with a simple annealing process during the film formation presents an opportunity for tuning the photon flux of luminescent plastics and even in the potential developments of energy efficient plastics.

Apart from these, as it is mentioned before, viscos flow activation energies calculated by using eq. 5.4. Fig 5.10 presents the $\ln(I_{tr})$ versus T^{-1} and Fig 5.11 presents the $\ln(I_P)$ versus T^{-1} plots for films from which ΔH_{tr} and ΔH_P activation energies were obtained. The energies can be obtained by considering the slope of linear part of graphs and these values also given in Table 1.

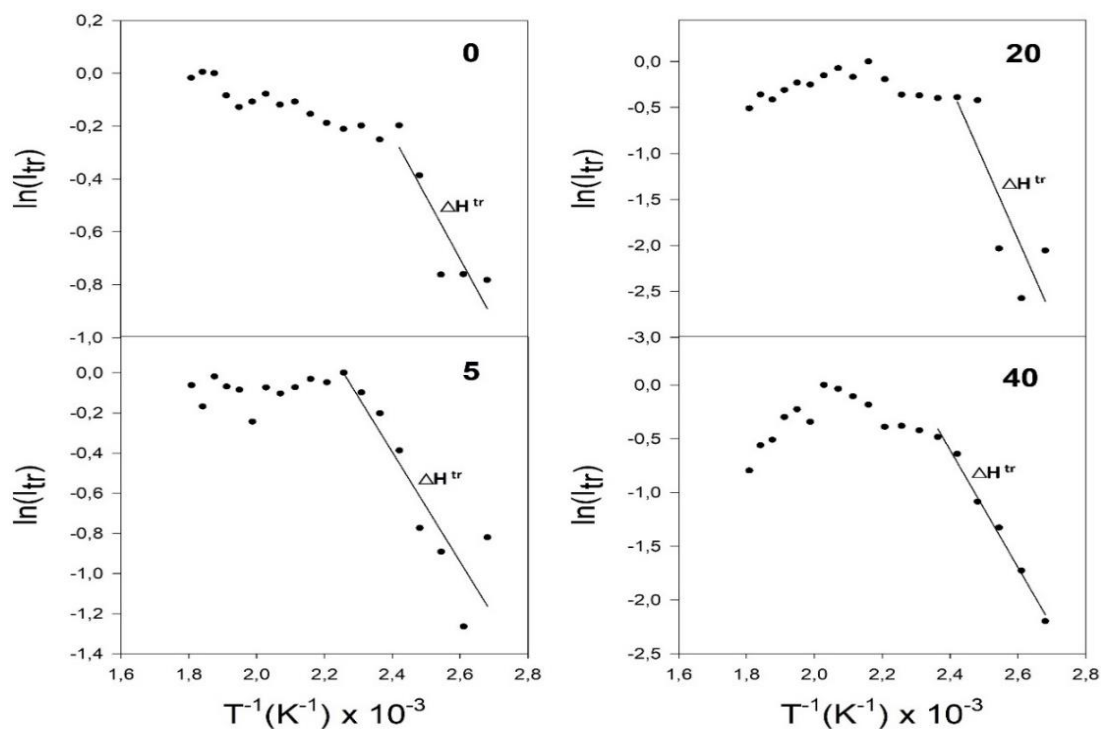


Figure 5.10 : Logarithmic plots of I_{tr} data in Fig. 5.3 vs inverse of annealing temperatures (T^{-1}) for various AgNPs content. Data are fitted to eq. 5.4 to produce ΔH_{tr} and are listed in Table 5.1.

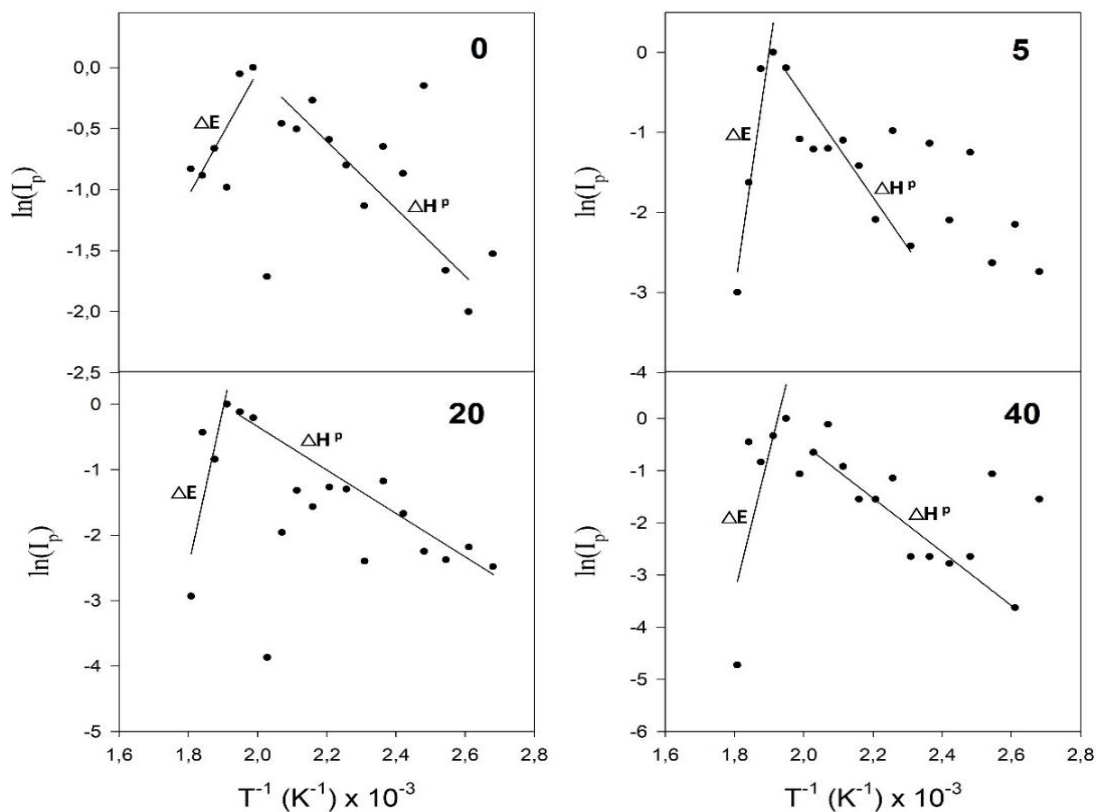


Figure 5.11 : The $\ln(I_p)$ versus T^{-1} plots of the data in Fig. 5.3 for the composites with 0, 5, 20 and 40 wt% of AgNPs content, respectively. The slope of the straight lines on the right and left hand side of the graph produce ΔH_p and ΔE values, respectively.

5.1.4 Film morphology

Figures 5.12-5.14 illustrate scanning electron microscopy (SEM) images of composite films with 0, 3, 20 and 30 wt% of AgNPs content annealed at 100, 200 and 280 °C, respectively. The white spots in SEM images are the AgNPs nanoparticles embedded into the PS matrix. At 100 °C (see Fig. 5.12), no deformation in PS particles is observed and PS particles are distributed randomly for all film samples. However, with increasing AgNPs content, the nanoparticles are sit on and/or between the surface of PS particles. With annealing the films at 200 °C (see Fig. 5.13), all voids disappear and the coalescence of PS particles occurred for all film samples. SEM micrographs of 0, 3 and 20 wt% of AgNPs content film surfaces appear relatively smooth and flat. For 30 wt% of AgNPs content film, despite the smooth surface for this composite film small AgNPs aggregations are seen in the film.

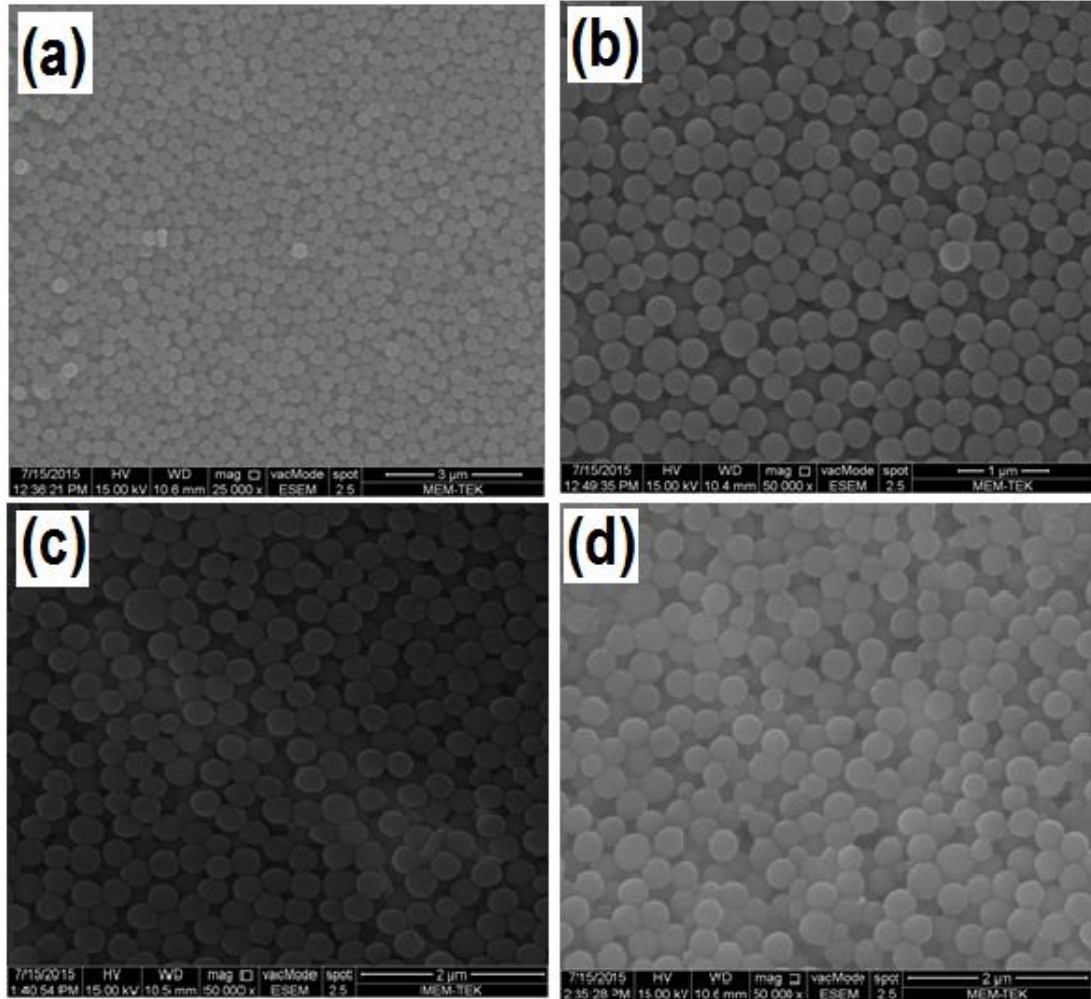


Figure 5.12 : Scanning electron micrographs (SEM) of 0, 3, 20 and 30 wt% of AgNPs content films annealed at 100 °C for 10 min.

Upon annealing the films at 280°C (Fig. 5.14) 0, 3, 20 and wt% of AgNPs content films show regular and continuous surface structure and AgNPs (white spots) appear to be well dispersed throughout the film indicating that PS particles coalesce and envelope the AgNPs very well. However, in the 30 wt% of AgNPs content film, it seems that PS latexes fail to completely coalesce due to the AgNPs aggregation that creates porosity in the film.

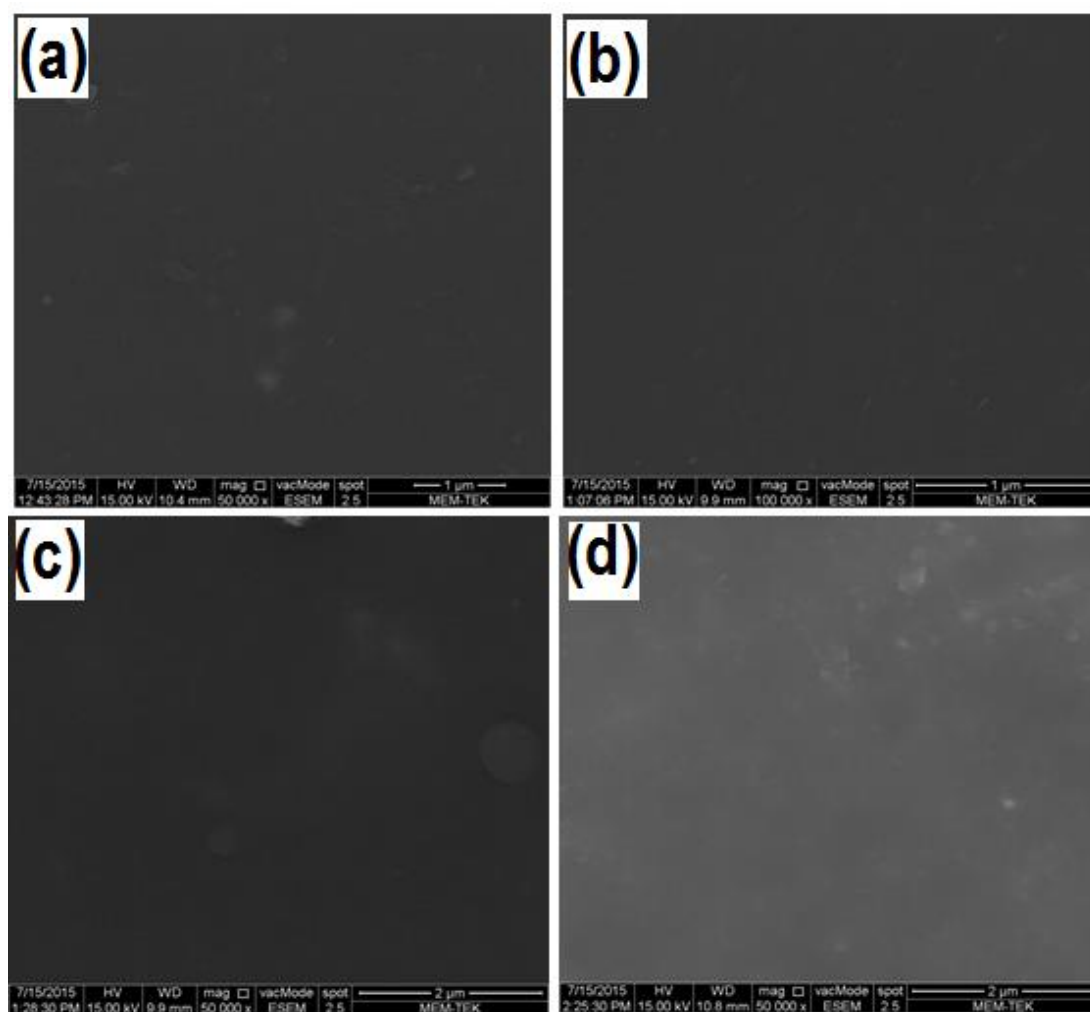


Figure 5.13 : Scanning electron micrographs (SEM) of 0, 3, 20 and 30 wt% of AgNPs content films annealed at 200 °C for 10 min.

It is understood that, increasing AgNPs concentration above 30 wt% creates more porosity with limited coalescence between PS particles. So, during the film formation agglomeration of AgNPs occurs. In particular, within their diffusion distance, metal atoms may encounter each other leading to aggregation and formation of metal clusters which are embedded into the polymer matrix during the film formation process. Such structure leads extensive light scattering from the composite films which is consistent with the optical transmission results given in Fig. 5.5.

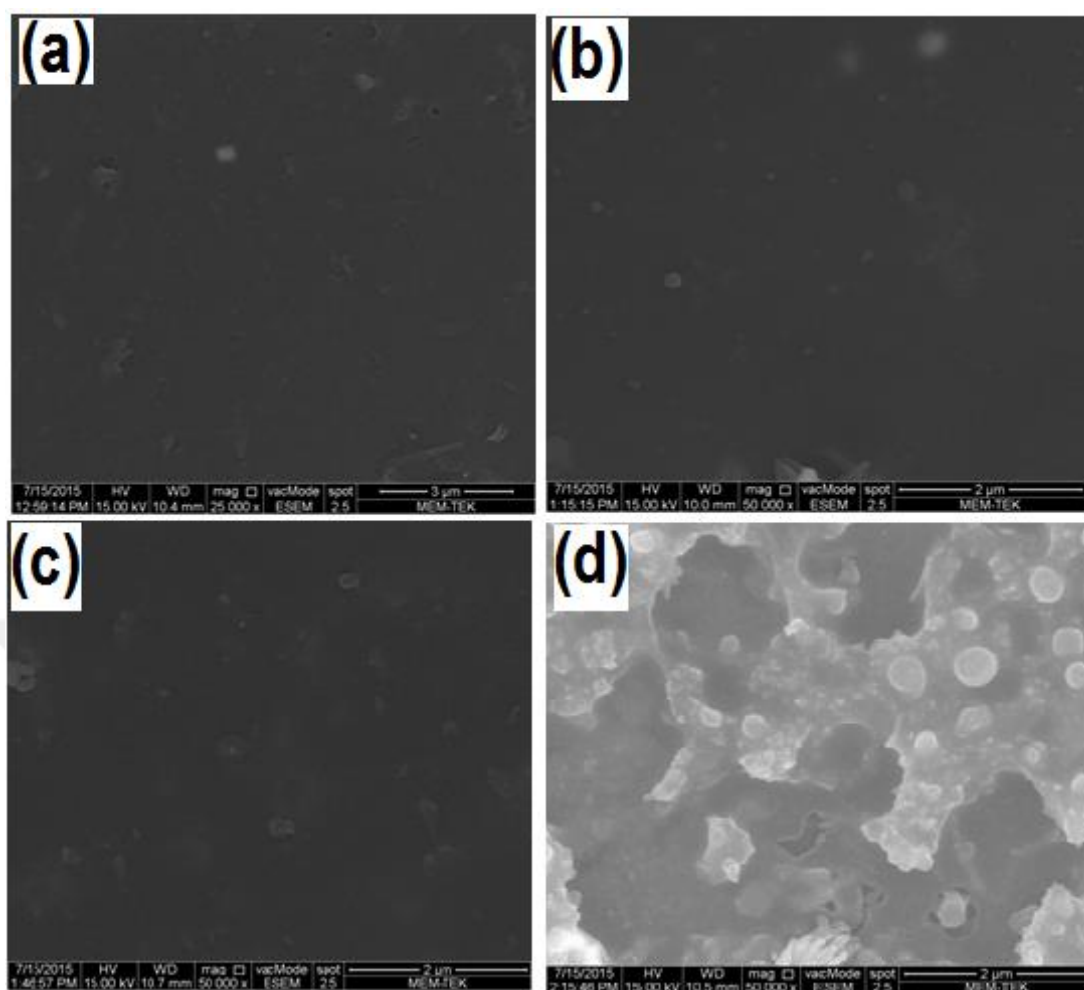


Figure 5.14 : Scanning electron micrographs (SEM) of 0, 3, 20 and 30 wt% of AgNPs content films annealed at 280 °C for 10 min.

5.1.5 Electrical conductivity

Fig. 5.15 shows electrical conductivity of PS/AgNPs composite films as a function of AgNPs content annealed at 280 °C. In the studied concentration range of 0-50 wt% of AgNPs, dielectric behavior and very little change in conductivity was observed. In particular, when increasing the Ag NPs content from 0 to 50 wt %, the conductivity of the films was found to increase from $1,26 \times 10^{-14}$ to $4,54 \times 10^{-14}$ S. The resulting conductivity is quite low, in the same order of magnitude (10^{-14} S) that of pure PS film. This low conductivity is due to the isolated nature of the PVP covered (which prevents the particles from aggregating, but puts an insulating layer around the particles) silver (Ag) nanoparticles with small sizes and relative large separations in the dielectric PS matrix. At these AgNPS contents, the possibility of AgNPs to become contacted or coalesced to form an interconnected metallic pathway is very low. The electron mean

free path is significantly reduced due to the effective hindrance of the dielectric polymers. Therefore, no apparent substantial change in conductivity is observed.

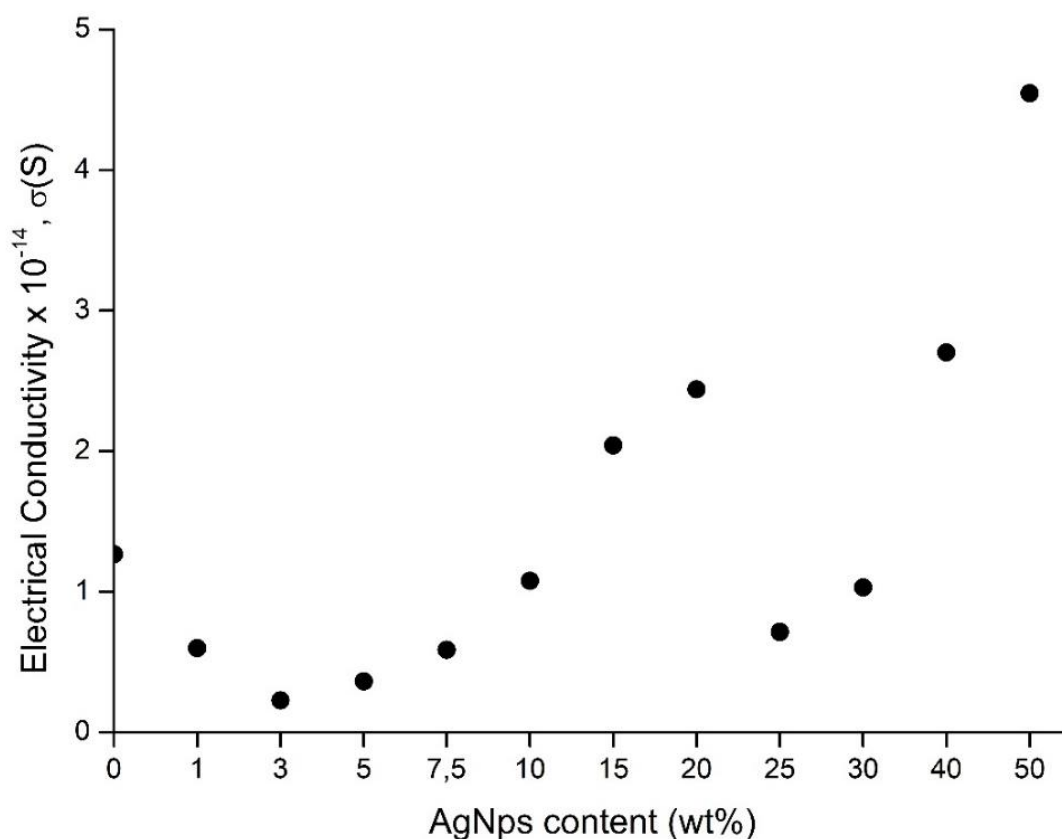


Figure 5.15 : Electrical conductivity (σ) of PS/AgNPs composite films as a function of AgNPs content annealed at 280 °C for 10 min.

The film conductivity is closely related to the morphology of the films. The SEM images in Fig 5.14 confirms the inherent correlation between film microstructures and conductivity. From these images, it is clearly seen that, AgNPS particles completely imbedded in the polymer matrix and direct contact between them is prevented to form a conducting path.

5.2 Film Formation Process of PS/AgNPs Composites Exposed to Organic Solvent Vapor

In this part, we studied the film formation process of PS/AgNPs composites exposing to solvent vapor. In this experiment, 7 different composite films including 0, 1, 5, 10, 20, 30 and 50 wt% of AgNPs content were prepared in the form of powder. As it is shown in Fig. 5.16, all composite films are exposed to chemical vapor by confining in a quartz cell. Chloroform which is a very good solvent for PS is used in order to start the film formation process. Heptane which is a poor solvent for PS is used in

order to slow down the diffusion of solvent molecules into the films. For each 1cm x 1cm quartz cell, 0,350 ml (0,175 ml chloroform + 0,175 ml heptane) solvent mixture is used. Mean lifetimes and transparency of films were measured by using spectroscopic techniques as it is mentioned in the previous sections. Film formation behaviour of composite films were determined due to B (●) , R (◻) values and SEM images of composite films.

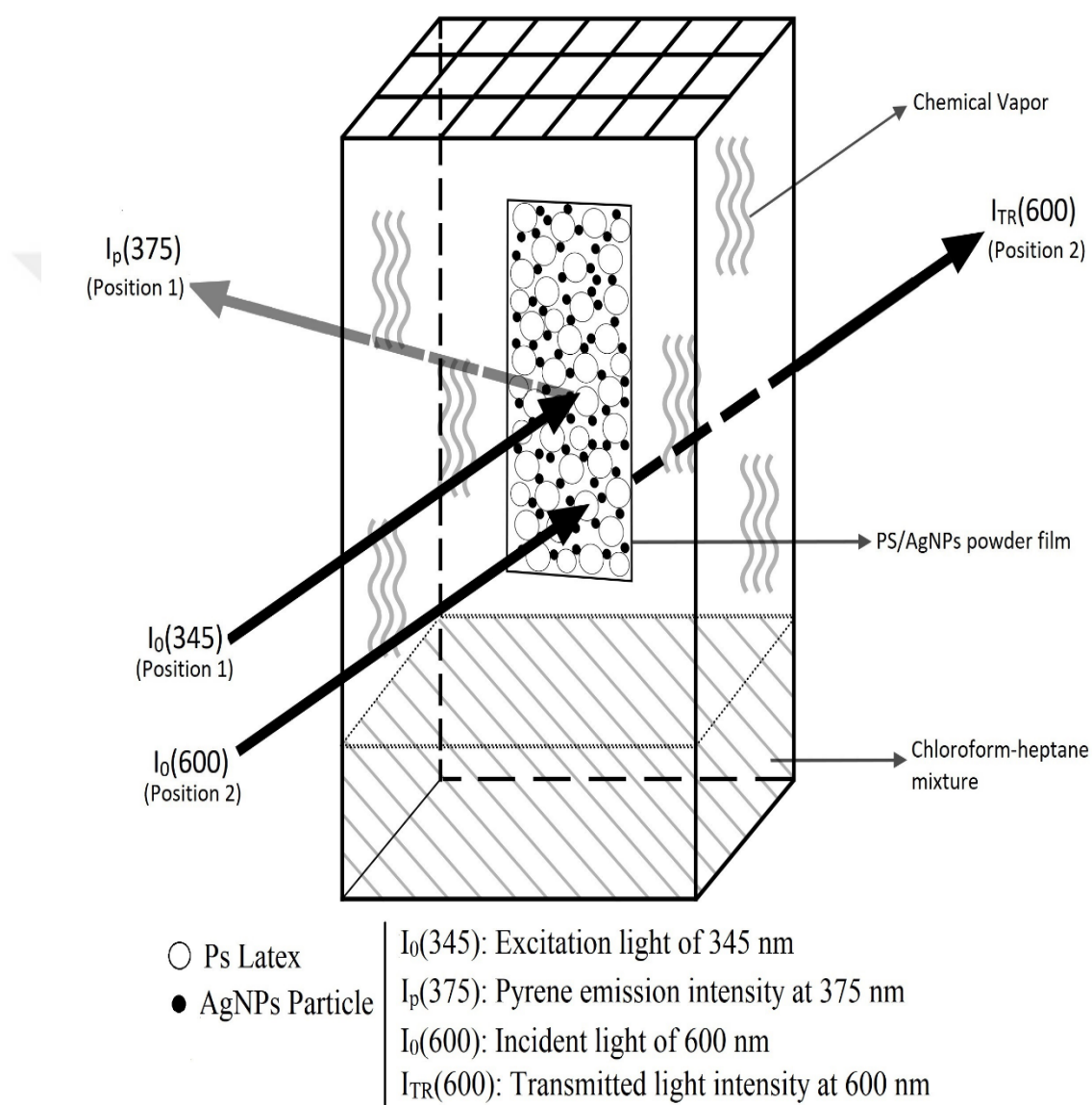


Figure 5.16 : The position and the illumination of the composite film sample exposed to solvent vapor are shown in SMS (position 1) and UVV (position 2) systems. $I_0(345)$, $I_p(375)$, $I_0(600)$, and $I_{tr}(600)$ are the excitation, pyrene, incident and transmitted light intensities, respectively.

5.2.1 Fluorescence lifetime measurements

Fig. 5.17 presents the fluorescence decay profiles of P in pure latex film at various film formation steps. It is observed that as the vapor exposure time, t is increased, excited P decay faster, indicating that the quenching of excited P increases. Here, the vapor molecules act as an energy sink for rapid vibrational relaxation, which occurs after the rate-limiting transition from the initial state.

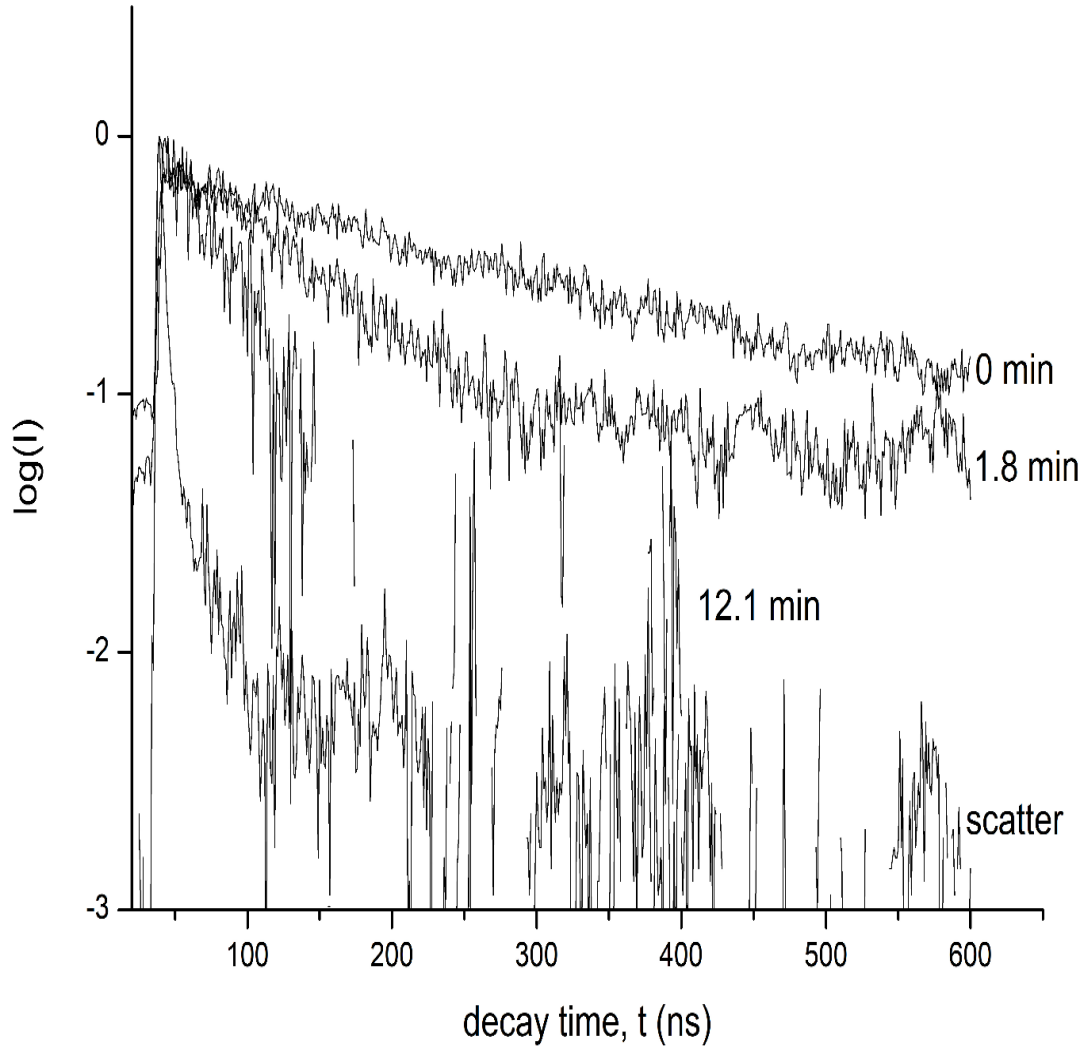


Figure 5.17 : Fluorescence decay profiles of P from pure PS film at various film formation steps. The number on each curve represents the vapor exposure time, t , in minutes. The sharp peaked curve is the lamp profile.

A typical decay curve and its fit to eq. 5.8 is shown in Fig. 5.18. (A_1, A_2) and (τ_1, τ_2) values were produced at each film formation step using the non-linear least squares analysis. The uniqueness of the fit of the data to the model is determined by χ^2 ($\chi^2 < 1.20$), the distribution of weighted residuals, and the autocorrelation of the residuals.

Mean lifetimes of P were calculated from the eq. 5.8. Using (A_1 , A_2) and (τ_1 , τ_2) values for the film formation experiments, $\langle \tau \rangle$ values are measured and plotted in Fig. 5.19 versus solvent exposure time (t) for various AgNPs contents. It is observed that $\langle \tau \rangle$ values for all film samples decrease exponentially as t is increased. In order to understand the effect of AgNPs content on the quenching of excited P molecules, $\langle \tau \rangle$ values were also plotted as a function of AgNPs content in Fig. 5.20 for various solvent exposure times. From these figures, it is seen that $\langle \tau \rangle$ values show no substantial change with varying AgNPs content and the quenching process is mostly originated from the solvent molecules.

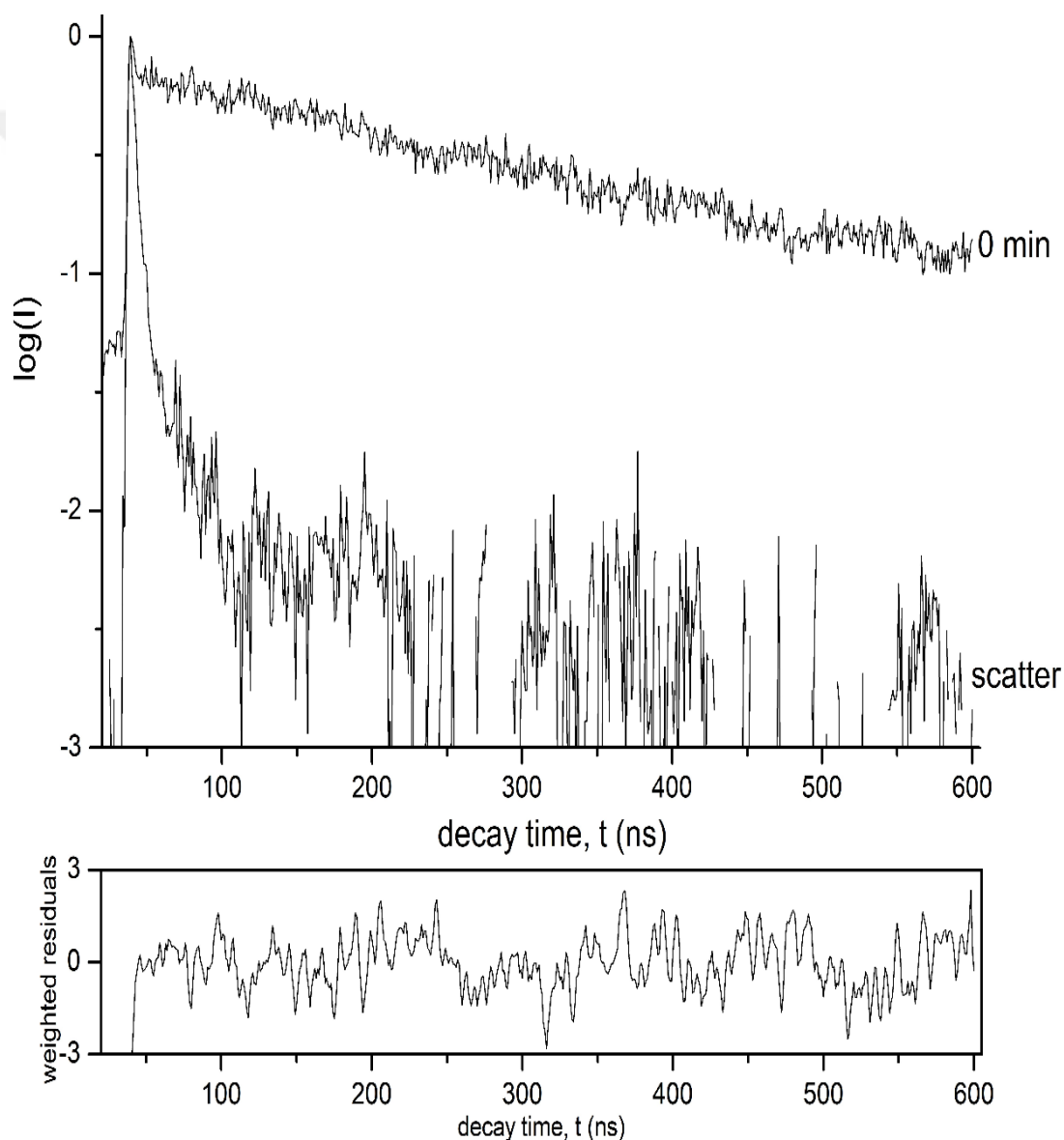


Figure 5.18 : Typical fluorescence decay curve and its fit to eq. (5.8), from which τ values are determined.

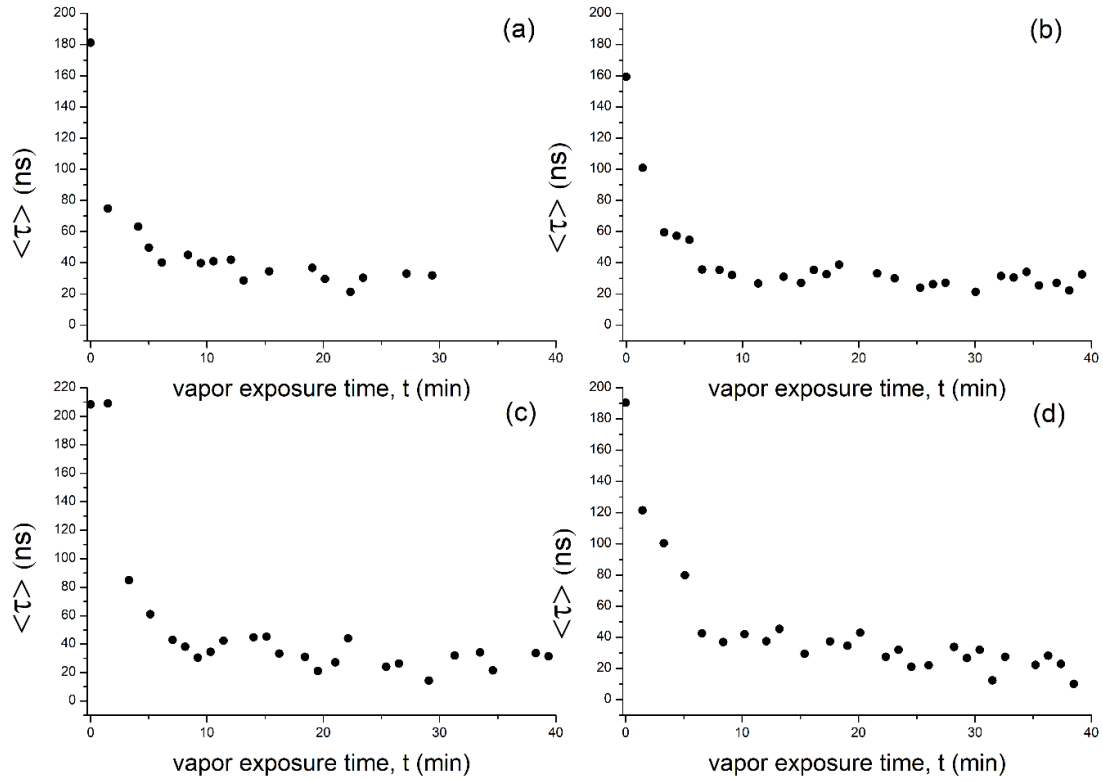


Figure 5.19 : Plots of $\langle \tau \rangle$ values versus vapor exposure time, t , for the composite films with (a) 0, (b) 10, (c) 30 and (d) 50 wt% of AgNPs content.

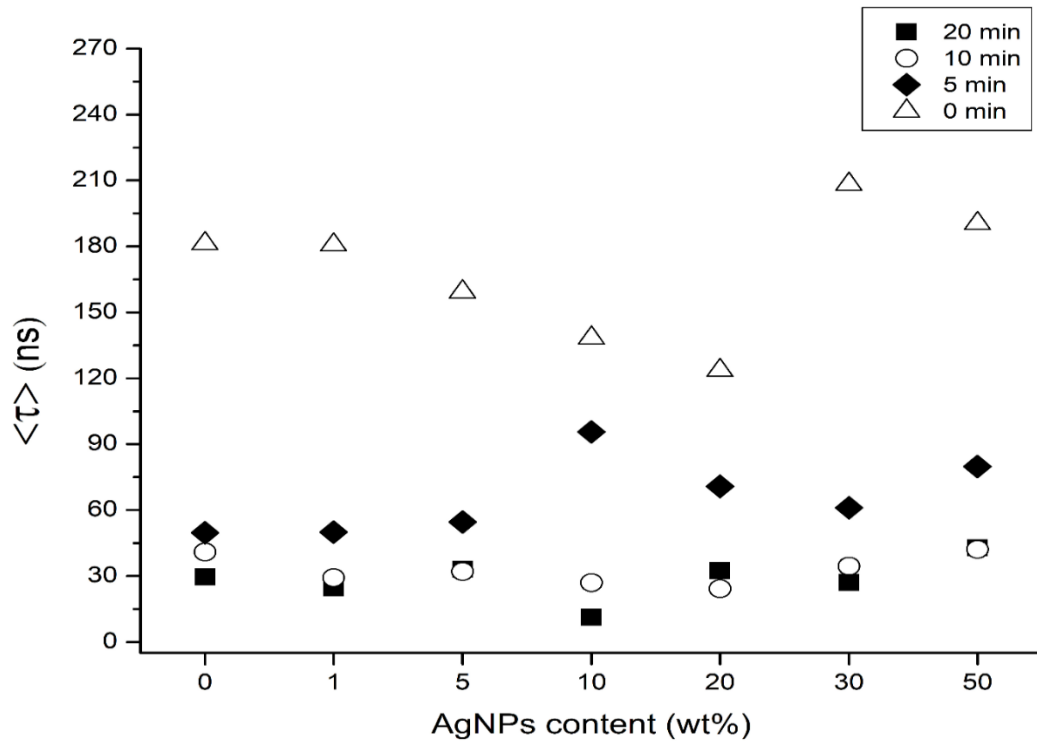


Figure 5.20 : Plot of $\langle \tau \rangle$ values as as function of AgNPs content at various vapor exposure times.

To quantify these results, a Stern–Volmer type of quenching mechanism is proposed for the fluorescence decay of P in composite film during vapor-induced film formation, where eq. 2.8 can be employed. For low quenching efficiency, $\tau_0 k_q [M] < 1$; eq. 2.8 becomes:

$$\tau \approx \tau_0 (1 - \tau_0 k_q [M]) \quad (5.10)$$

Here, since we assume that solvent molecules are responsible for the quenching process, $[M]$ represents the quencher (vapor) concentration at time t . The relation between the lifetime of P and $[M]$ in film can be obtained approximately using the volume integration of eq. (5.10) and the relation:

$$\frac{\langle \tau \rangle}{\langle \tau_0 \rangle} = 1 - C \frac{M}{M_\infty} \quad (5.11)$$

where $C = \tau_0 k_q M_\infty / V$. Here V is the volume of the film. The vapor sorption is calculated over the differential volume as:

$$M = \int_0^d [M] dV \quad (5.12)$$

where dV is the differential volume in the film and the integration is performed from 0 to d , where d is the film thickness. M_∞ is the amount of vapor sorption at time infinity.

In order to compare our results with the crossing density of the PT model, we can re-write eq. (3.7) as:

$$\frac{\sigma(\tau)}{\sigma(\infty)} = R t^{1/2} \quad (5.13)$$

where $R = (8\nu/\pi)^{1/2} N^{-1}$. Combining eq. 3.7 with eq. 3.12 and assuming that vapor penetration is proportional to the chain interdiffusion due to plasticization, i.e., the increase in vapor sorption causes the increase in crossing density, $\sigma(t)$, then the following relation can be produced:

$$1 - \frac{\langle \tau \rangle}{\langle \tau_0 \rangle} = B t^{1/2} \quad (5.14)$$

where $B = CR$, is obtained. Plots of the data in Fig. 5.19 according to eq. 5.14 are shown in Fig. 5.21. Fits are nice, and support the PT model, where chain transport obeys the $t^{1/2}$ time dependence. The slopes of the linear relations in Fig. 5.21 produce B values with the accuracy of R^2 close to 1.0 in which the only variable is the reptation

frequency, ν . The other parameters in C and R are constant during film formation processes.

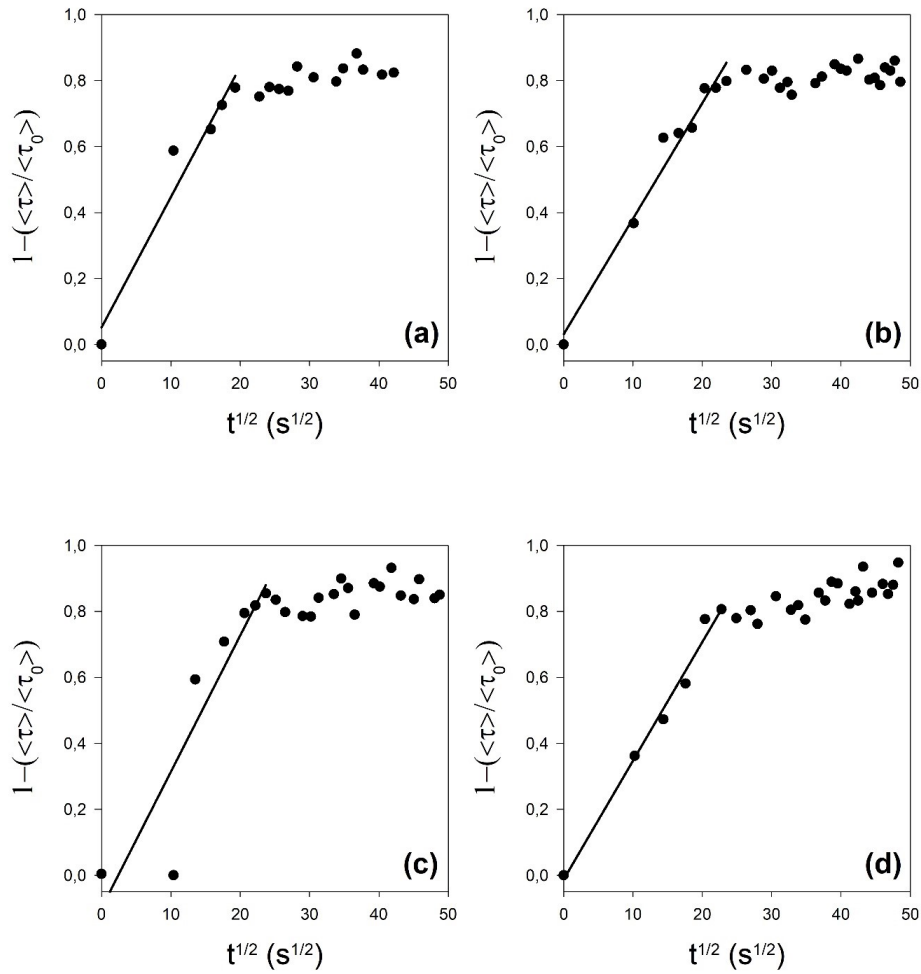


Figure 5.21 : Plots of the data in Fig. 5.19 according to eq. 5.14, where linear least squares fits are performed. The slope of the linear relations produce B values.

The produced B values are given in Table 5.2 and also plotted versus AgNPs content in Fig. 5.22. It is seen that as AgNPs content is increased, B values first decrease up to the critical 10 wt% of AgNPs content, then start to increase. In this figure, circles and squares are experimental data and lines are guides for the eyes. Most probably large B values are caused by high crossing densities due to fast reptation of polymer chains. In other word, film formation accelerates in these films as a result of high solvent vapor absorption due to plasticization effect. The decrease in B values for 0-10 wt% of AgNPs range can be explained by the reptation of polymer chains at lower frequencies during film formation processes, which result in low B values. Here one may argue that due to steric hindrance by the AgNPs particles, the interdiffusion of polymer chains across the junction is retarded. As a result, polymer chains reptate slower at the

polymer/polymer interface, which results in low B values with increasing of AgNPs content from 0 to 10 wt%. The increase in B (or ν) values above 10 wt% of AgNPs content can be explained by the formation of AgNPs aggregates which results in formation of voids in the film (see Fig. 5.26). Due to these voids, the solvent molecules diffuse faster into the composite films and enhance the reptation of PS chains.

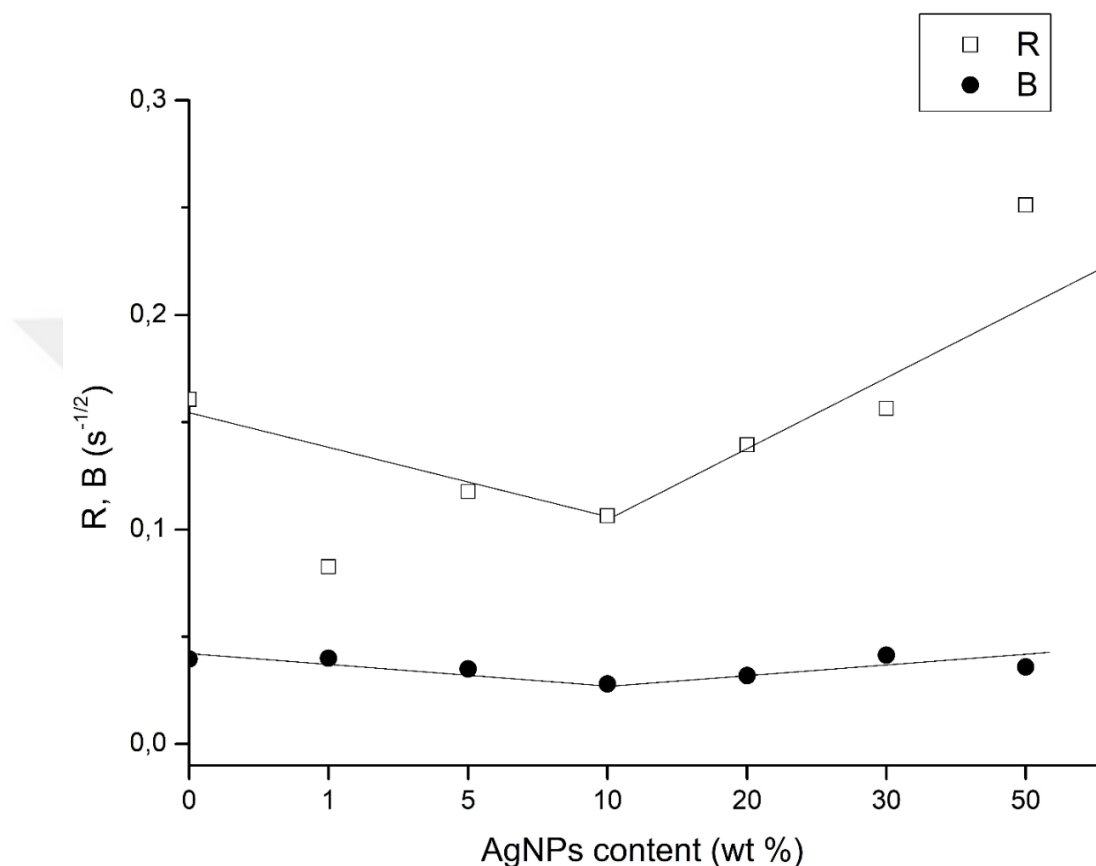


Figure 5.22 : Plot of B (●) and R (□) values versus AgNPs content in the composite film.

Table 5.2 : B (●), R (□) values and film thicknesses of PS/AgNPs composite films used in this study.

AgNPs (wt%)	B (s ^{-1/2})	R (s ^{-1/2})	d (μm)
0	0,040	0,161	5,3
1	0,040	0,083	12,1
5	0,035	0,118	10,3
10	0,028	0,106	9,1
20	0,032	0,139	10,4
30	0,041	0,157	19,2
50	0,036	0,251	25,2

5.2.2 Transmitted light intensities

In order to support above findings, transmitted light intensity (I_{tr}) data were obtained. Fig. 5.23 presents I_{tr} versus time (t) plots for various AgNPs content. It can be seen that all curves increase as the vapor exposure time is increased and reach a plateau by suggesting that the composite films become more transparent to light. These behaviors can be explained with the chain interdiffusion between latex particles during vapor induced film formation. As the polymer chains interdiffuse, transparency of the film increases with time, which results in less light scattering from the composite film. This also indicates that vapor-induced film formation occurred in all film samples.

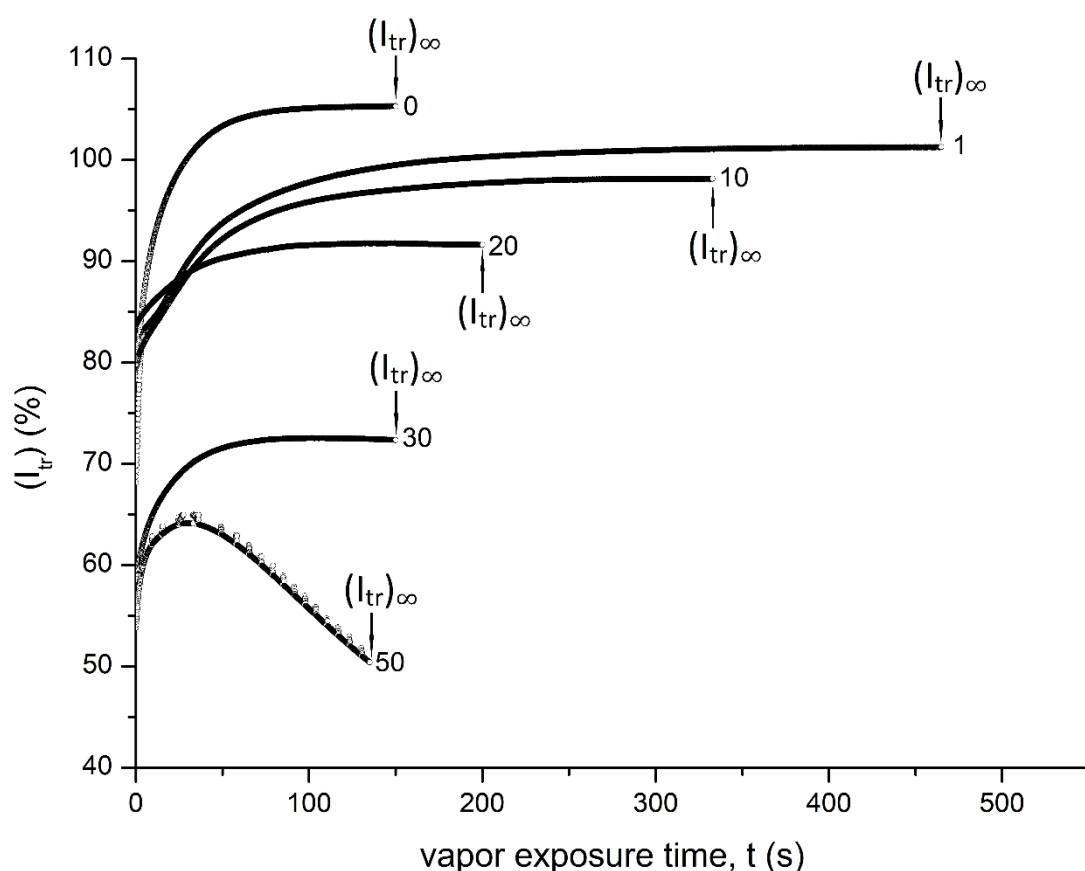


Figure 5.23 : Plot of transmitted light intensities, I_{tr} , versus vapor exposure time, t , in seconds. The number on each curve indicates the AgNPs content in the film.

Here it is interesting to note that all I_{tr} curves start above 50% at 0 time, which may indicate that the diffusion of solvent vapor into films is too fast. Furthermore, as AgNPs content increased above 10 wt%, I_{tr} increases faster with solvent exposure time (t) by presenting smaller saturation values. Intuitively, this behaviour of I_{tr} predicts that film samples with high AgNPs content exposed to solvent vapor create less transparent film in very short times. Beside this, it is worthy to note that I_{tr} curve of

50 wt% of AgNPs content film first increases reaching a maximum and then decreases with vapor exposure time. Since the solvent provides a medium for the solubilization of the AgNPs particles and at the same time plasticizes the polymer chains, it causes the migration and combination of AgNPs particles forming clusters (aggregates) at long vapor exposure time resulting strong scattering of the light. Therefore, the I_{tr} decreases with increasing vapor exposure time due scattering of the light from these clusters.

To make this point clear, the saturation values, $(I_{tr})_{\infty}$ of transmitted light intensity (I_{tr}) curves in Fig. 5.23 were plotted versus AgNPs content in Fig. 5.24. It is seen that as increasing the AgNPs content from 0 to 20 wt%, the transmittance of composite films decreased almost gradually from 105% to 92%. However, the transmittance decreased rapidly from 92% to 72% increasing AgNPs content from 20 to 30 wt% and then to 51% at 50 wt% of AgNPs. The composite films with transmissions above 85% correspond to transparent films, whereas films with transmission below 20% and in between them correspond to turbid and translucent films, respectively. In our case, the results indicate that transparent composite films (105%-92%) were successfully achieved for 0-20 wt% of AgNPs contents, but translucent films (72-51%) were obtained for 30-50 wt% of AgNPs contents. As it is known that the transparency of composite films depends mainly on three factors: differences in refractive indices, sizes of phases, and the number and size of air voids in the composite films [54,55]. Here, despite the refractive indices of PS polymer ($n=1.59$) and AgNPs particles ($n_{PVP}=1.53$, $n_{Ag}=0.072$ and $n_{AgNPs}=1.17$) [56] are somewhat different (about 0.42), we suggest that the low I_{tr} for higher AgNPs content films is mostly associated with aggregation of AgNPs [57] in the films which can scatter the light. As argued above, due to the plastization effect of the solvent vapor, the voids are completely filled by the PS polymer during vapor induced film formation and almost no voids are present in the films. Therefore, optical transmission in these films can be qualitatively related to AgNPs clusters. Drawing upon the SEM results shown in following section (see Fig. 5.27), we can conclude that the clustering of AgNPs particles scatter light significantly, so that the optical transmission is reduced with increasing AgNPs content. As the size of AgNPs clusters is large with respect to the wavelength of the visible light, they scatter the light that causes low I_{tr} . Because of the continuous film formation of PS, transparency is high (>90%) for composite films with AgNPs content

in the range of 0-20 wt%. As the AgNPs content is increased above 20 wt%, the transmission decreases dramatically (around 51%) which results in translucent films. Thus, it can be concluded that the AgNPs and the PS phases existed as two separate phases in these films as seen in SEM images in the following section.

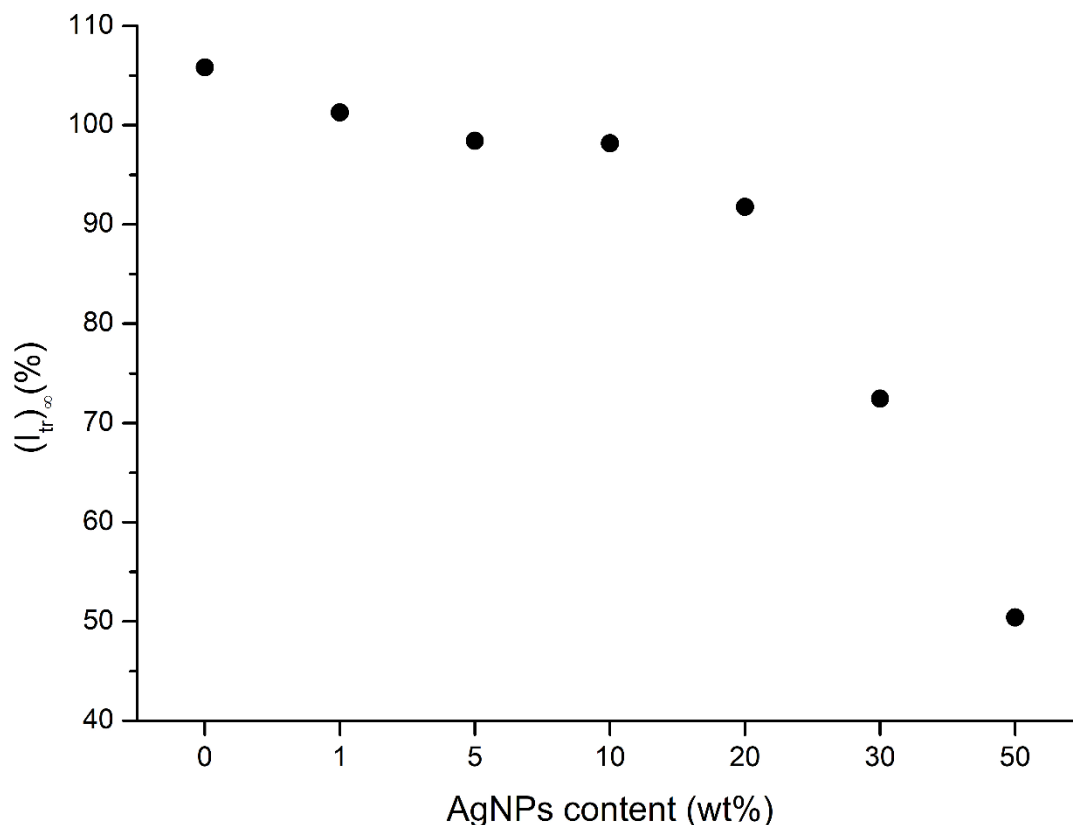


Figure 5.24 : Plot of saturation values, $(I_{tr})_{\infty}$ of I_{tr} curves as a function of AgNPs content.

To compare our results with Prager-Tirrel model, we assume that $I_{tr}(t)$ ($=[I_{tr}(t) - I_{tr}(0)]$) is proportional to the crossing density, $\sigma(t)$, in eq. 3.7. then the following phenomenological equation can be written [58]:

$$\frac{I_{tr}(t)}{I_{tr}(t_{\infty})} = R t^{1/2} \quad (5.15)$$

The above assumption requires the disappearance of particle–particle interfaces due to the chain interdiffusion which cause an increase in I_{tr} . The plots of eq. 5.15 for the data in Fig. 5.23 are shown in Fig. 5.25 for 0, 10, 20 and 30 wt% of AgNPs content films, respectively. The slopes of linear regions in Fig. 5.25 produce R values given in Table 5.2. R values were also plotted in Fig. 5.22 together with B values versus AgNPs content.

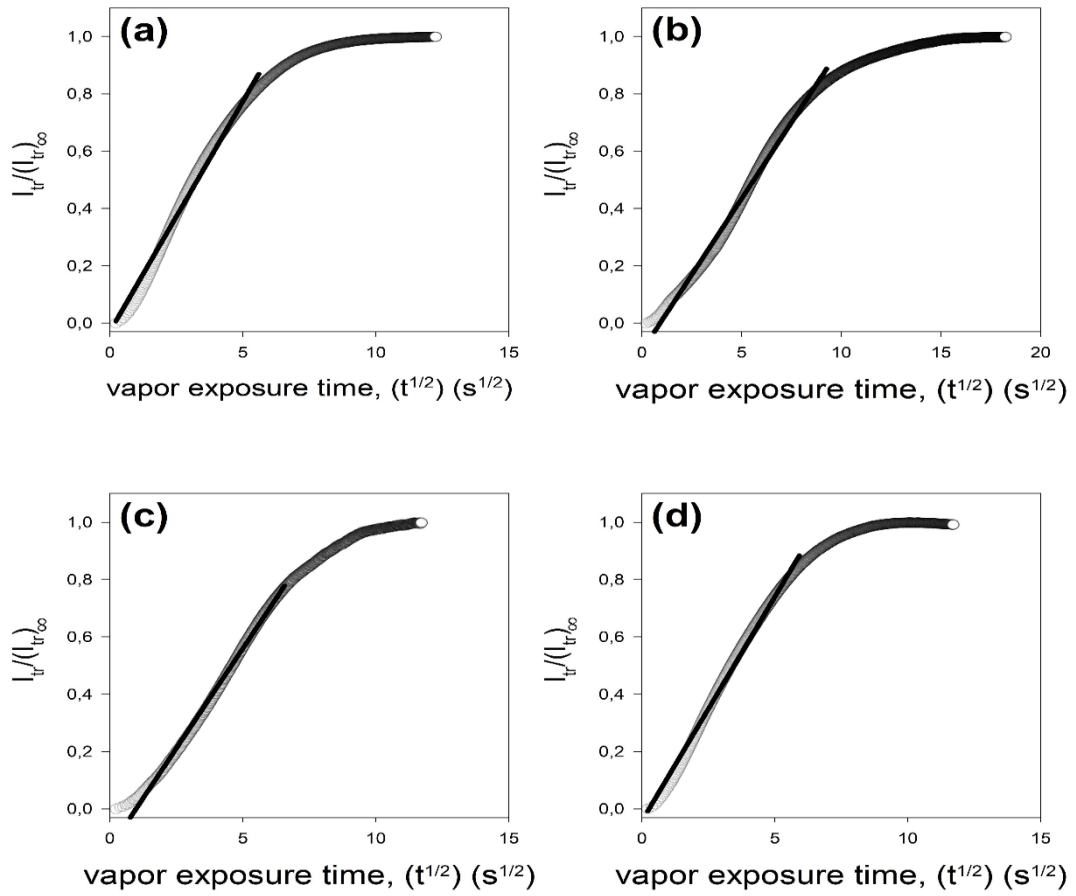


Figure 5.25 : Plot of I_{tr} data in Fig. 5.23 according to eq. 5.15 for the (a) 0, (b) 10, (c) 20 and (d) 30 wt% of AgNPs content. The slope of the linear relations produce R values (see Fig. 5.22). R (□) and B (●) values versus AgNPs content are plotted in Fig. 5.22 together to illustrate the behavior of fluorescence quenching and transparency.

For the composites with 0 to 10 wt% of AgNPs, R values decrease and then as the weight fraction of AgNPs increased from 10 to 50%, the value of R increases again. From the Fig. 5.22, it is seen that R values show similar behavior as B values produced from fluorescence quenching (lifetimes) data. As was predicted in the previous section, B values or reptation frequency, ν , first decrease as AgNPs content is increased up to 10 wt%, then increases with further increase in AgNPs content. Here, the decrease in R (or ν) values can also be explained by the AgNPs particles merely acted as nanofiller to increase the solvent resistance of the composite films. AgNPs occupy the interstitial space between the PS latexes and act as a barrier for diffusion of solvent molecules and slow down the plasticization effect of solvent molecules for AgNPs content in the range of 0-10 wt%. As a result, PS chains reptate slower at polymer/polymer interface which results in low R and/or B values in these composites. However, the increase in

R and/or B values above 10 wt% can be explained by the formation of AgNPs aggregates which causes voids in the films that promote the diffusion of solvent molecules into the films. As a result, as seen in Fig. 5.22, reptation frequency is shown to increase with increasing AgNPs content for these films. Furthermore, it can be seen that highest slope (R) is produced for 50 wt% of AgNPs content film proposing that polymer chains reptate at higher frequency during film formation process, which result the largest R value. This will be explained in detail in the light of SEM images in the next section.

5.2.3 Film morphology

In order to support our findings above, SEM was used to examine the morphologies of composites before and after vapor exposure. The images which are given in this section for the films with 0, 10, 30 and 50wt% of AgNPs content, respectively. Before vapor exposure at $t=0$, for 0, 10 and 30 wt% of AgNPs content films (see Fig. 5.26) the hard PS spheres seem to be randomly distributed and contain a lot of voids, which give lower I_{tr} values at this stage.

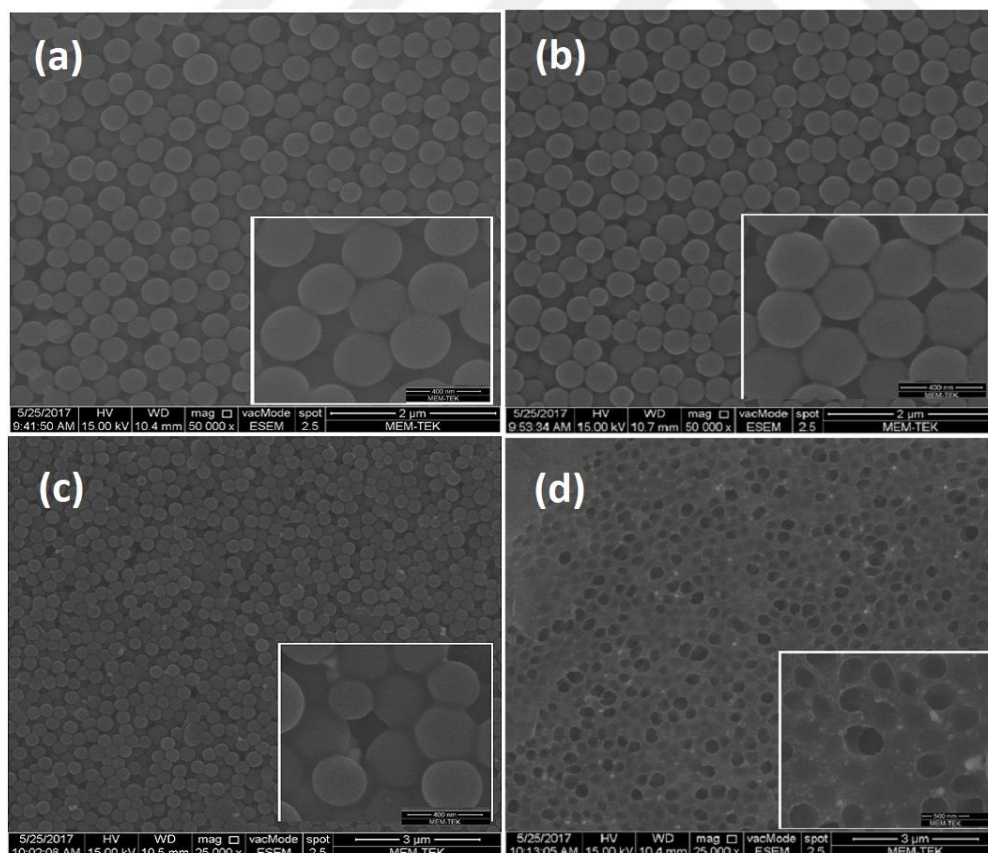


Figure 5.26 : SEM images of PS/AgNPs nanocomposites with (a) 0, (b) 10, (c) 30 and (d) 50 wt% of AgNPs content before exposure of solvent vapor. (Insets show the images taken in higher magnification).

In addition, some bright spots are clearly visible on the surface and/or between PS latex particles for 10 and 30 wt% content films. Here, the bright spots represent the Ag particles embedded in PVP polymer. The AgNPs occupy the interstitial voids between the PS particles and link them via soft PVP polymer reducing the voids in the 10 wt% of AgNPs content film (inset of Fig. 5.26(b)). This causes the restriction of PS polymer chains during the film formation process exposed to solvent vapor and gives the lowest R and B values for this film (see Fig. 5.22) as stated before. However, in Fig. 5.26 (c), PS particles tend to cluster and more voids are observed for 30 wt% of AgNPs content film which present larger R and B values.

For 50 wt% of AgNPs content film, no PS particles are observed, instead nearly circular porous surface structure is seen. Here, the influence of low- T_g ($\sim 20^\circ\text{C}$) PVP on the morphology of these composites is expected to be important due to its relatively high concentration. At the highest AgNPs concentration (50 wt%), since 75 wt% of AgNPs is composed of PVP, PVP makes up 37.5 wt % of the composite film. The high fraction of soft PVP polymer was found to affect film formation of PS latex/AgNPs composites, analogous to the film-forming behavior of hard/soft latex blends [59]. Thus, the formation of the circular pores on the surface of 50 wt% of AgNPs content film may be interpreted as follows: When the water in the PS/AgNPs film on glass substrate evaporates, soft (low- T_g) PVP polymer flow and deform concurrently with the evaporation of the water. Coalescence of the soft PVP occurs at the room temperature and form a continuous phase in the composite film with embedded Ag particles in it. However, the hard (high- T_g) PS latexes remain undeformed after evaporation of water and prevented to come into contact with each other by AgNPs particles. Since they have higher molecular weight (2.66×10^5 g/mol) than PVP polymer (around 3000-4000 g/mol), they are buried in soft PVP matrix leaving circular pores at the surface of the composite film. These pores are around 350 nm sized as the size of PS particles. Thus, a highly porous film is formed ultimately in this case. This type of structure is responsible for the highest value of R due to the faster diffusion of solvent molecules into the films through these voids which confirms our arguments above.

Fig. 5.27 shows the SEM images of composite films after solvent vapor treatment. It is seen that substantial changes occurred in morphology of the composite films. The hard PS particles lost their initial spherical shape and formed a more or less continuous

phase depending on AgNPs content. The flat and smooth surfaces of all film samples indicate that interdiffusion of the PS polymer chains take place. Despite the flat surface of composite films, AgNPs aggregations are seen with increasing AgNPs content. Here, bright areas in Fig. 5.27 (b,d) are due to the presence of a relatively soft AgNPs clusters. Moreover, in the 50 wt% of AgNPs content film, the circular pores are seen to disappear. It is understood that, upon exposure of solvent vapor, polymer becomes plasticized and sufficiently mobile to self assemble at the room temperature. PS particles come into contact with each other and coalesce forming a continuous network. As AgNPs content increased, AgNPs particles form clusters during the vapor exposure and small clusters are obtained on the surface of 10 wt% of AgNPs content film in Fig. 5.27 (b). During vapor exposure, the AgNPs clusters grow in size, and form larger clusters with further increase in AgNPs content (see Fig. 5.27(c,d)).

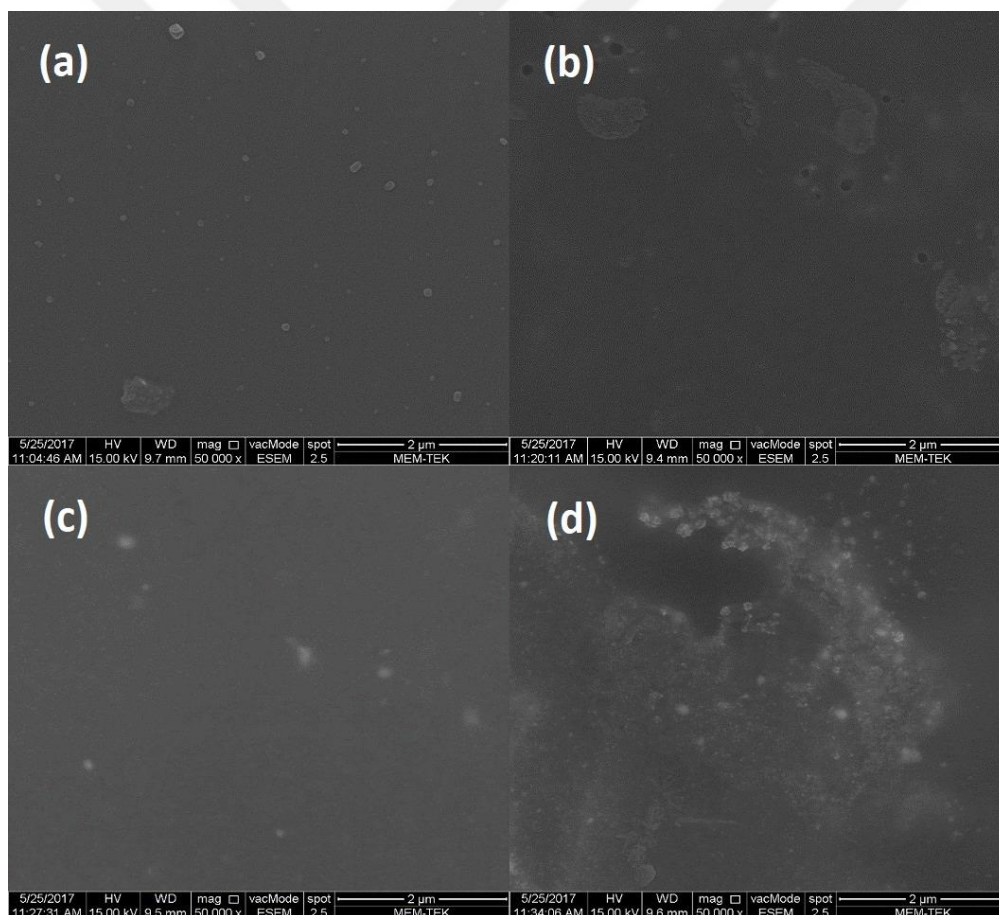


Figure 5.27 : SEM images of PS/AgNPs nanocomposites with (a) 0, (b) 10, (c) 30 and (d) 50 wt% of AgNPs content after exposure of solvent vapor.

Neighboring clusters meet and touch leading to the percolative AgNPs network which contributes to higher electrical conductivity. The existence of such clusters also explain the decrease in $(I_{tr})_{\infty}$ values with increasing AgNPs content (see Fig. 5.24) due

to the light scattering from surface of the films. This indicates that chloroform-heptane vapors induce the phase separation of AgNPs and PS polymer, and the interconnected AgNPs clusters can enhance the conductivity of PS/AgNPs films. This observation suggests that this phase separation is induced by the solvent vapor treatment. In conclusion, SEM micrographs confirmed the UVV and fluorescence quenching data and also the increase in conductivity of composites.

5.2.4 Electrical conductivity

The effect of the AgNPs content on the electrical conductivity of PS/AgNPs composite films was also analyzed. The electrical conductivities of film samples were measured by two probe method after the vapor exposure as a function of AgNPs content and the results are shown in Fig. 5.28. In particular, when increasing the AgNPs content the electrical conductivity of nanocomposites was found to increase from $\sim 10^{-14}$ S for pure PS (0 wt% of AgNPs content) film to $\sim 10^{-11}$ S for pure (100 wt%) AgNPs film. This shows that the conductivity of PS increases by 3 order of magnitude when the AgNPs concentration reaches to 100 wt%. This indicates the enhanced conductivity of PS matrix with increasing AgNPs content. With increasing nanoparticle content, the AgNPs particles form clusters and spacing between them decreases, so that the electron tunnelling between neighbouring clusters and conducting paths through the composite films occur (see Fig. 5.27(b,d)). This results in an increase in the conductivity of the composite films. However, this conductivity values are typical for insulators so that the composite films behave like an insulator even at 100 wt% of AgNPs content. Here, it should be noted that the stabilization of silver (Ag) particles by PVP polymer negatively affects electrical conductivity. This is because PVP is an intrinsically insulating stabilizer which puts an insulating layer around the Ag particles, so that Ag particles remain isolated within the polymeric film. So, the possibility of Ag particles to become contacted to form an interconnected conducting pathway is low due to the effective hindrance of the surrounding dielectric PVP. Therefore, no apparent transition zone of a rapid conductivity change is observed for these films at all. The conductivity could be increased further with reducing PVP stabilizer concentration or using a conductive stabilizer.

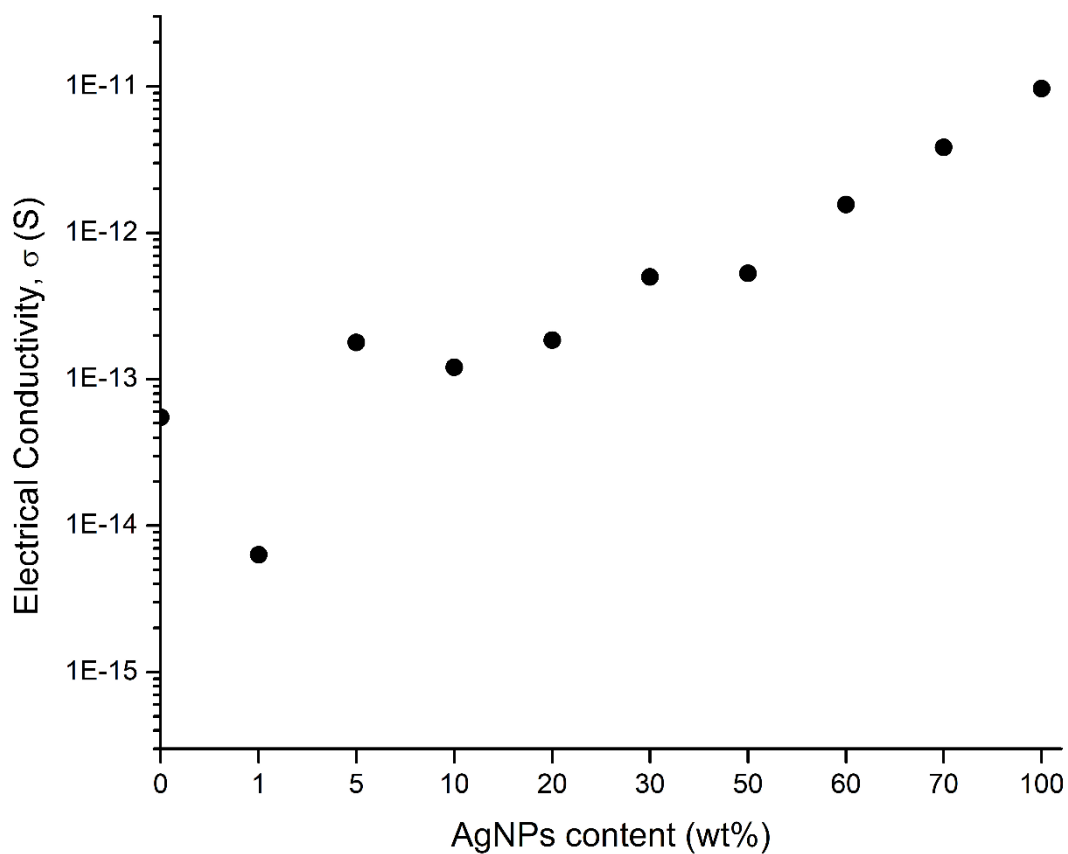


Figure 5.28 : Variation in electrical conductivity, σ (S) of PS/AgNPs nanocomposites with AgNPs content (wt %).

6. CONCLUSIONS

In this study, we investigated the film forming, morphological and electrical properties of PS/AgNps composites dependent on AgNPs content using steady state (SSF) and fast transient fluorescence (FTRF) techniques in conjugation with UV-vis (UVV) and scanning electron microscope (SEM) techniques. The effect of AgNPs content on these properties were studied in two different ways by annealing the films and exposing the films to a solvent vapor and the results were compared.

In the first experiment, PS/AgNPs composites with different AgNPs content were prepared in powder form and annealed above T_g of PS polymer at various temperatures between 100 °C and 280 °C. In order to monitor the film formation process of these composites, fluorescence spectra, fluorescence decay curves and optical transmission measurements were performed after each annealing step.

From optical data, it was observed that classical latex film formation occurred in the range of 0-30wt% of AgNPs content and above this range no film formation takes place. The surface morphology of the films was found to vary with the AgNPs content. The results also showed that there is a good correspondence between the optical data and SEM images. Our study presents useful information and ideas about the kinetics of film formation in metal based composite systems. The emission spectrum became narrower with increasing AgNPs content. Fluorescence enhancement and reduced lifetime were also observed with increasing AgNPs content in the range of 3-30 wt%. This can be understood in terms of increased radiative rates due to interactions between the pyrenes and the electron plasma in nearby silver nanoparticles. Therefore, this study can be used to develop novel dye-labeled polymer/metal composite films with bright and narrow emission bands. In addition, this approach provides a general and effective approach for preparing functional materials, which can be applied to various other materials. In this respect, this work presents a simple and efficient method to produce surface enhanced fluorescence (SEF) in PS thin films using plasmonic AgNPs nanoparticles. This approach could be useful to start a new research field in exploring the capabilities of these polymers for fluorescence sensing mainly in bio-applications.

In the second experiment, the powder PS/AgNPs films were prepared in the same manner and exposed to a solvent vapor. The time dependence of the transmittance of these films were recorded. Seven different composite films were determined. In order to monitor the film formation behavior of the composites, fluorescence decay curves and optical transmission measurements were done during vapor exposure time. It is clearly seen that solvent vapor can successfully initiate the film formation process since the polymer chains obey the $t^{1/2}$ law during interdiffusion.

As it is seen from photon transition measurements data, in the range of 0-30 wt% of AgNPs content obeyed the classical latex film formation. The reptation frequencies of the composites which are obtained from spectroscopic data were found compatible with the SEM images. In the range of 0-30 wt% of AgNPs content, transparent films were obtained (above 85% transparency). However, above this range films were lost their transparencies due to aggregations of silver nanoparticles. Electrical conductivity of the composite films were also determined. The conductivity of composites showed an increase of 3 orders of magnitude with increasing AgNPs content. However, composite films were still found as dielectric. The increment of the electrical conductivity with increasing AgNPs content can also be supported by SEM images. The aggregations in film morphology that mentioned above is given a rise to the electron tunnelling between neighbouring clusters and conducting paths through the composite films. It can be concluded that chemical vapor deposition in order to obtain composite films is a strong alternate way in particular for coating industry.

The transparency of the composite films which are obtained by solvent vapor were found higher than the thermal annealed films. For both experiments, it is shown that the film formation is seen in the range of 0-30 wt% of AgNPs content. Electrical conductivity of thermal annealed films almost did not alter with the increasing AgNPs content. Despite, the films which are exposed to solvent vapor were found 3 orders of magnitude conductive. However, for both experiments, all films were found dielectric due to the insulating behavior of PVP. Decreasing PVP ratio of AgNPs can lead to increase on the conductivity of these films. So that, with further researches metal reinforced PS composites can potentially be used as coatings especially for the electronic devices.

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PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- Akaoğlu, C., Uğur Ş. 2017. Solvent Vapor Induced Film Formation of PS/AgNPs Composites Using Spectroscopic Techniques, *Journal of Applied Polymer Science*. (Submitted article)
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