

Modification of TPE Using Selected Additives

By

Lim Chun Piao

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Supervisor: Prof. Dr. Rosiyah Yahya

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ABSTRACT

Blends of well characterized hydrogenated polystyrene-polybutadiene-polystyrene (SEBS) triblock and additives consisting tackifiers provide unique rubbery and glassy network interaction with controlled amounts of volume fraction (ϕ) of certain phase. Such systems also provide quantitative information correlated from the concentrations of trapped chain entanglements in polymer additives blend. Two different resins (aliphatic type, Sukorez SU420 and aromatic type, Norsolene W85) were blended carefully in various amounts with a typical SEBS triblock copolymer (TSCR's Taipol 3152H) to form three series of samples for viscoelastic study. The unusual behaviours in dynamic mechanical properties suggest that complex morphology of gyroid exists in certain blending ratio.

The mechanical properties of these blended materials were studied in sinusoidal oscillation of film tension mode at 1 Hz over a temperature range from room temperature to about 110°C. The effect of tackifier mixture on the mechanical properties depends upon their compatibility and concentration in the network, as well as partial interaction with other phase. It acts as a diluent, lowering the storage modulus in the rubbery region. Several unexpected mechanisms appeared as a result of suspected gyroid structure formation, and their existence resulted from certain critical volume fraction of components. The various mechanisms (chain architecture, morphology formation, chain topology) associated with the polystyrene chains have been incorporated from previous efforts whose parameters were given in terms of the structural and compositional features of complex morphology formation. The correlation in between compatibility, morphology and rheology properties successfully predicts the level and the location of the dynamic response for the various blends studied here.

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LIST of SYMBOLS & ABBREVIATIONS

BCC	body centred cubic
C5	aliphatic petroleum resin
C9	aromatic petroleum resin
°C	degree celcius
δ	tan delta
DCPD	dicyclopentadiene
DMA	dynamic mechanical analysis
etc	<i>et caetera</i> ; and the others
G'	dynamic storage modulus
G''	dynamic loss modulus
G_{Mix}	plateau modulus of mixture
HPC	hexagonal packed cylinders
i.e.	for example
log	logarithms
M_n	number average molecular weight
M_w	weight average molecular weight
No.	number
OBDD	ordered bicontinuous double diamond
PB	polybutadiene

PS	polystyrene
SBS	poly(styrene-butadiene-styrene)
SEBS	poly(styrene-ethylene/1-butene-styrene)
SIS	poly(styrene-isoprene-styrene)
ref.	reference
TPE	thermoplastic elastomers
Tg	glass transition
wt	weight
vs	versus
ϕ	volume fraction

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1. INTRODUCTION

Complementary theoretical¹⁻³ and experimental⁴⁻⁵ efforts are continually preceded to complement the current understanding of block copolymer phase behaviour and its dynamics properties under a wide variety of conditions. The driving force of such efforts is to produce controllable microstructure polymeric materials with the superior properties needed to develop new,⁶ as well as improve existing applications which are more demanding nowadays.⁷

The presence of solvent affects segmental interactions and may alter interfacial geometry of both phases existed in block copolymer, thereby influencing morphological development, especially if the solvent is only preferentially compatible with one phase of the copolymer. From that, the study used two types of different solvents to modify its inherent properties, with typical focus on polystyrene (PS) phase changes.

While numerous studies have elucidated the effect of a parent homopolymer on the morphological characteristic and mechanical properties of microphase-ordered block copolymer blends, few comparable efforts have focused on dynamic effect for presence of low molecular weight block selective, high glass transition (T_g) solvent in similar blends⁸. In fact, the key factors for their versatile application are indeed the interfacial properties⁹ of the two highly segregated blocks, therefore dynamic mechanical, morphology and correlation in between them are important aspects to study, even though it is not well understood in spite of a detailed knowledge of phase behaviour of simple linear block copolymers. Hence, it is of prime importance from materials scientific stand point that such correlation is intensively investigated.

1.1 The Purpose of this study

The introductory chapter provides some basic background information which should help to gain more complete appreciation of the goals of this study and of the particular approach taken here to achieve these goals.

The motivation of studying such mixture derived from the desire to design compounds or blends whose properties are even superior than that either components, rather than utilizes much more cost and manpower involved with research and facility setup for mass production plant to commercialize the new class of polymer. An interesting and valuable example of the blends are polystyrene-poly(*n*-butylmethacrylate) diblock copolymer, in which the tensile strength is found to excess both independent components in a certain composition.¹⁰

For block copolymer blends, both blends being microphase separated, may offer the chances to tailor desired mechanical properties. For this reason, the primary goal of this work was to investigate the effect of blending tackifiers on the dynamic mechanical behavior of block copolymers as a function of their molecular architecture, compatibility and both with total compositional morphology correlation. The focus was especially placed on the role of various types of tackifiers and their effects on the dynamic mechanical of polymer blending. Thus, the study is limited to amorphous styrene-ethylene/1-butene (SEBS) block copolymers in a narrow blending range of different types and dosages of additives (resins).

2. LITERATURE REVIEWS

2.1 Block Copolymer

A block copolymer is composed of different homopolymer segments linked sequentially to become macromolecule. For example, triblock copolymer of the A-B-A type, where the blocks A are thermodynamically incompatible with the blocks B resulting in a rubber consists of two substantial distinguishable phases: a continuous elastomeric phase (blocks B) and a basically discontinuous hard, glass-like plastic phase (blocks A) called domains embedded in rubbery phase, forms a unique and versatile group of polymers possessing interest nano-scale microphase separation morphology.¹⁰

Since introduction of block copolymer, its unique characteristic have attracted and established multibillion dollar industry, where styrenic based block copolymer make up of approximately 50%.¹¹ With almost none modification required, it can adapt the use of conventional thermoplastic processing techniques including extrusion, injection-molding, and blow-molding clearly demonstrate part of the major advantages in the application of it¹², as its reason will be elaborated below.

2.1.1 Properties

Polymers are complex chain molecules formed from the polymerization of smaller simple molecules called monomers. The classification of polymer can be categorized by reaction to temperature, chemistry of synthesis, structure, and area of application. Among them, block copolymers are partly consist of a “hard” segments which may be glassy, quasi-crystalline or hydrogen bonded phase.¹³ This “hard” blocks normally form individual domain together act as physical crosslinks for an elastomeric block forming the continuous majority entangled phase or matrix, as represented in Figure 2.1.

Block copolymer is more famously called as *thermoplastic elastomers* (TPE) due to its combination of processible characteristic of *thermoplastics* (plastics) at elevated temperatures where the hard phase is softened as processing temperature is above their glass transition (T_g), and a physical *elastomers* (rubbers) properties at lower temperature, provided the temperature is not lower than T_g of soft block.



Figure 2.1: Two-phase schematic morphology in thermoplastic elastomers: quasi-crystalline or glassy (hard segments) and amorphous (soft segments) regions.

In other words, TPE is a kind of polymer alloy possessing elastomeric or rubber-like properties at room temperature due to the soft block, where the hard block in different chain tends to agglomerate or anchor together to act as reinforcing filler as well as “reversible” crosslinking sites. Due to the hard block unique thermally reversible characteristic, this mechanically crosslink segment gives the TPE typical strength comparable to vulcanized rubber and processing flexibility, but with the weakness of lack of heat resistance compared to conventionally vulcanized rubber. Unlike chemically, irreversible crosslinking vulcanized rubbers, the physical crosslink of TPE’s hard domain breaks upon heating leading to become a flowing melt of homogenous blend with thermoplastic characteristic, and therefore can be molded without involving vulcanization step. It can be recyclable¹⁴ after used as well due to the same reason, thus greatly reduce waste and more environmental friendly compared to vulcanized rubbers.

Another unique characteristic of TPE is that a very narrow, almost near monodispersity of molecular weight distribution can be obtained for each of the segment in it, due to the particular methods used in synthesis.

2.1.2 Background

The era of TPE began with the advent of block and grafted copolymers, with the discovery of Szwarc,¹⁵⁻¹⁶ or rediscovered¹⁷⁻¹⁸ for the living anionic polymerization. These studies utilised sodium metal naphthalene initiators to prepare poly(styrene-isoprene-styrene) (or SIS), which was the first TPE come with a defined structure. However, this unlucky newborn block copolymer did not have commercial value, as most of the polyisoprene units were 3,4-addition, which meant inherent poor elastomeric properties. The classical TPE properties: high tensile strength and elongation at break, rapid elastic recovery, and no chemical vulcanizing were finally realised with the polymerization by alkyllithium chemistry. Officially, Bailey¹⁹ announced the birth of these exciting materials in 1966 while Holden²⁰ published the corresponding theory in 1967 and then extended to other block copolymer models as well. Nowadays, most styrenic block copolymers are synthesized in industrial scale by living anionic polymerization catalysed by metal organic initiators.²¹ Catalysts like n-butyl and sec-butyl lithium²²⁻³¹ are among the famous, and other major synthesis techniques of block copolymer were summarized by Hillmyer.³²

For anionic polymerization, this type of reaction is carried out in solvent with only two steps involved: initiation of the catalyst to start reaction by forming “living” anion radical, and followed by propagation step where reactive species keep consume the monomer available under sequential addition until chain terminated by protic terminating agent. Figure 2.2 shows the example of anionic polymerization steps by which can produce precise molecular weight of each block for the TPE.

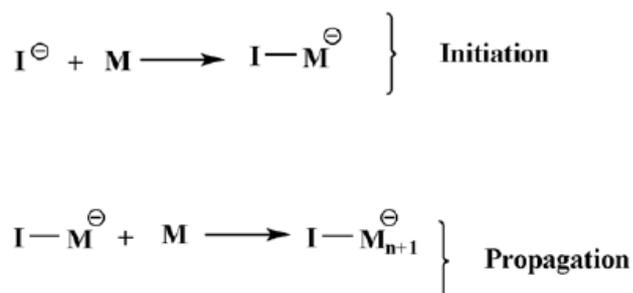


Figure 2.2: Schematic diagram showing two steps of anionic polymerization involving initiation and propagation, respectively.

2.1.3 Architecture and Morphology

Through above steps and combine with two basic routes: sequential polymerization of all blocks and sequential polymerization followed by coupling,³³ the various well-defined architecture of TPE can be synthesized. They may range from simple two-component linear molecules diblock copolymer to the multi-component radial and branched chains (star, cyclic, graft etc.)³⁴, as illustrated in Figure 2.3. To be defined as block copolymer architecture, it must contain at least two or more different polymer chains attached at their end. For instance, linear block copolymers comprise two or more polymer chains in sequence, whereas star-block copolymers have more than two linear block copolymers attached at a common branch point, and the number of branches or arms of star-block copolymer is dependent on the functionality of coupling agent.^{24, 28, 32}

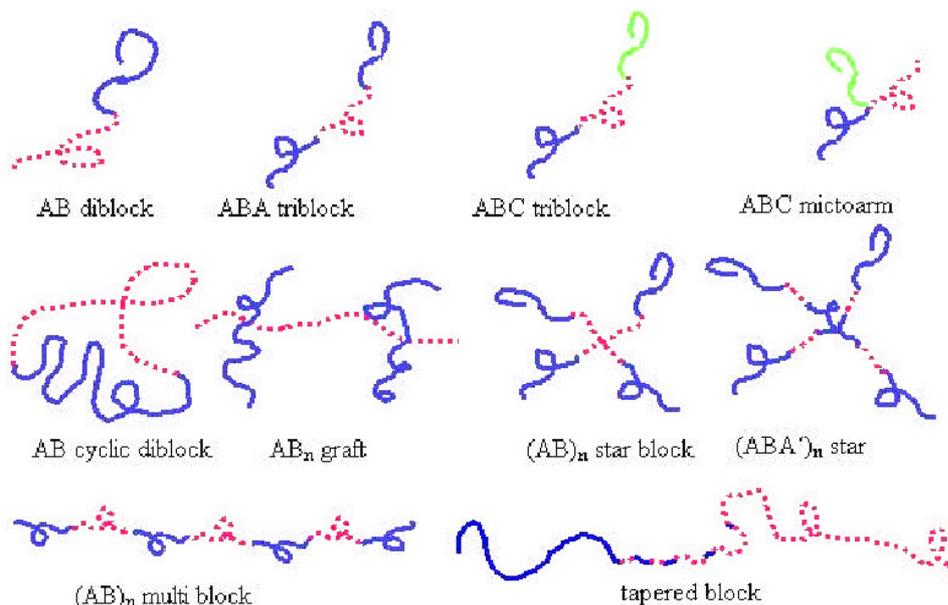


Figure 2.3: Block copolymers of various molecular architectures (A denotes the glassy block).

Further architectural modification (modification of interface, chain topology, block symmetry etc.) may lead to a significant deviation in nanoscale-ordered morphology and physical properties of the

block copolymers, where it involves major factors such as volume fraction and geometry of the endblock domains as they are dispersed in the elastomer midblock matrix. For examples, the basic morphological compositions observed in a two-component block copolymer are shown in Figure 2.4.



Figure 2.4: Scheme showing various classical morphologies for block copolymers; white and black colours stand for glassy hard phase and rubbery soft phases, respectively.

From left to right in Figure 2.4, the trends of changes of morphologies are influenced by increasing the minor phase concentration. The most asymmetric block copolymer owns spherical morphology comprising body centred cubic (BCC) spheres or spheroids of the minor component dispersed in the matrix of the major component. As the volume fraction of the minor component increases cylindrical morphology (hexagonal packed cylinders, HPC) evolves. Symmetric block copolymer exhibits a lamellar morphology consisting of alternating layers of the components. With volume fraction of the minor component keeps increasing the morphology appears in reversed order,³⁵ as shown on right side diagrams of Figure 2.4. In short, with increasing minor component content, these are glassy spheres in a bcc arrangement, followed by HPC, a tricontinuous structure, and lamellae. With increasing content, the minority domains gain in dimensional spheres as 0-D, cylinders as 1-D, lamellar as 2-D, and bicontinuous as 3-D reinforcing complex structures.³⁶

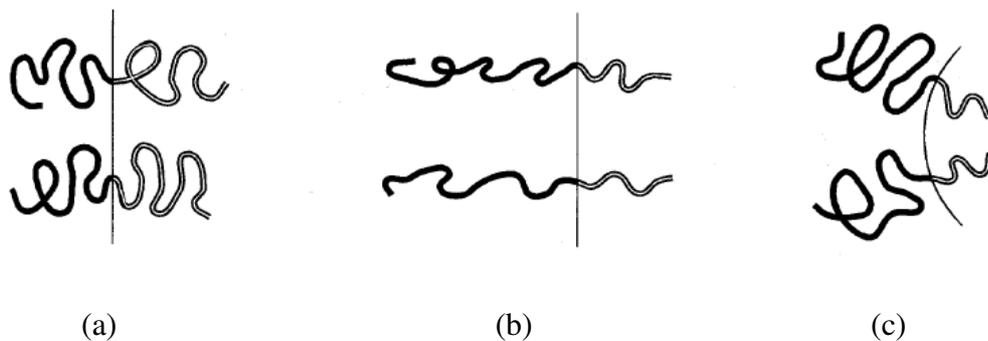


Figure 2.5: Schematic of chain conformation at the microphase-separated state; (a) stable flat interface from a compositionally symmetric AB block copolymer, (b) an unstable flat interface in the case volume fraction of polymer block A, $\phi_A \gg \phi_B$ and (c) a stable curved interface in the case of $\phi_A \gg \phi_B$.

It is easier to conclude that the shape of the block copolymer interface varies with the relative chain length of the component copolymer. As the symmetric diblock copolymer forms a flat interface most likely as illustrated in figure 2.5a, the increase of one component volume relative to that of the other phase will form the curved interface, resulted from the chain stretching which to form the planer interface. In this case the conformational entropy loss of the major component (say of A) is too high, the A chain therefore tends to expand along the direction parallel to the interface to compensate that entropy under conditions that segment densities of both of the block chains have to be kept constant and must be the same as that of the bulk densities of its parent homopolymers. Thus, as a consequence the interface have to become convex towards the minor component B (Figure 2.5c). This kind of interface curvature effect will be more pronounce as the composition of the block copolymer becomes further asymmetric, which can be seen in figure 2.4.

There are of course more complex morphologies existed and reviewed by literatures,³⁷⁻³⁹ but for this study the discussion will be carried out in Results and Discussion section.

2.1.4 Chain entanglements

It was recognized in the early 40's that a system of uncross-linked polymer could exhibit temporary network structures⁴⁰, and that temporary junctions were assumed to be manifestation of strong and widely separated points of coupling among the long-chain molecules. Thus, chain entanglements referred to the temporary constraints of long range molecular motions as mentioned.

For vulcanized elastomer with certain entangled points, they are capable to slip along the chains in order to accommodate the stress applied and hence, introduce additional time dependant mechanism (long time relaxation) in dynamic mechanical behaviour. This phenomenon offers the elastomer much higher proportion of stress-bearing properties than the covalent chemically cross-link site exactly does. For example, in the case of styrenic block copolymers, an increase in the styrene/rubber ratio results in increasing modulus and ultimate tensile strength and decreased its flexibility.⁴¹ The thermo-mechanical

properties and performance of block copolymers are significantly affected by the block lengths and weight fractions of both hard and soft blocks, where the chain entanglements come to play a major role in it.

In fact, the uncross-linked continuous rubbery phase in TPE could also bear stress at each of several entanglement points formed within it, in addition to the glassy phase. And the position of the chains entanglements are randomly fixed due to the possibility of slippage along the chains, for this behaviour it is quite similar to vulcanized rubber system. The effect of the slippage of chains entanglements in TPE will be further explained in the discussion section, where other factor like diluent effect will be taken into consideration.

2.1.5 Hydrogenation

Generally the rubbery block of TPE consists of butadiene or isoprene unit which are subjected to degradation upon exposure, due to their chemically reactive double bond of diene. In order to improve aging resistance quality, the diene bond always been treated with hydrogenation process. The hydrogenation may be achieved in the presence of any of the known catalysts include the Group VIII metals such as nickel, cobalt and platinum, the Group VI metals such as tungsten and molybdenum, the Group VII metals such as manganese and copper. These metals may be used together, as described in U.S. Pat. No. 4,629,766 which is incorporated herein by reference. The hydrogenation step is carried out with a high hydrogen pressure of 20-300 atmospheres, preferably 150-250 atmospheres.

2.2 Tackifiers

2.2.1 background

Tackifier is a general term used for resin that can promote strong tack when mixed with rubbery polymer. Its inherent viscous properties used as viscoelastic modifier to primarily raise Tg of the blend system. For tackifier performance determination, it must fulfil three basic requirements.⁴² It must be reasonably compatible with the component to be blended with. Second, it must have a very low

molecular weight relative to the base elastomer. And finally, the tackifier must have a glass transition temperature that is higher than rubber phase.

Commonly tackifier is referred to hydrocarbon resins which are blends of low mass (typically between 300 g/mol to 10 000 g/mol) thermoplastic copolymer or homopolymer compounds with a polydispersity higher than 1. Tackifier is sometimes referred as a high Tg solvent⁴³ due to its solvency effect on domain it compatible with. Tackifier can be divided into the three groups: hydrocarbon resins, rosin resins and terpene resins. Hydrocarbon resins are based on a petroleum feedstock, rosin resins are based on a natural feedstock: pine trees, and terpene resins are generated from a natural source, wood turpentine or from the kraft sulphate pulping process.⁴⁴ Commercially, hydrocarbon resins are classified by the chemical types of the starting monomer, which are derived mostly from petrochemical sources as shown in Figures 2.6 – 2.8 below:

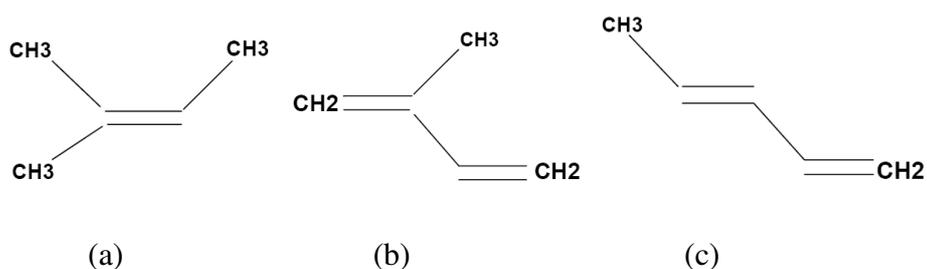


Figure 2.6: Aliphatic type of monomers: (a) isoamylene; (b) isoprene; (c) piperylene.

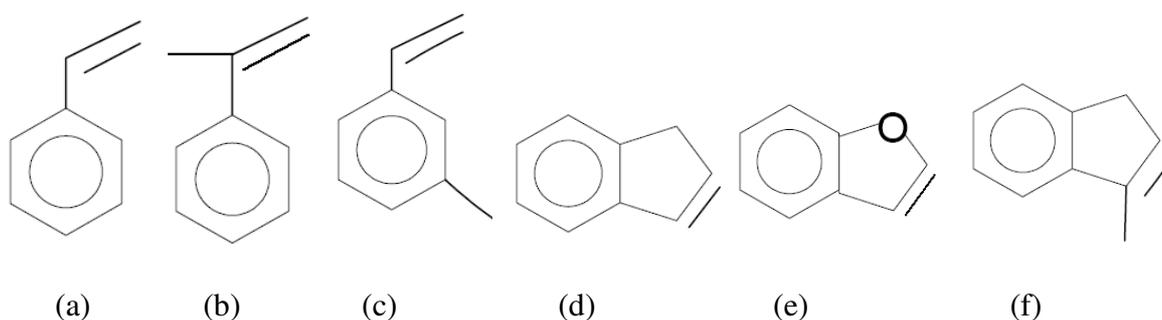


Figure 2.7: Aromatic type of monomers: (a) styrene; (b) alpha-methylstyrene; (c) vinyltoluene; (d) indene; (e) coumarone; (f) methylindene.

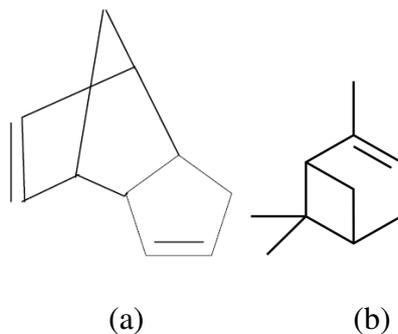


Figure 2.8: (a) dicyclopentadiene (DCPD) and (b) terpenic (bicyclic terpene).

From the above scheme, it is not difficult to understand why aliphatic resin is also been called as C5 resin, as it corresponds to the average of 5 carbon atoms per monomer. The same practice is also applied to aromatic resin which is called C9 resin. For dicyclopentadiene (DCPD) resin, it is actually polymerized from two C5 cyclopentadiene resins, thus the diagram of it showing the 10 carbons based molecular structure. The same logic can be applied to the terpene resin as well.

Lastly, rosin consists of mixture of organic acid called rosin acids, which can be further catalogued into abietic acid type and pimaric acid type, respectively. Because of the rosin natural structure, it is subjected to oxidation upon aging resulting in deterioration of the performance of TPE blend. Thus, modifications such as esterifications are generally applied to rosin to enhance its stability as well as increase the Tg.

The purpose of blending low molecular weight hydrocarbon resins or tackifiers in the TPE is to increase the monomer friction coefficient in the phase the tackifier is compatible with, and lower the number of trapped entanglements in its matrix⁴⁵ hence reducing the value of the total elastic modulus in the plateau zone, where the storage modulus stays relatively constant. Thus mixing of tackifier into elastomer system can improve the wettability and contact strength, which is critical factor in certain applications like pressure sensitive adhesive properties, such as peeling strength and tack.⁴⁶

The compatibility of tackifiers with elastomers can be investigated using solubility parameter theory.⁴⁷ For identical solubility parameter, both are very well miscible. Following scheme shows some examples of the compatible range for both tackifier and polymer:

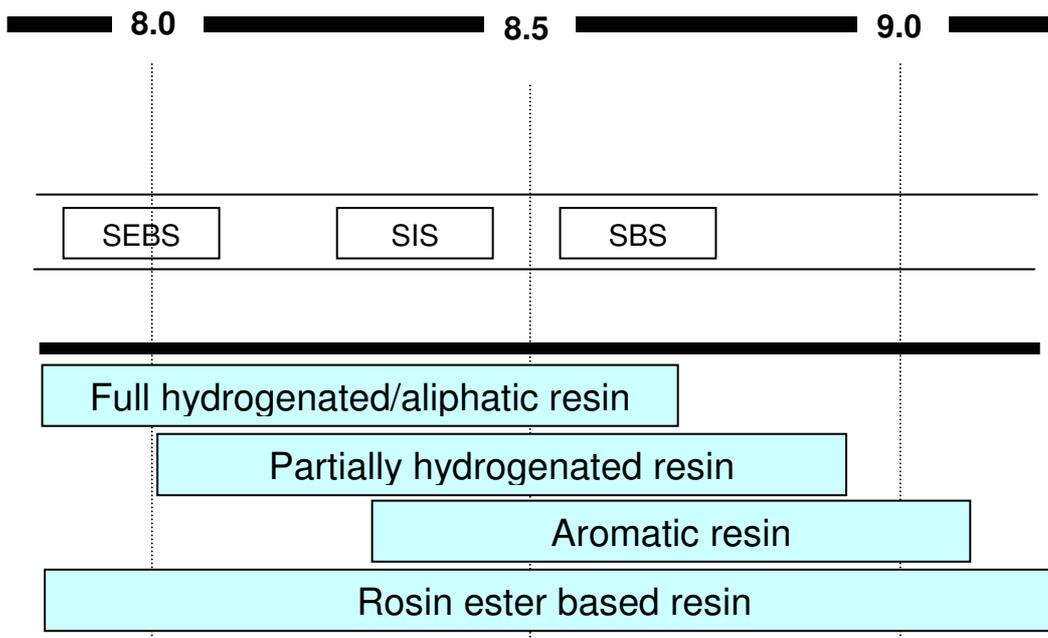


Figure 2.9: Solubility-parameter range with various elastomers and tackifiers.

In industrial scale, wide ranges of petroleum resins are produced by polymerization of various monomers feedstock using Lewis acid catalyst or by a free radical process under heat and pressure condition. For instance, the petroleum resin SU420 used in this study are produced under cationic polymerization of aromatic and DCPD monomers, then undergo further step of hydrogenation. The modification using more than one type of monomer gives diversity in petroleum resin properties as well as their compatibility in polymer system.

2.2.2 Synthesis

Generally synthesis of tackifier will undergo thermal polymerization for low cost consideration, and cationic polymerization for better quality in term of heat stability and light in color.⁴⁸ There are various techniques and advanced processes to produce desirable properties of tackifier to give better performance and improved quality.⁴⁸⁻⁵⁰ For example, as mentioned in US patent 5502140, it is known that for “a given family of hydrocarbon resins, i.e., all of those based on the same feedstock, as the softening point goes up, molecular weights and polydispersity also tend to increase,” and “there is a

trend toward higher softening points and molecular weights as reaction times and temperatures are increased during the thermal homopolymerization of dicyclopentadiene.”⁵¹ It is also known that higher molecular weight of resin will giving more compatible issue with the polymer to be blended. And for conversion of DCPD based resin, for example, to water-white and thermally stable derivatives, high cost of hydrogenation step will involved which is unfavourable from capital consideration.⁵¹

All above challenges can be overcome by careful study of the structural and selected component of resin, and correlated those properties with its compatibility in phase of blending.

3. EXPERIMENTAL

3.1 Materials

3.1.1 Block Copolymer

Commercial linear type of SEBS (mol. Styrene content = 29%, diblock content = 0%) was provided from TSCR (Taipol 3152H). It was chosen because of fully triblock content which will eliminate the untrapped entanglements effect provided by the terminal chains of diblock.

3.1.2. Tackifier Resins

The aromatic modified hydrogenated DCPD aliphatic resin (Sukorez SU 420) provided by Kolon Chemical Co. Ltd. It has softening point (ring and ball) of 120, Tg of 70, and weight average molecular weight (Mw) of 800. For water white aromatic resin (Norsolene W85) from Cray Valley, it has Mw of 1050, number average molecular weight (Mn) of 600, softening point (ring and ball) of 85, and Tg of 35. Both are commonly available in the commercial market.

3.2. Experimental Methods / preparation

3.2.1. Blend of Polymer and Tackifier

Table 3.1: Formulation of blends, by weight percentage.

Polymer/tackifier(s)	Blend ratio
3152H/SU420	100/0, 100/70, 100/155
3152H/W85/SU420	100/70/80, 100/70/90, 100/70/110
3152H/W85/SU420	100/90/80, 100/90/90, 100/90/110

The tackifier(s) were blended with the SEBS in different weight ratios to form total of 3 series of samples, as the detail of blending ratio is given in table 3.1. The blending was accomplished by dissolving known weight of tackifiers and SEBS in toluene to form a solution containing around 10% polymer. And the solution was stirred for few hours until all components are dissolved. It was then poured carefully on a flat teflon panel to avoid bubble formation, and solvent was allowed to evaporate

for several days. Uniform films about 1 mm thick were obtained, which is free of visible surface flaw and trapped air bubble. Annealing of the sample at 100°C for 24 hours was done before performing the test. It is as to remove radial orientation effects of polystyrene domain induced during the solvent casting procedure.⁵²

3.2.2. Thermal Analysis

The dynamic properties are generally described in terms of storage modulus, loss modulus and damping factor which are inter dependent on temperature, time and frequency. In this study, the dynamic storage modulus (G'), loss modulus (G'') and loss factor ($\tan \delta$) of the specimens were determined as a function of temperature.

The thermomechanical properties of the blends were determined as a function of temperature using DMA Q800 (TA Instruments) in the film tension mode. Most of the data were obtained at 0.5% strain and 1Hz frequency in temperature ramping of 5°C/minutes from room temperature to about 110°C.

A typical set of result obtained from the dynamic mechanical analysis (DMA) experiments is shown in Figure 4.1. The dynamic mechanical data such as logarithms of the storage modulus, G' loss modulus G'' and $\tan \delta$ are presented in DMA spectra as a function of temperature. The units of the modulus are in Pa, and the T_g of the blend was determined by reviewing $\tan \delta$ by temperature sweep at a constant frequency of 1 Hz and strain of 10 micron.

4. RESULTS AND DISCUSSION

The important features of these response curves will be discussed, with special focus placed upon the relationship between changes in the endblock network structure (PS) and the observed changes in the dynamic mechanical behaviour. For block copolymer network which behaves similarly to conventional vulcanized rubbers, the added advantage here is that changes in mechanical behaviour can be correlated with proper control in network structure explained in following cases. By using selected tackifiers, it will either entangle rubber networks to disentangle in the plateau region, or entangle glassy segment which leads to increase in the plateau region. Above changes lead to different phase behaviour and mechanical properties as discussed below.

DMA of the block copolymer of 3152H SEBS gives an important insight into their phase behaviour. The shift of glass transition temperature of the components relative to that of the corresponding tackifiers blend may provide valuable information on the compatibility of the constituent blocks. For a mixture of two compatible polymer with different T_g , the blends will exhibit only single T_g , which is influenced by each individual T_g value and weight fraction of the two components. Compatibility is identified by a pronounced shift of the $\tan \delta$ peak temperature, associated with a depression in the storage modulus in the plateau. An incompatible system is confirmed by a minimal shift of the $\tan \delta$ peak along with an increase in the storage modulus in the plateau.

T_g or glass transition is defined as the temperature which an amorphous, glassy material softens and becomes rubbery or viscous. It represents the onset of long range coordinated molecular motion. If compared to movement of motions, it involves only 1-4 chain atoms below T_g , some 10-50 chain atoms attain sufficient thermal energy to move in a coordinated manner in the glass transition region.

For DMA spectra, T_g is defined by the location of the loss tangent peak, $\tan \delta$. For typical microphase separation characteristic of TPE, it gives 2 T_g and a broad plateau region between two T_g . This indicates that the blocks were incompatible with each other and localized in separate microdomains. This microphase separation was called "segregation". The example can be seen in Figure 4.1, where the neat linear triblock copolymer Taipol 3152H has a T_g at about 105°C for PS domain. The

polybutadiene (PB) midblock Tg is not available as it happened at sub-ambient temperature which was out of the temperature range of study.

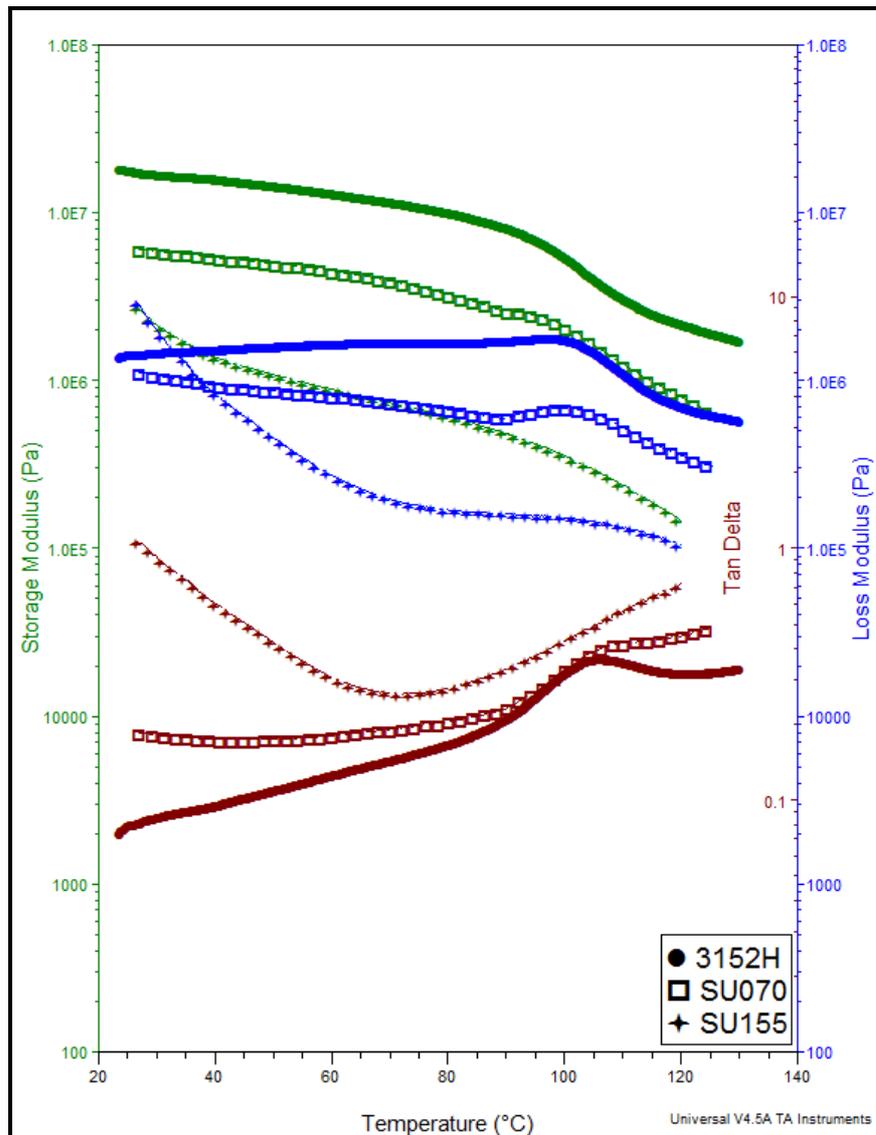


Figure 4.1: Dynamic mechanical spectra of Taipol 3152H/Sukorez SU420 blends (● 100/ 0, □ 100/70, + 100/155).

Temperature sweep of $\log G'$, G'' and $\tan \delta$ are given in Figure 4.1 for the pure Taipol 3152H SEBS triblock copolymer and mixtures of 3152H/SU420 in difference ratios. It can be seen that adding of SU420 PB midblock compatible resin into SEBS will have tremendously downward effect on the both G' and G'' , with even more of an order of magnitude of dropping in both plateau region was observed for ratio of 100/155 (wt/wt) 3152H/SU420 blend, suggesting compatibility in between SU420 and PB block. The degree of compatibility depends on the tackifier/rubber solubility, and the entanglement of

its molecular chains.⁵³ The plateau of loss modulus, which becomes more prominent with increased midblock compatible resin (SU420) content, are attributed to the frictional effects associated with the slippage of the entanglements.

While the T_g of the tackifier has less connection to the entanglement of chains, in contrast to the tackifier content.⁵⁴ And from literature⁵⁵ clearly demonstrated that for small molecular weights of homopolymers, these are easily dissolved in the microphase-separated structure of block copolymer. However when the molecular weight of a homopolymer is much greater than that of the corresponding block, macrophase separation occurs.

For example, blending of styrene-butadiene-styrene (SBS) with PS,⁵⁶⁻⁵⁷ the compatibility between PS and polystyrene domains of SBS is influenced by the relative molecular weight ratios of M_n of homopolymer over the M_n of copolymer. And it was tentatively explained on the basis of entanglement formation between the two components upon mixing, although no experimental confirmation of such hypothesis was presented. The modification of endblock polystyrene (PS) of block copolymer have even more pronounced improvement of the mechanical behaviour as the polar groups were inserted into the PS domains either by direct chemical modification, suggested by Weiss⁵⁸ and Passaglia⁵⁹ or by blending processes which studied by Picchioni.⁶⁰ Theory also suggests that compositional polydispersity is also important for effective compatibilization.⁶¹⁻⁶² It leads to a greater gradation in composition across the interface, and consequently a lower configurational entropy of the homopolymers.

As the experiment temperature range is limited from room temperature, the shifting of PB $\tan \delta$ on toward higher value was not be able to investigated. Nevertheless, from the trend of adding more SU420 resin into the blend, the $\tan \delta$ of PB observed is also on trend of shifting to higher temperature as the function of T_g of tackifier, and a decrease of the rubber plateau is recognizable which in agreement with literatures.⁶³⁻⁶⁵ This unseen higher peak height of this $\tan \delta$ shifted towards higher temperature range demonstrated that the PB block have more viscous property appearing to more mobility of molecular chains. It is due to the high pendant and bulky group of the tackifier that

interrupts and sterically hinders the segmental movement of chains.⁶⁵ Even though the entanglement plateau area was reduced or diluted by tackifier addition contributing to lower G' , the T_g increased and the height of the $\tan \delta$ peak increased with increasing tackifier concentration, as it introduced more viscous properties into the blend. Moreover, the onset of the terminal zone (G') did not move to lower temperature suggesting that PS segment did not interfere by diluted PB chains which can more readily slip by one another, implying to the less chains entanglement derived from swelling effect of SU420 tackifier in PB phase.

From Figure 4.1 also, the observed $\tan \delta$ of PS block is not detected on a blend of 100/155 (wt/wt) 3152H/SU420. It is interesting as the PS domain is likely to “disappear” in the DMA spectra, where the large drop of G' could not be seen. The literature⁶⁴ reported it is result from the non-existence of microphase-separated PS domains, meaning that PS is partially compatible with rubber matrix. From author interpretation, it is more likely due to the detection limit of DMA to detect the changes of PS, as volume fraction of the PS approaches to about 11% in that particular blend ratio. For the other blend of 100/70 (wt/wt) 3152H/SU420, the adding of SU420 hardly affects the T_g of PS block, evident from the $\tan \delta$ peak location. Indeed, $\tan \delta$ peak actually moves slightly higher than the neat 3152H, indicating the blending of the SU420 will introduce to the system more segregation, meaning more pure PS domain exists as lesser PS chain is entrapped into PB phase.

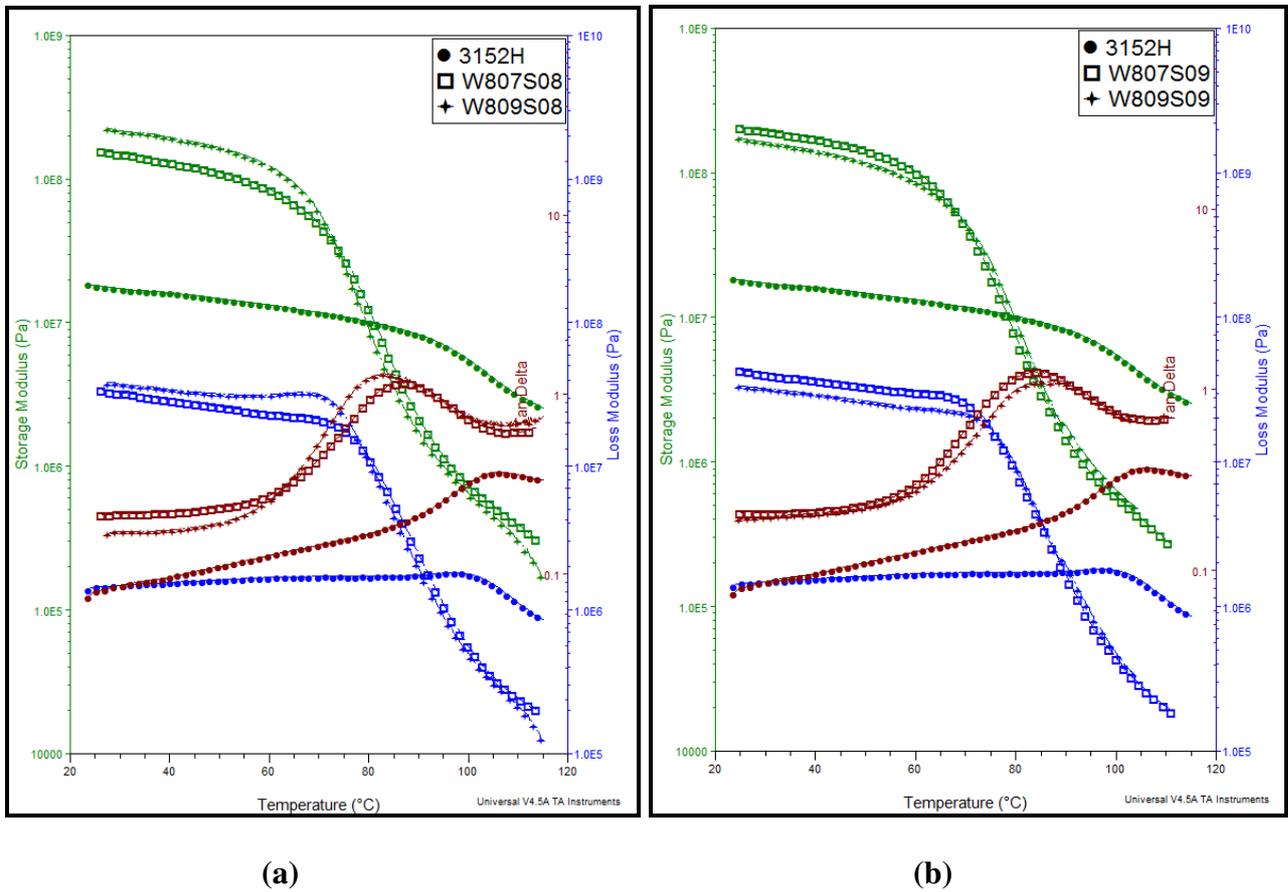


Figure 4.2: Dynamic mechanical spectra of Taipol 3152H/ Norsolene W85/ Sukrez SU420 blends:

Figure 4.2(a) (● 100/0/0, □ 100/70/80, + 100/90/80); Figure 4.2(b) (● 100/0/0, □ 100/70/90, + 100/90/90).

Results from DMA presented in Figure 4.2 are used to confirm the compatibility between 3152H and added aromatic resin in relation to the total volume of this low molecular weight tackifier. With increasing of W85 weight fraction, the $\tan \delta$ shifted down from about 105 °C for pure 3152H to the range of 80-85°C, and both $\tan \delta$ spectra (Figure 4.2(a) and Figure 4.2(b)) show tremendously increase of level due to the interfacial volume.⁶⁶ However, this increasing behaviour is not identical for different W85 composition across the two involved series. For Figure 4.2(a), the increase of W85 concentration resulting in increase of both G' and G'' corresponds to prediction trend, whereas for Figure 4.2(b), further increase of W85 concentration from sample W807S09 to W809S09 resulting in opposite trend, although both G' and G'' of Figure 4.2(b) are comparably higher than Figure 4.2(a). The significant drop in T_g reflects that low T_g of W85 was well miscible with PS domains of 3152H, resulting in only single T_g lying between this two components which is in line with the Fox equation⁶⁷ prediction:

$$1/T_{gm} = w_1/T_{g_1} + w_2/T_{g_2}$$

Where T_{gm} , T_{g_1} and T_{g_2} are glass transition temperatures of the mixture and of components 1 and 2, and w_1 and w_2 are the weight fractions of constituent components.

Interestingly, for comparison of Figure 4.2(a) and (b), the adding additional W85 aromatic resin to the blend of lower concentration of SU420 caused the PS T_g to shift downward to lower temperature, whereas for higher SU420 concentration environment in Figure 4.2(b), the T_g unexpectedly shifted to higher temperature with lower area of $\tan \delta$ peak. Above results actually suggest that certain blend ratio of SU420 in the series as shown in Figure 4.2(b) having synergies on the segregation of both phases, which is well correlated with Figure 4.1 final observation. But the rule is not followed by series as compared in Figure 4.2(a), revealing that some other types of factors are involved. If we assume that both morphology behaviours exist in the same manner, this kind of unexpected changes should not have happened.

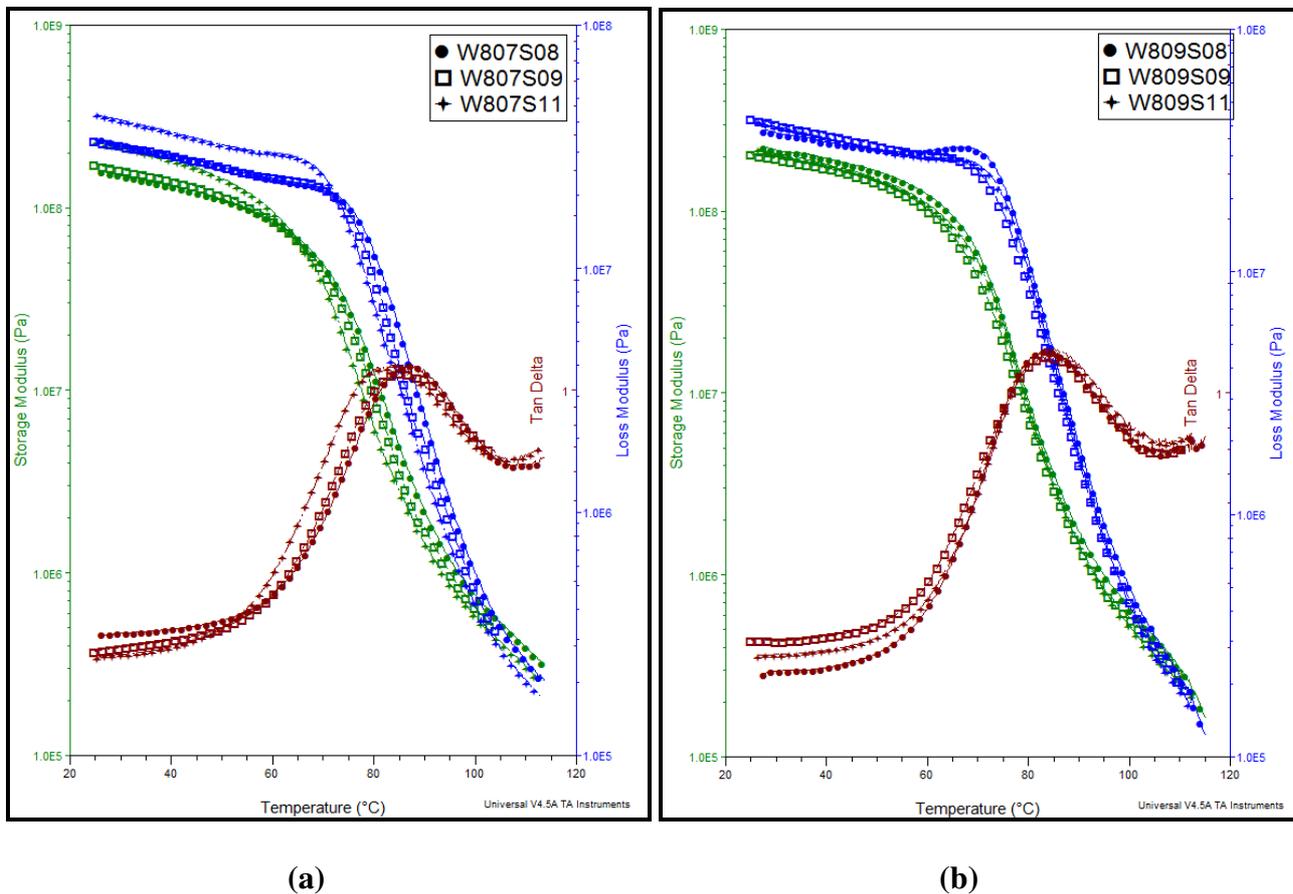


Figure 4.3: Dynamic mechanical spectra of Taipol 3152H/ Norsolene W85/ Sukorez SU420 blends:

Figure 4.3(a) (● 100/70/80, □ 100/70/90, + 100/70/110); Figure 4.3(b) (● 100/90/80, □ 100/90/90, + 100/90/110).

For SEBS/W85/SU420 blend in Figure 4.3, both series show plateau modulus (G_{Mix}) decreases (except sample W809S11 which gives increasing trend to be discussed later) with the increasing amount of SU420, which is similar to the behavior of SEBS/SU420 series blend. Comparing W809S11 and W807S11 blend with pure 3152H, both T_g of PS were shifted toward lower temperature in different degrees by adding more W85 endblock associated resin in the ternary mixture. This clearly demonstrates that adding even slightly more W85 in SEBS block copolymer will influence PS phase, and compatible blends of them gave lower T_g temperature suggesting that lower T_g of W85 has reduced the total T_g blend of PS/W85, which is in good agreement with previous observation in Figure 3152H vs 3152H/W85/SU420 (both 70 and 90 ratio series).

The dropping of $\tan \delta$ peak towards lower temperature also means that, the compatibility in between PS and W85 will lower the overall blend cohesive and heat resistance, compared to the pure 3152H

alone. Beside the diluting effect of low molecular weight of W85, the adding of W85 will cause lesser entanglements in between PS molecular chain and interaction of it with the resin. This will further contribute the weakening of the strength of PS/tackifier blend domain, as the T_g is on low shift trend leading to the more mobility of PS molecular chains in blend, resulting from total reduction of entanglements sites by present of low molecular weight of W85. The dropping of T_g of PS domains also contributed by the reducing overall chain packing of PS block derived from blending of short molecular chain of W85 that would introduce more spacing. (from page 51 of ref. 13)

For G_{Mix} of W809S11 blend, this really gives us a surprise, by which our prediction of further increase of SU420 dosage in Figure 4.3 (a) series will definitely lower both moduli implying it is a typical type of aliphatic resin that only compatible with rubbery midblock. From literature, it showed that only two reasons why the modulus of the mixtures increased with an increasing amount of tackifier: one is that the resin is miscible with the PS endblock and the other is that the resin itself forms a macrophase which contribute the modulus value (from page 5211 of ref. 46). For 1st reason, if it is miscible with PS block, then the $\tan \delta$ of PS peak should be higher due to more interaction of curvature interface, as shown in Figure 4.3 (b) that all $\tan \delta$ of PS are higher when more ϕ PS exist due to additional dosage of W85. And for second reason, the film cast from W809S11 blend did not show any turbidity as a sign of macrophase separation, thus also been rejected.

By combination of Figure 4.2 and 4.3 series and making comparison, the possibility is that there are other factors that dominate the unusual dynamic properties as discussed. From further study, it was found out that there are possibility of complex morphology changes in certain blend ratio, which is suggested by Thomas⁶⁸⁻⁶⁹. He found out that that the ordered bicontinuous double diamond (OBDD) structure appeared in the case of linear triblock copolymers in a composition range 0.32-0.36 independent of whether the minority components are the end blocks or the midblock. And previous study only found out that diblock and star block copolymers can form such gyroid morphology in certain ϕ .^{37, 11}

For example, in PS/Polysiprene blend, the gyroid can only been formed in the range of 0.28-0.34 of ϕ PS (from page 336-364 of ref. 66).

And now if we consider that all tackifiers in blend will 100% dissolve in their respective miscible phase only, then the volume fraction of each phase is actually added up of the tackifier and block phase volume. From the calculation it is found out that ϕ PS for W807S11 series actually falls into about 0.337, and another potential example is W807S09 with the PS volume fraction of about 0.362. And for gyroid morphology, the modulus is higher than other types i.e. BCC and HPC, resulting in contribution to higher modulus in both blends than as expected. OBDD structure also has more interface than BCC or HPC, which is in good agreement that higher $\tan \delta$ peak is observed in both W807S11 and W807S09 blends.

5. CONCLUSION

The study shows viscoelastic properties such as plateau modulus and glass transition of various blends, depend not only on the miscibility of components added, but also strongly affected by morphology factors. PS phase will be influenced by the concentration of added tackifier which is compatible, and shows one T_g in DMA spectra indicating complete miscible with the W85 aromatic resin. Adding of rubber compatible aliphatic resin will reduce G' of blend while no negative effect on PS phase. For ternary blend with one more addition of resin, the system is still predictable according to the classical theory. And the unforeseen higher G_{Mix} of few exemptions have also been deducted through implying gyroid morphology assumption.

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