تأثير خلط البوليبوليا ستايبرين مع المطاط على الخواص الميكانيكية والبنية

رسالة مقدمة
إلى قسم العلوم التطبيقية في الجامعة التكنولوجية
كجزء من مطالب نيل درجة الماجستير
في علم المواد

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**Abstract**

The thesis involved preparation of polymer blend as two systems, the first PS/ABS prepared by single screw extruder, the second PS/SBS prepared by Haake PolyDrive extruder. Different composition ratios were used with the aim of arriving at the best physical blending percentage.

In order to study the influence of blending on the mechanical properties, thermal properties and morphology several tests are performed including (tensile, impact resistance, Differential scanning calorimetry (DSC), optical microscopy and scanning electron microscopy).

The results from this work show that the mechanical properties for blend system PS/ABS at compositions 70/30, 60/40 and 50/50 have mechanical properties much better than the pure constituents. The mechanical properties for the blend system of PS/SBS, dependent on the amount of SBS content, indicate in general it nearly obeys rule of mixtures.

The (DSC) test for blend system of PS/ABS gives good indication of improving state of miscibility for most blend ratios; there is only one glass transition temperature between the two values for pure polymers. Also the DSC results for blends system of PS/SBS give good indications of improving state of partial miscibility.

The optical microscope and SEM results for both systems fully support the results obtained from the mechanical properties.

The FTIR results for PS/ABS blend system show that the PB phase in pure ABS has a cis configuration and these configurations change from cis to trans for all blend ratios.
الخلاصة
تضمنت الدراسة تحضير خلطات بولمية ثنائية بيئة نظامين تضمن النظام الأول خلط مادة (البولي ستايبرين). 

(ABS) Single screw extruder حضر بواسطة Haake PolyDrive extruder مع مادة باسبة (SBS) ستايبرين.

امة بالنسبة للنظام الثاني فقد تضمن خلط مادة (البولي ستايبرين) مع مادة (ستايبرين بروتايدين ستايبرين) حضر بواسطة ماكينة تمت الخلط بنسب مختلفة لغرض الحصول على أفضل نسب خلط فيزيائية.

ولأجل دراسة تأثير المزج في الخواص الميكانيكية والخواص الحرارية والبنية أجريت عدة فحوصات شملت (الشد، مقاومة الصدع، المسار الماسح التفاعلي، والفحص المجهري الضوئي، والمجهر الإلكتروني الماسح).

أظهرت نتائج فحص السلك الميكانيكي للنظام الأول أن نسب الخلط (30/70, 50/50, 60/40) تمتلك خصائص ميكانيكية أفضل من المواد الأصلية قبل الخلط. كذلك بينت نتائج فحص السلك الميكانيكي للنظام الثاني التأثير الواضح لمادة ستايبرين بروتايدين ستايبرين حيث اعتمدت الخصائص الميكانيكية بصورة مباشرة على نسبة خلط هذه المادة ضمن النظام، وبصورة عامة وتقريبية كانت نتائج فحص السلك الميكانيكي تابعة إلى قاعدة الخلط.

من خلال نتائج الفحص (للسعر الماسح التفاعلي) أظهرت نتائج هذا الفحص تحقيق ظاهرة الامتزاج بالنسبة للنظام الأول لمعظم نسب الخلط وذلك عن طريق تسجيل درجة انتقال زجاجية واحدة تمثل حالة وسطية مقارنة مع درجات الانتقال الزجاجي لكل المادتين. كذلك أظهرت نتيجة الفحص هذا حصول ظاهرة الامتزاج الجزئي بين مكونات الخلط للنظام الثاني.

اما نتائج الفحص باستعمال المجهر الضوئي والمجهر الإلكتروني الماسح فقد دعمت وتصوير كبيرة نتائج الفحص الميكانيكي لكلا النظمين.

كذلك أظهرت نتائج فحص FTIR بالنسبة للنظام الأول تغيرات لطور configuration البولي (البولي cis بروتايدين) من cis إلى trans جميع نسب الخلط لجميع مادة (البولي ستايبرين) النقي إلى ما بين مادة البولي ستايبرين.  

CHAPTER ONE  INTRODUCTION AND LITERATURE SURVEY  1

1.1  Introduction

Polymer blend represents a very important field in processing of new materials, which have better properties in comparison with the constituent polymers. They are significant also from ecological and economical viewpoint. Thus, for example, municipal commingled plastic waste, composed of various immiscible polymers can be recycled by mixing in molten state, and so it can be transformed to the material, which would satisfy the relevant application. High molecular weight polymers show low entropy of mixing [1], so that, most polymer blends show immiscible systems, whose properties are not only a function of the blend composition but also depend crucially on the degree of dispersion phase size, and phase interaction between the components of the blend. Also by controlling the morphology of polymer blend leads to practicability of controlling the polymer blend properties [2]. Many polymer pairs are not only immiscible but also incompatible. It means that they show high interfacial tension that leads to rough phase structure, poor adhesion at the interface, and therefore poor mechanical properties. Compatibility arises from thermodynamic interaction between the blend constituents, which is a function of their physical and chemical structure [3-5]. The main reasons lead to creating incompatible systems that can be summarized as: absence of any specific interaction between their blend constituents, dissimilarity in their structure, and broad differences in their viscosities.

Many articles were devoted to study the effect of different reasons on the compatibility, miscibility, morphology, and mechanical properties for the polymer blend.
1.2 Literature Review

In recent years there has been a great deal of interest in the structure and properties of polymer blends. The practical motivation for this interest is the achievement of desirable mechanical, morphological or other properties.

In (1990), Wycisk R, et.al.[6] prepared polymer blends from polyethylene (PE) and polystyrene (PS). There are three samples of different molecular weights of (PS) and that (PS) with (PE) decrease crystallization degree of (PE) but the relationship is non linear that means (PS) leads to fluctuation of crystalline arrangement of (PE). Also the morphology of the blends changed between that of spherical domains of one component dispersed in continuous matrix of the other to a highly non homogeneous mixture fibrous or cabbage-like macro domains of both components. This change in morphology depends on the composition and molecular weight of PS.

In (1993), R.N.Santra et.al. [7] studied the effect of Ethylene-Methyl Acrylate copolymer as a chemical compatibilizer on some properties of Low-Density Polyethylene blend with Polydimethylsiloxane Rubber; the results for these studies show that by addition of 6%w from (Ethylene-Methyl Acrylate Copolymer) to 50:50 blend of (LDPE: PDMS) many properties of this blend were improved, such as increase in shear adhesion between the phases, also dynamic mechanical analysis showed a single Tg peak at -119°C.

In (1998), R. Asaletha et.al.[8] studied the thermal properties of NR/PS blends with and without the addition of the compatibilizer (NR-g-PS). The thermal stability of the blends was analysed by thermogravimetry. Differential scanning calorimetry has been used to analyse the glass
transition temperatures of the blends. The effects of blend composition and compatibilizer loading on the thermal properties were analyzed.

In (1999), R. Asaletha et al.[9] studied the effect of different processing conditions on the morphology and mechanical properties of NR/PS blends. NR/PS blends were dynamically vulcanized using sulphur, peroxide and mixed systems. The effects of these different vulcanizing systems on the mechanical properties were also studied in detail.

In (2000), Je Kyum Lee and Chang Dae Han[10] prepared polymer blend by using a twin-screw extruder to study the morphology evolution in immiscible polymer blends. Morphology of a polymer blend was identified using scanning electron microscopy (SEM) or transmission electron microscopy (TEM).

In (2001) Hyun Tack et.al. [11] prepared polymer blend via melt extrusion by using a Minmax Molder in the system of syndiotactic polystyrene/polystyrene-block-poly(ethylene-co-butylene) block-polystyrene copolymers. The results for this study showed that the SPS block ratios and the total molecular weight of SEBS affected morphology significantly and the impact and tensile properties of SEBS toughened SPS. Also these studies show the blending of SPS by SEBS is a method for increasing the impact strength of SPS.

In (2002), Susan Joseph et.al.[12] studied the melt elasticity characteristics of PS/PB blends as a function of blend ratio, compatibilizer loading and dynamic vulcanization over a wide range of shear stresses and temperatures. The effects of blend ratio, shear rate and temperature on the melt elasticity of the system have been studied in detail. The effects of compatibilization by styrene butadiene rubber (SBR) and dynamic
vulcanization using different cross-linking systems on melt elasticity parameters were also studied in detail.

In (2003), Susan Joseph and Sabu Thomas [13] studied the rate of morphology development of PS/PB blends under dynamic conditions in a Haake mixer. The effect of blend ratio on the mechanical and morphological properties is studied in detail. The results of tensile experiments at room temperature are interpreted with regard to blend morphologies, as determined by scanning electron microscopy (SEM). The effects of mixing time, mixing temperature and rotor speed on the phase morphology development of PS/PB (30/70 wt.%) blends were also investigated.

In (2004), Qi Yang et.al.[14] studied the miscibility of polystyrene/poly(styrene-co-acrylonitrile) (PS/SAN) blend, one kind of A/A-B type blend. The calculation results from these studies suggested that PS/SAN blend shows the UCST behavior within the AN’s volume fraction range of 4–20%. PS/SAN blend was then studied with Small Angle Light Scattering method (SALS) to test the theoretical prediction. It showed that PS/SAN (AN:20 vol.% ) blend (49/51 wt.%) has UCST behavior with the UCST temperature of 171.8°C.

In (2004), Monsy Mathew and Sabu Thomas[15] studied the effect of styrene–acrylonitrile copolymer (SAN) as a potential compatibiliser for PS/NBR blends. The effect of this compatibilisation on the morphology, processing characteristics and mechanical properties was also studied.

In (2004), Gonzalo et.al.[16] studied blends of 3.5 and 10 weight % of styrene-butadiene Rubber (SBR) embedded in rigid polystyrene matrix which were first mixed in a co-rotating twin screw extruder and then injection molded. This study shows the mechanical properties of the blends to be dependent on structural characteristics and content of SBR employed
where increments of SBR content produce impact strength improvements on one hand, and decrease of tensile and flexural modules on the other. 

In (2005), S. Joseph et al.[17] analysed the morphology and mechanical properties of polystyrene (PS) /polybutadiene (PB) blends in the presence and absence of random and tri-block copolymers of PS and PB. 

In (2005), Azman Hassan and Wong Yean Jwu[18] studied the effects of blend composition upon mechanical properties of super high impact ABS/PC blend. 

In (2005), M.M.M,Khan et.al.[19] prepared polymer blends from ABS/PC by using twin extruder. The results from this study show that the processing ability of PC can be improved by addition of ABS. The tensile and yield strength results for the blends follow the rule of mixtures where they show a decreasing value with increasing ABS content. 

In (2006), Mahmoud Ansari et.al.[20] studied the effect of SBR as compatibilizer on the rheological properties of commercial PS/PB blends. 

In (2007), Xinhua Xu et.al.[21] analyzed quantitatively the influence of blend composition and processing conditions on phase morphology development of the polypropylene/ethylene-octene copolymer (PP/EOC) blends. 

In (2007), Susan Joseph et.al.[22] studied melt rheology and extrudate morphology of polystyrene (PS)/polybutadiene (PB) blends with special reference to the effect of blend ratio and two different types of compatibilisers. The results from this study show that the use of block copolymer, SBS as compatibiliser increases the melt viscosity of the blends. This increased viscosity has been attributed to the increased interaction between the PS and PB as a result of decreased interfacial tension and suppression of coalescence due to the introduction of the compatibiliser.
This is associated with the localization of the tri-block copolymer at the inter-phase.

In (2007), Wantinee et.al.[23] prepared polymer blend via melt extrusion using single screw extruder in the system polystyrene/high density polyethylene and polystyrene/polypropylene to assess the effect of composition and morphology on tensile and impact resistant. The result from this study show, in both systems, the tensile modulus was shown to follow approximately rule of mixtures behavior although the PS/HDPE blend curve reached the proportional level only at co-continuous compositions, whereas the tensile modulus of PS/PP blends was at or above the proportional relationship at all compositions on the PS rich side of phase inversions.

In (2008), Mediha KOK et.al.[24] studied thermal properties of PVC with blending a new polymer into PVC. Thermal conductivity, specific heat capacity, thermal diffusivity, and thermo-gravimetric analysis of PIBA and its blend with PVC are investigated and the dependence of thermo-physical properties of blend with PVC or PIBA is examined.

In (2008), M. Żenkiewicz and J. Richert[25] studied the effect of the preparation procedure for the samples of five engineering polymers on the values of offset yield stress at 0.2% strain, tensile stress at yield (σy), and tensile stress at break (σB) as well as tensile strain at yield (εy) and tensile strain at break (εB).

In (2007) Mustapha A.S [26] studied the effect of different compositions of PP/HIPS, a typical semi-crystalline amorphous polymer system on their physical properties.

In (2008), Cai-Liang Zhang et.al. [27] studied the efficiency of graft copolymers with different molecular structures and compositions at
stabilizing co-continuous morphology under quiescent annealing with emphasis on the length and density of grafts..

In (2008), Nina et.al.[28] prepared polymer blend by cast solvent from PS/PB with addition of styrene-butadiene block copolymer as a compmtibilizer. The results from these studies show the impact strength of the PS/PB blends compatibilized by four different copolymers is in all cases higher than that of un-compatibilized one and decreases in order (in block sequence): triblock/diblock + triblock, pent block copolymer. Incorporation, of all the used SB copolymer, leads to a significant decrease in the PB particle size as well as in width of their size distribution.

In (2009), Márcio Yee et.al.[29] studied the stress relaxation behavior of poly(methyl methacrylate) and polystyrene (PMMA/PS) blends, with or without random copolymer addition submitted to step shear strain experiments in the linear and nonlinear regime. The effect of the blend composition, viscosity ratio, and random copolymer addition was evaluated and explained in light of morphological observation.
1.3 Aims of Work:

The aim of the present work is to develop polymers of desirable properties at low cost by showing the effect of blend ratios on the mechanical properties for the systems of PS/ABS and PS/SBS and study the probability to creating compatible system for the polymer blend. Such system may be satisfied by correct choice of methods of polymer blends preparation.

1.4 Thesis Layout

The thesis is organized into five chapters including the present one. In chapter two show the theoretical background which has relation to this work. Chapter three including a detailed description of the experimental methodology is presented, which include, sample preparation methods and detailed description of test instruments used. Chapter four including all the experimental results that are obtained from the mechanical and physical tests for the polymer blends under investigation. Chapter five including the conclusions and suggestions for future work.
CHAPTER TWO THEORETICAL BACKGROUND

2.1 Introduction

The developments of a new polymer need a big amount of investment and have to spend a lot of time. Therefore, many plastics manufacturers are using blending polymers to develop polymer properties, which is more economical, convenient and widely accepted. Polymer blending is of growing importance today, because the blend can be tailored to meet the requirements of specific applications. In addition, since the properties of blend system are functions of the composition, the blend can be easily and quickly modified to meet performance and cost objectives required by new or changing markets. Nowadays, polymer blends constitute over 30% of polymer consumption and the annual growth rate of about 9%, in the past 12 years is constantly and continuously increasing. Benefits of blending can be discussed from the perspective of properties and economics it can bring to the manufacturer. To date, blending can be used to gain economy by diluting expensive engineering plastic with commodity ones [30]. There is no doubt that the main reason for blending compounding and reinforcing is economy. If a material can be generated at a lower cost with properties meeting specifications manufacturing, it must remain competitive. In general the following economy related reasons can be listed [31]:

- Extending engineering resin performance by diluting it with a low cost polymer;
- Developing materials with a set of desired properties;
- Forming a high performance blend from synergistically interacting polymer;
• Adjusting the composition of the blend to customer specification;
• Recycling industrial and/or municipal plastics scrap.

2.2 Types of Polymer Blends.

A. Homogeneous blend: A mixture of two homologous polymers, usually narrow molecular weight distribution fractions of the same polymer. In this blend, both blend components lose part of their identity and the final properties usually are the arithmetical average of both blend components.

B. Heterogeneous blend: The properties of all blend components are present. Weakness of one polymer can, to a certain extent, be camouflaged by strength of the others.

C. Miscible polymer blend: Polymer blends which are homogeneous down to the molecular level are associated with the negative value of free energy of mixing: \( \Delta G_{\text{Mix}} \approx \Delta H_{\text{Mix}} \leq 0 \).

D. Immiscible polymer blend: Any polymer blend whose \( \Delta G_{\text{Mix}} \approx \Delta H_{\text{Mix}} > 0 \).

E. Compatible polymer blend: A term indicating a commercially attractive polymer mixture with enhanced physical properties over the constituent polymers.

F. Polymer alloy: An immiscible polymer blend having a modified interface and/or morphology.
2.3 Methods of Blend Preparation.

Most polymer pairs are immiscible, and therefore, their blends are not formed spontaneously. Moreover, the phase structure of polymer blends is not in equilibrium and depends on the process of their preparation. Five different methods are used for the preparation of polymer blends: melt mixing, solution blending, latex mixing, partial block or graft copolymerization, and preparation of interpenetrating polymer networks [5,32]. It should be mentioned that due to high viscosity of polymer melts, one of these methods is required for size reduction of the components (to the order of μm), even for miscible blends.

Melt mixing is the most widespread method of polymer blend preparation in practice. The blend components are mixed in the molten state in extruders or batch mixers. Advantages of the method are well-defined components and universality of mixing devices—the same extruders or batch mixers can be used for a wide range of polymer blends. Disadvantages of the method are high energy consumption and possible unfavorable chemical changes of blend components.

Solution blending is frequently used for preparation of polymer blends on a laboratory scale. The blend components are dissolved in a common solvent and intensively stirred. The blend is separated by precipitation or evaporation of the solvent. The phase structure formed in the process is a function of blend composition, interaction parameters of the blend components, type of solvent, and history of its separation. Advantages of the process are rapid mixing of the system without large energy consumption and the potential to avoid unfavorable chemical reactions. On the other hand, the
method is limited by the necessity to find a common solvent for the blend components, and in particular, to remove huge amounts of organic (frequently toxic) solvent. Therefore, in industry, the method is used only for preparation of thin membranes, surface layers, and paints.

A blend with heterogeneities on the order of 10 μm can be prepared by mixing of latexes without using organic solvents or large energy consumption. Significant energy is needed only for removing water and eventually achievement of finer dispersion by melt mixing. The whole energy balance of the process is usually better than that for melt mixing. The necessity to have all components in latex form limits the use of the process. Because this is not the case for most synthetic polymers, the application of the process in industrial practice is limited.

In partial block or graft copolymerization, homopolymers are the primary product. But, an amount of a copolymer sufficient for achieving good adhesion between immiscible phases is formed. In most cases, materials with better properties are prepared by this procedure than those formed by pure melt mixing of the corresponding homopolymers. The disadvantage of this process is the complicated and expensive startup of the production, in comparison with other methods, e.g. melt-mixing. Another procedure for synthesis of polymer blends is by formation of interpenetrating polymer networks. A network of one polymer is swollen with the other monomer or prepolymer; after that, the monomer or prepolymer is cross-linked. In contrast to the preceding methods it is used for thermoplastics and uncross-linked elastomers, blends of react plastics are prepared by this method.
2.4 Kinetics of Phase Separation

The phase boundaries and the kinetics of phase separation of polymer blends are very rich areas of investigation, with, additionally important technological applications. Fig (2.1) shows schematically the variation of the free energy of mixing, $\Delta G_m$, with composition for a typical high molecular weight binary polymer blend and the corresponding phase diagram. Both the binodal (outer, dark grey) and spinodal (inner, light grey) curves are shown in the lower region of Fig (2.1). The binodal denotes the limits of miscibility and is determined by the points of common tangent to the free energy curve, where the chemical potentials of the two co-existing phases will be equal. The spinodal denotes the limits of meta-stability of the system, where the curvature changes from positive to negative and the second derivative of $\Delta G_m$ is zero. Inside the spinodal, the system is unstable to all concentration fluctuations and the blend spontaneously separates into co-existing phases via the process known as spinodal decomposition. The process left to develop fully would eventually lead to very large regions of the two co-existing phases; however, the spinodal structure can be frozen in by rapidly cooling the mixture below its glass transition temperature or causing a chemical reaction between the components. In some systems spinodal structures have proved to have interesting material and electrical properties due to the high degree of internal phase boundaries [4,33]. It is clear that to understand and control such behavior of polymer mixtures appropriate statistical thermodynamic models are required.
Fig (2.1): Schematic showing the Gibbs free energy of mixing as a function of composition at a chosen temperature $T_0$ (upper panel). Given in the lower panel is the corresponding phase diagram showing the binodal (outer, dark grey) and spinodal (inner, light grey) curves; marked are the binodal and spinodal compositions at $T_0$ ($B'$, $B''$ and $S'$, $S''$) which are related to the features in the free energy curve above[33].

2.5 FLORY-HUGGINS –STAVERMAN THEORY

The earliest theories of the thermodynamics of polymer mixtures were given by Flory, Huggins, Staverman and Santen in 1941. The thermodynamics of polymer mixture was developed in terms of a lattice
model with each monomer repeat unit of the chains occupying a single lattice site. The entropy of mixing, $\Delta S_m$, is assumed to be purely combinatorial and is calculated by enumerating the number of arrangements of the molecules on a lattice. The enthalpy $\Delta H_m$ is simply Van der Waals energy of contact, and the difference between like and unlike pairs is summarized into a single term, the Flory–Huggins (FH) interaction parameter, $\chi$. The free energy of mixing (per monomer), $\Delta G_m$, is then given by

$$\frac{\Delta G_m}{k_B T} = \left( \frac{\varphi_a}{r_a} \right) \ln \varphi_a + \left( \frac{\varphi_b}{r_b} \right) \ln \varphi_b + \varphi_a \varphi_b \chi_{ab}, \quad \text{............................................(2.1)} [33]$$

where $r$ is the degree of polymerization and $\varphi$ the volume fraction of the species. For a miscible system $\Delta G_m$ must always be negative, and further it must also have positive curvature over the whole concentration range, but for a partially miscible system it will have a region of negative curvature, and hence show the double minima seen in Fig (2.1). It is notable in equation (2.1) that the entropy terms become very small for higher molecular weight polymers because of the terms in $r$ in the denominator. Since the enthalpy term is normally positive, owing to unfavorable interactions between unlike pairs of molecules, and the entropy term, which is negative, drives mixing, high molecular weight polymers become less likely to mix. Another feature of equation (2.1) is that it can predict only upper critical solution temperature behavior (UCST), i.e. phase separation on cooling. The interaction term has an inverse T dependence when formulated as in equation (2.1) by FH, and, as a consequence, the enthalpy of mixing becomes less unfavorable at high T. In practice, however, most partially miscible blends phase separate on heating, thereby exhibiting a lower critical solution temperature (LCST). This
discrepancy between theory and experiment arises mainly because the FH description ignores any volume changes on mixing and simplifies the interactions in the system to a single enthalpic parameter. The problems with the FH lattice theory have typically been dealt with arbitrarily in the literature by allowing $\chi$ to take a complex temperature (and often concentration) dependence. Alternative theories, which take account of volume changes on mixing, have followed a number of different routes—either reformulating lattice models to include holes, for example, or starting with an equation of state formalism which can also account for volume changes[4,34]. However, all the subsequent modifications to FH theory have not improved the predictive capacity very much, and they all still rely on some sort of fitted interaction parameter, which may contain both enthalpic and entropic terms.

2.6 Assessment of Miscibility in Polymer Blend Systems

It is difficult to determine $\Delta G_m$ from experiment. Various techniques have been used to determine miscibility and phase behavior of polymer blend systems. Common techniques that are used include the determination of the glass transition temperatures, microscopy, light or radiation scattering, nuclear magnetic resonance spectroscopy, and infrared spectroscopy. Each experimental technique has limited sensitivity to detect a domain size. Therefore, the phase behavior determined from different measurement techniques may vary, and thus may not accurately reflect the thermodynamic phase behavior of the blend. According to literature survey [35, 36] the methods for determining polymer-polymer miscibility are summarized below.
(a) Miscibility Determination by Glass Transition Temperatures

The presence of a single Tg intermediate between that of the pure components suggests miscibility of the polymer pair. A few expressions have been proposed for the composition dependence of the glass transition temperature for miscible blends[35].

The determination of Tg may be done by calorimetric method. The sensitivity of differential scanning calorimetry (DSC) is reported only detecting a domain size approximately larger than 10 nm. This is a widely used technique because of its simplicity.

(b) Miscibility Determination by Microscopy

Electron micrographs taken via scanning and transmission electron microscopy can observe the phase segregates. The contrast of scanning electron microscopy (SEM) depends on differences of surface topography or texture [37]. This can be emphasized by breaking the specimen in its glassy state, or etching one phase away. When the domain-phase is chemically etched, dimples can be observed by SEM.

(c) Miscibility Determination by Scattering Methods

The methods can determine the average domain size in a blend. Small angle light-scattering (SALS) is less sensitive than small-angle x-ray scattering (SAXS), which means SALS cannot detect small particles such as the case of blends with specific interactions. Techniques utilized are cloud-point methods via SALS, conventional light scattering method, phase-induced
critical scattering (PICS), neutron scattering methods particularly small-angle neutron scattering (SANS), and SAXS[36].

\[(g) \text{ Miscibility Determination by Heat of Mixing by Calorimetry}\]

Some studies use DSC to measure the thermal energy released upon blending. They conclude that the exothermic reaction during blending indicate interaction in a blend[35].

\[(h) \text{ Miscibility Determination by Melting Point Depression}\]

This method applies to the blend systems that contain crystalline polymers. The utility of the melting point depression allows the calculation of the interaction parameters between polymer species[36].

\[2.7 \text{ Melt Processing Mechanism of Plastic}\]

In order to understand the melt process mechanism of plastics it is first necessary to consider: (1) the basic special properties of plastics extruded; and (2) the typical physical changes which they undergo during processing. Their most important property is the reversible change of plasticity with temperature, i.e., their rheological behavior or the deformation and flow of material. A plastic is more or less rigid at room temperature, becomes elastic, and then viscous or 'plastic’ as temperature increases. At too high a temperature, the plastics become damaged through degradation (depolymerization) or decomposition (breakdown of the monomer or
oxidation). According to the type of plastic, the transitions between physical states of the plastics are defined [38].

Rheology is the science that deals with the deformation and flow of matter under various conditions, such as a plastic’s melt flow. These plastics combine the properties of an ideal viscous liquid (pure shear deformations) with those of an ideal elastic solid (pure elastic deformation). Plastics are therefore said to be ‘viscoelastic’. Viscoelastic materials simultaneously exhibit a combination of elastic and viscous behavior. While all substances are viscoelastic to some degree, this behavior is especially prominent in polymers. Generally, viscoelasticity refers to both the time and temperature dependence of mechanical behavior. The five regions of viscoelastic behavior for linear amorphous polymers are shown in Fig (2.2). In region 1 the polymer is glassy and frequently brittle. In the glassy state, molecular motions are largely restricted to vibrations and short-range rotational motions. Region 2 in Fig (2.2) is the glass transition region. The behavior of polymers in this region is best described as leathery, although a few degrees of temperature change will obviously affect the stiffness of the leather. The glass transition temperature, \( T_g \), is often taken at the maximum rate of turndown of the modulus at the elbow. Qualitatively, the glass transition region can be interpreted as the onset of long-range, coordinated molecular motion. While only 1 to 4 chain atoms are involved in motions below the glass transition temperature, some 10 to 50 chain atoms attain sufficient thermal energy to move in a coordinated manner in the glass transition region. Region 3 in Fig (2.2), is the rubbery plateau region. After the sharp drop that the modulus takes in the glass transition region, it becomes almost constant again in the rubbery plateau region. In the rubbery plateau region, polymers exhibit long-range rubber elasticity, which
means that the elastomer can be stretched, perhaps several hundred percent, and snap back to substantially its original length on being released. As the temperature is raised past the rubbery plateau region for linear amorphous polymers, the rubbery flow region is reached—region 4. In this region the polymer is marked by both rubber elasticity and flow properties, depending on the time scale of the experiment. For short time scale experiments, the physical entanglements are not able to relax, and the material still behaves rubbery. For longer times, the increased molecular motion imparted by the increased temperature permits assemblies of chains to move in a coordinated manner (depending on the molecular weight), and hence to flow. At still higher temperatures, the liquid flow region is reached—region 5. The polymer flows readily, often behaving like molasses. In this region, as an idealized limit, the equation below is obeyed.

\[ \eta = \frac{\tau}{\frac{dy}{dt}} \]  

\[ \text{(2.2) \ [36]} \]

Where \( \tau \) and \( \gamma \) represent the shear stress and strain, respectively, and \( t \) is the time. The increased energy allotted to the chains permits them to reptate out through entanglements rapidly and flow as individual molecules [36]. In this region the polymer molecules can form a temporary entanglement network with entanglement junctions whose number can change with time in various flow situations [39].
2.8 Mechanism of Polymer Dissolves

Once placed in a solvent, polymers dissolve in several steps. First, the solvent must wet the polymer. Second, the solvent diffuses into the polymer, swelling it. For polymers of high molecular weight, this process may take several hours or longer, depending on sample size, temperature, and so on. Contrary to many low molecular weight substances, the solvent does not initially diffuse into the polymer.

There are two distinguishable modes of solvent diffusion into a polymer. If the polymer is amorphous and above its glass transition temperature (i.e., a polymer melt), the diffusion of the solvent into the polymer forms a smooth composition curve, with the most highly swollen
material at the outer edge. This is referred to as Fickian diffusion, following Fick’s laws. If the polymer is significantly below its glass transition temperature, however, the non-Fickian phenomenon known as case II swelling may predominate. In this situation the diffusion into the glassy polymer is slow. First the solvent must plasticize the polymer, lowering its glass transition temperature until it is below ambient. Then swelling is rapid. A rather sharp, moving boundary results between highly swollen material and that substantially not swollen. Frequently the stresses at the swelling boundary cause the sample to craze or fracture. A similar phenomenon is sometimes found with semi-crystalline polymers. Finally the polymer diffuses out of the swollen mass into the solvent, completing the solution process. If the polymer is cross-linked, the polymer only swells, reaching an equilibrium degree of swelling. There are also some polymers, particularly with high melting temperatures or strong internal secondary bonds that cannot be dissolved without degradation [40].

2.9 Blend Morphology

Blend of two or more polymers are mostly immiscible system, whose properties are not only a function of blend composition but also depend crucially on the degree of dispersion, phase particle size, and phase interaction between the components of the blend. Controlling of morphology is therefore the control of polymer blend properties [26].

The morphology of polymer blends depends on the arrangement of the phases, whether continuous or discontinuous and the degree of order in the phases, namely crystalline or amorphous [38].
The spatial arrangement or morphology of the phases may consist of one phase dispersed as simple sphere in a matrix of the other polymer, as shown Fig (2.3, a).

Fig (2.3): Different types of polymer blend morphology, (dark regions) in the matrix of an immiscible polymer. (a) The spherical droplets (b) rod-like (c) co-continuous phases.

On the other hand, the dispersed phase may take the form of rod-like domains of one polymer surrounded by a continuous phase of the other. This happens when the immiscible blend is put under stress in only one direction, such as during mixing as shown in Fig (2.3, b).

Another distinct morphology appears when the domains of each phase are joined together, also these phases are joined together for the formation of co-continuous phases. Fig (2.3, c).

The development of morphology depends upon the type of mixing device: interfacial tension between the phases, rheological characteristics of the components, processing conditions, etc, and reflects a dynamic balance.
between phase deformation or break-up caused by stresses imposed and phase coalescence or rearrangement driven by the tendency to minimize surface energy [38].

The morphology generated during mixing depends on the interfacial tension between the phases, the viscosity and elasticity.

2.10 Polystyrene

Polystyrene is amorphous thermoplastic, hard, rigid, free of odor and taste, ease of heat fabrication, thermal stability, low specific gravity, excellent thermal and electrical properties for insulating purposes, and low cost. It is in solid (glassy) state at room temperature, but flows if heated above its glass transition temperature (for molding or extrusion), and becomes solid again when it cools off. Pure solid polystyrene is a colorless, hard plastic with limited flexibility. Polystyrene can be transparent or can be made to take on various colors. The chemical makeup of polystyrene is a long chain hydrocarbon with every other carbon connected to a phenyl group (the name given to the aromatic ring benzene, when bonded to complex carbon substituents). Polystyrene's chemical formula is:

\[
\text{[-CH_2-CH-]}_n
\]

it contains the chemical elements carbon and hydrogen. Because it is an aromatic hydrocarbon, it burns with an orange-yellow flame, giving off soot, as opposed to non-aromatic hydrocarbon polymers such as polyethylene, which burns with a light yellow flame (often with a blue tinge) and no soot. Complete oxidation of polystyrene produces only carbon dioxide and water.
vapor. Extruded polystyrene (PS) is economical, and is used for producing plastic model assembly kits, plastic cutlery, CD "jewel" cases, smoke detector housings, license plate frames, and many other objects where a fairly rigid, economical plastic is desired. Production methods include stamping and injection molding [42,43].

2.11 Acrylonitrile Butadiene Styrene (ABS)

ABS is a heterogeneous thermoplastic, which consists of two phases terpolymer, consisting of dispersed rubbery phases made up of polybutadiene (PB) rubber graft with styrene acrylonitrile (SAN) and then dispersed in a continuous plastic of more SAN. Chemical formula \((C_8H_8)_x\cdot(C_4H_6)_y\cdot(C_3H_3N)_z\).

\[
\begin{array}{c}
\text{C} = \text{N} \\
\text{\begin{array}{c}
\text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_2 \\
\text{CH} - \text{CH}_2 \\
\end{array}}
\end{array}
\]

ABS is a graft copolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene. The result is a long chain of polybutadiene, criss-crossed with shorter chains of poly(styrene-co-acrylonitrile). The nitrile groups from neighboring chains, being polar, attract each other and bind the chains together, making ABS stronger than pure polystyrene. The styrene gives the plastic a shiny, impervious surface. The butadiene, a rubbery substance, provides resilience.
even at low temperatures. For the majority of applications, ABS can be used between −25 and 60 °C as its mechanical properties vary with temperature. The properties are created by rubber toughening, where fine particles of elastomer are distributed throughout the rigid matrix. Generally ABS would have useful characteristics within a temperature range from -40 to 100 °C [41, 43].

2.12 Poly (Styrene-Butadiene-Styrene).

Poly(styrene-butadiene-styrene), or SBS, is a hard elastomer. It is a copolymer called tri block copolymer made of three segments. The first is a long chain of polystyrene, the middle is a long chain of polybutadiene, and the last segment is another long chain of polystyrene. Chemical formula for SBS is;

\[
\begin{array}{c}
\text{Polystyrene: } \left\{ \text{CH}_2-\text{CH} \right\}_n \\
\text{Polybutadiene: } \left\{ \text{CH}_2-\text{CH} \right\}_n \\
\text{Polystyrene: } \left\{ \text{CH}_2-\text{CH} \right\}_n
\end{array}
\]

Polystyrene is a tough hard plastic, and this gives SBS its durability. Polybutadiene is a rubbery material, and this gives SBS its rubber-like properties. Since SBS contains rubber and plastic, it acts like both materials [43].
2.13 Mechanical Properties

The design of machines and structures so that they will function properly require that the mechanical behavior of their materials being used is understood, i.e. the only way to determine how materials behave when they are subjected to loads is to perform experiments in the laboratory. The usual procedure is to place small specimens of the material in testing machines, apply the loads, and then measure the resulting deformations (such as changes in length and changes in diameter). For most traditional materials, the objective of the design method is to determine stress values, which will not cause fracture. However, for plastics it is more likely that excessive deformation will be the limiting factor in the selection of working stress.

2.13.1 Stress-Strain Curve

A method of measuring the resistance of a yarn or fabric to a force tending to stretch the specimen in one direction is called tensile test. The results are obtained from this test represented by stress–strain curves, a graphical representation, showing the relationship between the change in dimension (in the direction stress–strain curves of the applied stress) of the specimen from the application of an external stress, and the magnitude of that stress. In tension tests, the stress can be expressed in units of force per unit cross-sectional area,

\[ \sigma = \frac{F}{A} \]  

Where:

\( \sigma \) : tension stress( N/m\(^2\) )
F : tension force ( N )

A : cross-sectional area ( m² )

And the strain can be expressed either as a fraction or as a percentage of the original specimen length.

\[ \% \varepsilon = \frac{\Delta L}{L_o} \times 100 \% \] ................................. 2.4 [45]

Or by the change specimen length divided by original length

\[ \varepsilon = \frac{L - L_o}{L_o} = \frac{\Delta L}{L} \] ................................. 2.5 [45]

Where

\( \varepsilon \) : the strain

\( L_o \) : in initial length

\( L \) : final length

The behavior of the tensile specimen according to stress–strain curves is that for small strains the deformation is elastic and reverses if the load is removed. At higher stresses plastic deformation occurs. This is not recovered when the load is removed [45].

When the deformation is proportional to the applied load, the material is said to exhibit Hookean elasticity or ideal elasticity. Elasticity equals stress divided by strain at linear portion of stress-strain curve.
2.13.2 Impact test

The impact test measures the amount of energy necessary to cause failure, which is dependent upon ultimate stress value and slope of load deformation curve. The energy of deformation upon the break point is given by [43]:

\[ W = \frac{1}{2E} S_{\text{nm}}^2 \]  \hspace{1cm} 2.6

W= energy necessary to cause failure in impact test.

Where E is the apparent modulus and \( S_{\text{nm}} \) is ultimate stress. The resistance to impact is one, key for properties of materials.

Impact properties can be very sensitive to test specimen thickness and molecular orientation [45].

These tests depend on the sample geometry and the method of measurement. The most common tests are the Izod, the Charpy and falling weight test. These are very important in determining the applications and limitations of polymers. Thus, Izod and Charpy tests employ a weighted pendulum. In Izod test a notched bar is held vertical while being clamped at one end. The notch serves as a stress concentrator. In Charpy test the specimen is clamped at both ends [45].

2.14 Differential Scanning Calorimetry (DSC).

Differential scanning calorimetry (DSC) analyzes thermal transitions occurring in polymer samples when they are cooled down or heated up under inert atmosphere. Melting and glass transition temperatures can be determined as well as the various transitions in liquid crystalline mesophases [46]. If unit mass of any substance is heated slowly at constant pressure in such a way that
the rate of supply of energy $Q$ is $dQ/dt$ and the rate of rise of temperature $T$ is $dT/dt$, the specific heat of the substance at constant pressure $C_p$ is given by

$C_p = \frac{dQ/dT}{dT/dt} = \frac{dQ/dt}{dT/dt}$ \hspace{1cm} \text{2.7 [47]}

It follows that if $dT/dt$ is maintained constant and equal to $a$, and $dQ/dt$ is plotted against $T$, the graph will show the value of $a$ and $C_p$ as a function of $T$. This will, however, be true only provided that there are no first-order phase transitions, such as melting, in the temperature range scanned. If there is such a transition, energy will be required to change the phase without any change of temperature taking place, so that, for constant $dT/dt$, the value of $dQ/dt$ would have to be infinite. A schematic diagram of the corresponding plot is shown in Fig. (2.4, a). It has been assumed for simplicity that the value of $C_p$ is constant on each side of the transition but has slightly different values on the two sides. In reality, the best that can be done experimentally is to place the sample in a holder and to measure the temperature of the holder, rather than that of the sample as shown in Fig (2.5). This has two effects on what is observed. The first is that the holder will have its own heat capacity, which must be allowed for in deducing the specific heat of the sample, and the second is that heat must be transferred from the holder to the sample, so that there will be a lag between the average temperature of the sample and the temperature of the holder. It is now possible to raise the temperature of the holder at a constant rate even when the sample is undergoing a first-order transition. Once the transition is complete, $dQ/dt$ becomes proportional to the new specific heat of the sample, assuming that the heat capacity of the holder has been allowed for. The plot of $dQ/dt$ against $T$ during a first-order transition will therefore appear as shown schematically in Fig (2.4, b).
Because T changes uniformly with time, the area under the curve of $\frac{dQ}{dt}$ against T for any temperature range is proportional to the total energy supplied in the corresponding time. It follows that this simple type of experiment can give the values of three important quantities: (i) the temperature dependence of the specific heat $C_p$, (ii) the temperature of any first-order transition and (iii) the change in enthalpy during the transition.

When the glass transition temperature of the polymer sample is reached in the DSC experiment, the plot will show an incline. It is obvious that the heat capacity increases at $T_g$, and therefore DSC can monitor the $T_g$ of a polymer. Usually the middle of the incline is taken to be the $T_g$. Above $T_g$, the polymer chains are much more mobile and thus might move into a more ordered arrangement [47].

Fig (2.4) Rate of supply of energy $\frac{dQ}{dt}$ plotted against temperature T or time t for a substance undergoing a first-order transition: (a) the theoretical plot for a substance uniformly and directly heated with a constant value of rate of change of temperature $\frac{dT}{dt}$; (b) an idealised plot for a substance heated indirectly with a thermal resistance between it and a holder whose temperature is changed at the constant rate $\frac{dT}{dt}$ [47].
2.15 Infrared Spectroscopy

Infrared (IR) spectroscopy is a popular method for characterizing polymers. This technique is based on the vibrations of the atoms of a molecule. An infrared spectrum is obtained by passing infrared radiation through a sample and determining which fraction of the incident radiation is absorbed at a particular energy. The energy, at which any peak in an absorption spectrum appears, corresponds to the frequency of vibration of a part of the sample molecule. Most infrared spectroscopy is carried out by using Fourier-transform infrared (FTIR) spectrometers. This method is based on the interference of radiation between two beams to yield an interferogram, i.e. a signal produced as a function of the change of path-length between the two beams. The two domains of distance and frequency are inter-convertible by the mathematical method of Fourier transformation. The basic components of an FTIR spectrometer are shown schematically in Fig (2.6). The radiation emerging from the source is passed through an interferometer to the sample
before reaching a detector. Upon amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data are converted to a digital form by using an analog-to-digital converter and then transferred to the computer for Fourier transformation to take place.

Fig (2.6): Schematic of a typical Fourier-transform infrared (FTIR) spectrometer.

The output from an infrared instrument is referred to as a spectrum. Inverse wavelength units (cm\(^{-1}\)) are used on the x-axis - this is known as the wavenumber scale. The y-axis may be represented by % transmittance, with 100% at the top of the spectrum. It is commonplace to have the choice of absorbance or transmittance as a measure of band intensity. The transmittance is traditionally used for spectral interpretation, while absorbance is used for quantitative work. The infrared spectrum can be divided into three regions, namely the far-infrared (< 400 cm\(^{-1}\)), the mid-infrared (400-4000 cm\(^{-1}\)) and the near-infrared (4000-13000 cm\(^{-1}\)). Most infrared applications employ the mid-infrared region, although the near- and far-infrared regions can also provide specific information about materials. The near-infrared region consists largely of overtones or combination bands of fundamental modes appearing in the mid-infrared region. The far-infrared region can provide information regarding lattice vibrations. Spectrum interpretation is simplified by the fact that the bands that appear can be assigned to particular parts of the molecule, thus producing what are known as group frequencies.
The mid-infrared spectrum may be divided into the following four regions [4, 48]:

- X-H stretching region (4000-2500 cm\(^{-1}\))
- triple-bond region (2500-2000 cm\(^{-1}\))
- double-bond region (2000-1500 cm\(^{-1}\))
- fingerprint region (1500-600 cm\(^{-1}\))

Fig (2.7): Region for IR spectrum of important groups in polymer [48].
3.1 Introduction

In this chapter, a detailed description of the experimental methodology is presented, which include, sample preparation methods and detailed description of test instruments used.

3.2 The Materials Used

Many materials are used in this research which included polystyrene, acrylonitrile butadiene styrene (ABS), and Styrene- polybutidene-Styrene (SBS). All these material are obtained from Iraqi markets, these in view of cost and availability.

3.3 Polymer Blend Preparation

Two different methods are used to prepare polymer blend, the first is by solvent casting, which involves dissolving the polymers in a common solvent and casting a film from solution. The second is by melt mixing, which involves mixing of two polymers in the molten state under shear and is usually achieved with the help of either plasticizer type batch mixer or an extruder.

3.3.1 Solvent Casting

Different proportions of PS and ABS were mixed together as listed in table 3.1. After mixing, the material were dissolved in dichloromethane of (7% wt solution). The mixture was kept overnight, then the mixture was stirred for 12 hr using a magnetic stirrer, then each mixture was poured into a Petri-dish in order to dry in air at room temperature to form a cast film.
Table 3.1: Polymeric blends percent prepares by cast solvent.

<table>
<thead>
<tr>
<th>Polymeric blends percents for (PS/ABS)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(100/0)%</td>
</tr>
<tr>
<td></td>
<td>(90/10)%</td>
</tr>
<tr>
<td></td>
<td>(80/20)%</td>
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<tr>
<td></td>
<td>(70/30)%</td>
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<td>(60/40)%</td>
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<td>(50/50)%</td>
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<td>(40/60)%</td>
</tr>
<tr>
<td></td>
<td>(20/80)%</td>
</tr>
<tr>
<td></td>
<td>(0/100)%</td>
</tr>
</tbody>
</table>

3.3.2 Preparing Polymer Blends by Extruder

Ideally, thorough melt mixing of two components requires large shear forces which would be created by specially designed mixing rollers. Furthermore, it is desirable that melt blending be carried out in vacuum to avoid thermal degradation. However, using equipment available melt mixing was carried out after several attempts adjusting the blending temperature and the residence time of the polymer inside the extruders. The conditions of the two methods used were carried out in the following manner.
3.3.2.1 Single Screw Extruder

Two polymers were mixed and prepared by melt extrusion using single screw extruder, Internal structure of Single screw shown in Fig (3.1), for the polystyrene / poly(acrylonitrile-butadiene-styrene), (PS /ABS) system of different composition ratios, as summarized in Table 3.2.

Fig (3.1): Internal structure of Single screw Extruder machine
Table 3.2: Extrudusion procedure of blends preparing via single screw extruder.

<table>
<thead>
<tr>
<th>Polymeric blends percentages for (PS/ABS)</th>
<th>Temperature °C</th>
<th>Screw speed Cycle per min (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>zone 1</td>
<td>zone 2</td>
</tr>
<tr>
<td>(100/0)%</td>
<td>200</td>
<td>225</td>
</tr>
<tr>
<td>(90/10)%</td>
<td>190</td>
<td>210</td>
</tr>
<tr>
<td>(80/20)%</td>
<td>190</td>
<td>210</td>
</tr>
<tr>
<td>(70/30)%</td>
<td>180</td>
<td>200</td>
</tr>
<tr>
<td>(60/40)%</td>
<td>170</td>
<td>190</td>
</tr>
<tr>
<td>(50/50)%</td>
<td>170</td>
<td>190</td>
</tr>
<tr>
<td>(40/60)%</td>
<td>140</td>
<td>160</td>
</tr>
<tr>
<td>(20/80)%</td>
<td>130</td>
<td>150</td>
</tr>
<tr>
<td>(0/100)%</td>
<td>130</td>
<td>150</td>
</tr>
</tbody>
</table>

3.3.2.2 Haake PolyDrive extruder.

Blends of PS/SBS were prepared with different ratios of compositions as shown in table 3.3. Each blend was first blended in Haake PolyDrive extruder. The extruder operation conditions were 50 rpm and temperature of the front zone, mix chamber zone and rear panel zone are chosen to be 200°C.
Afterwards the blends were molded by using hot press machine at temperature 200 °C and 10 ton pressure. Thickness of the sample used through tensile test equals 1mm and for sample used through impact test equals to 2mm as shown in Fig (3.2).

Table 3.3: Polymeric blends percentages prepared by Haake PolyDrive extruder.

<table>
<thead>
<tr>
<th>Polymeric blends percents for (PS/SBS)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(100/0)%</td>
<td></td>
</tr>
<tr>
<td>(90/10)%</td>
<td></td>
</tr>
<tr>
<td>(80/20)%</td>
<td></td>
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<tr>
<td>(70/30)%</td>
<td></td>
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<tr>
<td>(60/40)%</td>
<td></td>
</tr>
<tr>
<td>(50/50)%</td>
<td></td>
</tr>
<tr>
<td>(40/60)%</td>
<td></td>
</tr>
<tr>
<td>(20/80)%</td>
<td></td>
</tr>
<tr>
<td>(0/100)%</td>
<td></td>
</tr>
</tbody>
</table>
3.4 **Tensile Test.**

The tensile test is carried out on specimens, which were prepared by extrusion methods, according to ASTM-D638 standards using Instron (model PLTE-329.TSQ) testing machine, using cross head speed of 0.5 mm/min. The load applied was (0-50000) N.

<table>
<thead>
<tr>
<th>Test</th>
<th>Sample dimensions</th>
<th>Standard Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>impact</td>
<td><img src="image" alt="Impact sample dimensions" /></td>
<td>ISO-179</td>
</tr>
<tr>
<td>tensile</td>
<td><img src="image" alt="Tensile sample dimensions" /></td>
<td>ASTM-D638</td>
</tr>
</tbody>
</table>

Fig (3.2): Sample dimensions and standard specifications for the testing specimens.
3.5 Impact Test.

(Izod test) is performed according to ISO-179 standards using (Zwick 5113 pendulum impact tester) model IMI. This instrument consists mainly of pendulum and software to analyse the results. Izod impact test consists of standard test piece that would be broken with one blow of a swinging hammer. The test piece is supported at one end in a way that the hammer strikes it at the middle. The testing method of this instrument includes lifting of the pendulum to its maximum height and fixing it firmly.

3.6 DSC Test.

The measurements of glass transition temperature and melting point were carried out with a Perkin-Elmer differential scanning calorimeter model (DSC-6) and (DSC 60). Detailed description of theory and operating principles of differential scanning calorimeter were given in chapter two.

Throughout the DSC work, samples were encapsulated in aluminum sample pans and placed in the holder. An empty aluminum pan of the same weight as that used with the sample, was used as reference holder. Each holder has its own heater and temperature sensor.

The glass transition temperatures for the blend system PS/ABS was determined by DSC instrument model (DSC-6) with approximately 20 mg, each sample was scanned from initial temperature of (30°C) at a heating rate of 10° C/min. This heating rate was chosen to achieve good resolution through DSC test. Nitrogen at flow rate of 20 ml /min was used as a purge gas.
The glass transition temperatures for the pure and blend system PS/SBS were determined by DSC instrument model (DSC 60) with approximately 20 mg, each sample was scanned from initial temperature (-70°C) for the instrument at a rate of 10°C/min. This heating rate was chosen to achieve good resolution through DSC test, liquid Nitrogen was used as a cooling system for the measurement of Tg below room temperature.

### 3.7 Fourier Transforms Spectroscopy (FTIR) Test

Fourier transform (FTIR) spectroscopic measurements were carried out using 8400S –FTIR-Perkin-Elmer spectrophotometer. This instrument operates over wave number range of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). The samples was mounted on a special FTIR-holder so that the reconstructed beam is directed through the sample and focused onto detector.

The output data is in the form of graphical chart, in which the x-axis represents the wave number, while y-axis represents the transmission % in the IR region. Data, comprising points of wave number and transmission % values, have been read out in the same way as mentioned above.

### 3.8 Optical Microscope Instrument

Optical microscope model IM 7000 MEIJI TECHNO JAPAN, was used in the study of the morphology of polymer blends prepared by cast solvent for the system PS/ABS.
3.9 Scanning Electron Microscope (SEM).

Scanning electron microscope (SEM) model (KARL ZEISS EVO 50) JAPAN, was used to observe morphology of blend specimens, cut under liquid nitrogen atmosphere, in order to enhance the phase contrast between two phases. Diagram of a scanning electron microscope shown in Fig (3.3)

![Diagram of a scanning electron microscope](image)

In order to investigate the internal structure of pure and blend specimens peeling was done by means of razor blade. Peeling at room temperature may introduce disruption in the molecular arrangement near the torn surface; to overcome this, the specimens were submerged in liquid nitrogen for 8 min then the peeling was done while the sample was frozen. The sample to be investigated was then mounted carefully on the adhesive side of the sample holder, and then introduced to the scanning electron microscope. Several specimens of each type were scanned to enhance the reproducibility of results obtained.
4.1 Introduction

This chapter includes all the experimental results that are obtained from the mechanical and physical tests for the polymer blends under investigation. The experimental tests and the results of blends systems were used to investigate at first, the mechanical properties including (tensile test, impact test) and physical properties including (differential scanning calorimeter (DSC) test, Fourier transforms spectroscopy (FTIR) Test) and finally the most important morphology for polymer blend were performed by using optical microscopy and Scanning electron microscopy (SEM).

In this chapter, the results of two blend systems are reviewed. 
- PS/ABS
- PS/SBS

All results are discussed together with presentation of, the data obtained from measurement.

4.2 Results and Discussion for PS/ABS System

4.2.1 Mechanical Properties

The mechanical properties in this work were curried out mainly to investigate the behavior of PS/ABS blend, extruded by single screw extruder with different compositions, on the stress-strain curves. The results for the pure polymer and the blends with different compositions are summarized in table 4.1. These results show that:
1- The 60/40 blend composition has the highest value of Young’s modulus and ultimate strength, while the 70/30 blend composition has the highest value of ultimate strain.

2- The 70/30, 60/40 and 50/50 blends have better Young’s modulus, ultimate strength and ultimate strain than the pure PS or ABS materials.

3- The 90/10 and 40/60 blend compositions have very poor mechanical properties, which are worse than those for the pure materials.

4- The 80/20 and 20/80 blend compositions show the same mechanical behaviors, i.e. they have Young’s modulus and ultimate strain % higher than those of the pure materials, while the ultimate strengths are the same as that for ABS but slightly less than that for PS.

Table 4.1: Mechanical Properties of PS/ABS Blends

<table>
<thead>
<tr>
<th>Polymeric blends percents for (PS/ABS)</th>
<th>Young’s modulus MPa</th>
<th>Ultimate Strain %</th>
<th>Ultimate strength MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100/0)%</td>
<td>12.69</td>
<td>3.25</td>
<td>39.5</td>
</tr>
<tr>
<td>(90/10)%</td>
<td>10.6</td>
<td>3.4</td>
<td>19.6</td>
</tr>
<tr>
<td>(80/20)%</td>
<td>17.63</td>
<td>11.25</td>
<td>35.3</td>
</tr>
<tr>
<td>(70/30)%</td>
<td>17.51</td>
<td>20</td>
<td>43.98</td>
</tr>
<tr>
<td>(60/40)%</td>
<td>21.1</td>
<td>10.1</td>
<td>50.8</td>
</tr>
<tr>
<td>(50/50)%</td>
<td>17.9</td>
<td>13.2</td>
<td>45.68</td>
</tr>
<tr>
<td>(40/60)%</td>
<td>10.1</td>
<td>8.5</td>
<td>18.9</td>
</tr>
<tr>
<td>(20/80)%</td>
<td>16.7</td>
<td>17</td>
<td>34.68</td>
</tr>
<tr>
<td>(0/100)%</td>
<td>14.42</td>
<td>13</td>
<td>35.8</td>
</tr>
</tbody>
</table>
One of the physical characteristics of immiscible blends has weaker mechanical properties than pure polymers, although there are some methods that make immiscible blends stronger and compatible. One of these methods is to process these by mechanical mixing in the melt.

From the results of Young’s modulus in table 4.1, it may be seen that the incompatibility of 90/10 and 40/60 blend compositions may be attributed to that during extrusion the solidification of the matrix phase PS before minor phase ABS may result in bad adhesion between two phases. Bad adhesion between two phases results in lower interfacial tension and hence the lower is the internal stress.

The compositions 70/30, 60/40 and 50/50 of PS/ABS blends have mechanical properties that are better than the pure materials, which may be due to their processing with flow in one direction where the minor components form rods instead of spheres as in blending in co-solvents. These rods act like fibers of reinforced composite material, while when the two polymers are roughly in equal amounts, they form two co-continuous phases [52]. This means both phases will bear the load if any stress is applied on the material, then it will be stronger. Also it may be that by increasing the amount of ABS then the styrene proportions within ABS increase. This styrene will be capable to form interaction bonding with the polystyrene compound during extrusion which consequently enhances the adhesion between the two phases. This good adhesion of 60/40 blend component shows the highest value of strength and less strain %, which means with better adhesion between the two phases results in greater interfacial tension and hence higher internal stress which will lead to a lower extensibility. Morton and Hearle[51] interpreted the mechanical properties of polymer in terms of molecular motion. They explained the initial modulus
in terms of internal stresses. At low applied stress, polymers exhibit high resistance to deformation owing to the secondary bonds between the chains and the geometrical interaction between the molecular chains, which cannot move independently of their neighbors. The small motion of chain segments caused by the applied stress in this range is attributed to the diffusion of short chain segments into the “hole” in the polymer microstructure.

### 4.2.2 DSC Test Results and Discussion for PS/ABS

The DSC test in this work was carried out mainly to investigate the effect of PS/ABS blend, extruded with different compositions, on the value of glass transition temperature. The results for pure polymer and blends with different compositions are shown in Fig (4.1, a, b, c, d, e).

![Fig (4.1, a): glass transition temperature for pure polystyrene.](image-url)
Fig (4.1, b): glass transition temperature for sample of (80/20) PS/ABS blends.

Fig (4.1, c): glass transition temperature for sample of (70/30) PS/ABS blends.
Fig (4.1, d): glass transition temperature for sample of (60/40) PS/ABS blends.

Fig (4.1, e): glass transition temperature for sample of (50/50) PS/ABS blends.
The DSC results in Fig (4.1 a), for extruded polystyrene (PS), the glass transition temperature is found to be 119.3 °C. The DSC results for extruded PS/ABS blend samples are shown in Fig (4.1, b, c, d and e), for compositions 80/20, 70/30, 60/40 and 50/50 respectively. For these blend compositions, the Tg's are found to be 116.7, 115.8, 114.8 and 114.0 °C respectively. It is observed that the Tg value decreases with increasing ABS composition. The ABS Tg has been reported elsewhere 110 °C [19]. The Tg for the mixtures is calculated by using an approximate relationship between Tg for mixture and composition as given by the simple (rule of mixture) for binary mixture [53]

\[ \frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \]

Where W₁ and W₂ are the weight fraction of two polymers having Tg₁ and Tg₂ respectively. From these calculations the value of Tg’s for the above compositions are 117.0, 116.1, 115.2 and 114.3 °C. From these results, it seems that for all compositions the calculated Tg’s are slightly higher than that found by;

\[ T_{g\ (calc)} - T_{g\ (DSC)} = 0.3^\circ C \]

It is reported that Tg’s behavior for polymer blends has been used as a measure of miscibility. The appearance of a single Tg at a temperature intermediate between the Tg’s of pure components is indicative of molecular homogeneity, while the appearance of multiple Tgs reflects phase separation of the blend's components [54].
4.2.3 FTIR Results and Discussion for PS/ABS

According to bands values, recorded by Fourier transform spectroscopy (FTIR) for the pure polymers and blends prepared by method of extrusion with different composition of PS/ABS are summarized in tables 4.2 and 4.3, which were derived from Fig (1 to 6) in the appendix.

From these results, the PB phase in pure ABS shows a cis configuration where the band values recorded for this sample are:

The band at 1659 cm\(^{-1}\) is assigned to (C=C) cis stretching. The band at 3002 cm\(^{-1}\) is assigned to (CH) cis stretching. The band at 910 cm\(^{-1}\) is assigned to (CH\(_2\)) cis twisting, and the bands at 1070 and 1315 cm\(^{-1}\) are assigned to (CH\(_2\)) cis wagging. These configurations change from cis to trans for all blend ratios where the band value was recorded. The cis and trans-configuration for PB is shown in Fig (4.2)

![cis-trans configuration for PB](image)

Fig (4.2): The cis and trans configuration for PB

The bands at 1668 cm\(^{-1}\) for 60/40 and 50/50 are assigned to (C=C) trans stretching, also these bands appear with shift by (-2 and -1 cm\(^{-1}\)) in the blend ratios 40/60 and 20/80 respectively. The bands at 2997, 2952 and 2951 cm\(^{-1}\) are assigned to (CH) trans stretching. These values appear in the blend ratios 60/40, 40/60 and 20/80 respectively. The band at 1313 cm\(^{-1}\) is assigned to (CH\(_2\)) trans twisting; this band appears at the blend ratios 60/40 and 50/50 also these bands appear in the blend ratios but with shift by (-3 cm\(^{-1}\)). The
bands at 1240, 1328 and 1235 cm\(^{-1}\) are assigned to \((\text{CH}_2)\) trans wagging for the blend ratios 60/40, 50/50 and 40/60 respectively.

It is observed the \((\text{CH}_2)\) trans twisting and \((\text{CH}_2)\) trans wagging vibration mode don’t appear in the blend ratios 20/80. Also the \((\text{C=C})\) aromatic ring stretching and \((\text{CH})\) aromatic bending for SAN phase appear in the blend ratios 60/40 and 50/50 with the band values (1541, 1598, 1596) cm\(^{-1}\) and (1485, 1637, 1487) cm\(^{-1}\) respectively.

Table 4.2 FTIR results for pure polymers and PS/ABS blend

<table>
<thead>
<tr>
<th>Bond sample</th>
<th>Pure PS</th>
<th>Pure ABS</th>
<th>PS/ABS 60/40</th>
<th>PS/ABS 50/50</th>
<th>PS/ABS 40/60</th>
<th>PS/ABS 20/80</th>
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<tr>
<td>C=C stretching for PB</td>
<td>/</td>
<td>1659 cm(^{-1})</td>
<td>1668 cm(^{-1})</td>
<td>1668 cm(^{-1})</td>
<td>1666 cm(^{-1})</td>
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<td>3002 cm(^{-1})</td>
<td>2997 cm(^{-1})</td>
<td>/</td>
<td>2952 cm(^{-1})</td>
<td>2951 cm(^{-1})</td>
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<tr>
<td>CH(_2) stretching for PB</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>2914, 2902 &amp; 2837</td>
<td>/</td>
<td>2840 cm(^{-1})</td>
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<tr>
<td>CH(_2) twisting for PB</td>
<td>/</td>
<td>910 cm(^{-1})</td>
<td>1313 cm(^{-1})</td>
<td>1313 cm(^{-1})</td>
<td>1310 cm(^{-1})</td>
<td>/</td>
</tr>
<tr>
<td>CH(_2) wagging for PB</td>
<td>/</td>
<td>1070 &amp; 1315 cm(^{-1})</td>
<td>1240 cm(^{-1})</td>
<td>1328 &amp; 1240 cm(^{-1})</td>
<td>1235 cm(^{-1})</td>
<td>/</td>
</tr>
<tr>
<td>C=C stretching for PB</td>
<td>/</td>
<td>1027 cm(^{-1})</td>
<td>1155 cm(^{-1})</td>
<td>1155 cm(^{-1})</td>
<td>1156 cm(^{-1})</td>
<td>1155 cm(^{-1})</td>
</tr>
<tr>
<td>CH aromatic stretch for SAN and PS</td>
<td>3064 cm(^{-1})</td>
<td>3082 cm(^{-1})</td>
<td>3078 &amp; 3066 cm(^{-1})</td>
<td>3076 cm(^{-1})</td>
<td>3082 cm(^{-1})</td>
<td>3026 cm(^{-1})</td>
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<tr>
<td>CH alphatic stretch for SAN</td>
<td>/</td>
<td>2943 &amp; 2852 cm(^{-1})</td>
<td>/</td>
<td>2966 cm(^{-1})</td>
<td>2920 cm(^{-1})</td>
<td>3923 cm(^{-1})</td>
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<td>CH overtone or Combination for SAN and PS</td>
<td>1942 cm(^{-1})</td>
<td>1728 cm(^{-1})</td>
<td>1944 cm(^{-1})</td>
<td>1944 cm(^{-1})</td>
<td>/</td>
<td>1942 cm(^{-1})</td>
</tr>
<tr>
<td>C=C aromatic ring stretching for SAN and PS</td>
<td>1494 cm(^{-1})</td>
<td>1492 &amp; 1600 cm(^{-1})</td>
<td>1541 &amp; 1598 cm(^{-1})</td>
<td>1596 &amp; 1541 cm(^{-1})</td>
<td>1492 &amp; 1600 cm(^{-1})</td>
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<tr>
<td>CH aromatic bending for SAN and PS</td>
<td>1442 &amp; 1593 cm(^{-1})</td>
<td>1450 cm(^{-1})</td>
<td>1637 &amp; 1485 cm(^{-1})</td>
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<td>CH scissoring and bending for SAN and PS</td>
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<td>1363 cm(^{-1})</td>
<td>1348 &amp; 1433 cm(^{-1})</td>
<td>1434 &amp; 1367 cm(^{-1})</td>
<td>/</td>
<td>1367 cm(^{-1})</td>
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<td>C-C or CH out of plan bending for SAN and PS</td>
<td>621 &amp; 1002 cm(^{-1})</td>
<td>621 &amp; 1002 cm(^{-1})</td>
<td>621 &amp; 1002 cm(^{-1})</td>
<td>621 &amp; 1002 cm(^{-1})</td>
<td>698 &amp; 966 cm(^{-1})</td>
<td>700 &amp; 759 cm(^{-1})</td>
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</tbody>
</table>
Table 4.3: The effect of composition on the FTIR bands

<table>
<thead>
<tr>
<th>Wave number cm(^{-1})</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1659,3002,910,1070</td>
<td>Not found in pure PS Initially found in cis PB in pure ABS</td>
</tr>
<tr>
<td>1315, and 1027</td>
<td></td>
</tr>
<tr>
<td>1668,1666,1667,2997,2952</td>
<td>Change from cis to trans for all composition</td>
</tr>
<tr>
<td>2951,1313,1310,1240,1328</td>
<td></td>
</tr>
<tr>
<td>1235,1027, and 1155</td>
<td></td>
</tr>
<tr>
<td>1494,1492,1442,1450,1593</td>
<td>Found in pure PS &amp;ABS, as well in composition:40/60 and 20/80</td>
</tr>
<tr>
<td>1452</td>
<td></td>
</tr>
<tr>
<td>1541,1596,1598,1637,1485</td>
<td>Found in composition:60/40 and 50/50</td>
</tr>
<tr>
<td>1487</td>
<td></td>
</tr>
<tr>
<td>1942 and 1944</td>
<td>Found in pure PS and for all blend ratio</td>
</tr>
<tr>
<td>1728</td>
<td>Found in pure ABS</td>
</tr>
<tr>
<td>621 and 1002</td>
<td>Does not change in all composition</td>
</tr>
</tbody>
</table>

4.2.4 Optical Microscopic Results and Discussion for PS/ABS

Optical microscopy results for polymer blend prepared by cast film from solutions show that the blend ratio of 90/10 (PS/ABS), Fig (4.3.b), where the PS represents a major phase while ABS represents minor phase, and they separate into little spherical globules. When increasing the ABS ratio 80/20 and 70/30 (PS/ABS), the sphere gets bigger and bigger as shown in Fig (4.3.c, d) respectively, until they get so big that they become joined together. Now they are not isolated anymore, but a continuous phase. These continuous phases are observed very clearly in Fig (4.3.e and 4.3.f). This indicates good adhesion between the two phases of PS and ABS rather than the isolated spheres of the minor phase, embedded in the matrix phase. The
mechanical properties previously mentioned enhances this suggestion that these two compositions have the highest tensile strength.

Fig (4.3): Light micrograph (x 600) for: (a) pure PS (b) PS/ABS [90/10]% (c) PS/ABS [80/20]% (d) PS/ABS [70/30]% (e) PS/ABS [60/40]% (f) PS/ABS [50/50]%.
4.2.5 SEM Results and Discussion for PS/ABS

Scanning electron micrographs of melt mixed by single screw extruder of pure polymer and blends of PS and ABS in (100/0, 0/100, 90/10, 80/20, 70/30, 50/50, and 20/80 of PS/ABS) composition ratio are given in Fig (4.4, a, b, c, d, e, f, g) respectively. Figs (4.4, a, b) show the morphology of pure PS and ABS. In Fig (4.4, c, d), it is clear that the effect of polymer flow in one direction (the direction of extrusion) where the ABS as minor components appear as fibres instead of spheres as in blending in cast film from solution. Thus the dispersion of the ABS component in the matrix of PS is finer in the blend with 80% PS than that with 90%. These results enhance the suggestion of reinforced composite material, where these rods act like fibres of reinforced composite material. The co-continuous morphology occurs at blend ratio 70/30 as shown in Fig (4.4, e), and appear clearly in blend ratios 50/50 as shown in Fig (4.4, f).
Fig (4.4): SEM photomicrographs for: (a) pure PS (b) pure ABS (c) PS/ABS [90/10]% (d) PS/ABS [80/20]% (e) PS/ABS [70/30]% (f) PS/ABS [50/50]%. (g) PS/ABS [20/80]%.
4.3 Results and Discussion for PS/SBS System

4.3.1 Mechanical Properties

The mechanical properties in this work were curried out mainly to investigate the effect of PS/SBS blend, extruded by Haake PolyDrive extruder with different compositions, on the stress-strain curves and impact behaviors.

4.3.1.1 Tensile test

Due to the tensile properties of PS, which is highly brittle, it was found very difficult to obtain a stress-strain curve, while the mechanical test results for (SBS) show good elastic properties and good resilience but poor process ability characteristics. For SBS and its high composition blends the yield point was not well defined, in this case the yield point was determined by finding the intersection of the linear portions of the stress-strain curve before and after yield via computer.

The results of strain-stress curves are shown in Figs (7 to 16) in the appendix. The Young’s modulus of tested sample (i.e. the slope of linear part of the stress-strain curve) is plotted against blend composition in Fig (4.5). It is seen that the Young’s modulus decreases dramatically with increasing SBS content, i.e. for composition of 10/90(SBS/PS) the modulus is around 2640 MPa while 90/10(SBS/PS), composition is 4 MPa. The Young’s modulus for pure SBS is 0.3 MPa.
The effect of blend composition on the yield strength and break strength is shown in Fig (4.6). The two curves are very similar and may be seen that both strengths decrease very steeply with increasing SBS composition, specially for 10 and 20 % SBS composition but above 50% the break strength becomes nearly stable.

Fig (4.5): Effect of SBS content on Young’s modulus

Fig (4.6): Yield strength and Break strength as a function of SBS content.
On the other hand, the elongation at break % is found to increase with increasing SBS proportion, as shown in Fig (4.7), which shows that pure PS and blend with low proportion of SBS are brittle i.e. for 10 % SBS the elongation% is around 4 %, while for high proportions of SBS 90 %, the blend is ductile and the elongation is around 1315 % which indicates it is near being elastomer.

Fig (4.7): Effect of SBS content on Elongation at break.

The addition of small proportion of SBS to PS, less than 30 %, the material behaves like hard and strong but not as brittle as pure PS. The addition of large proportion of SBS tends to make the material ductile and elastic but stronger than pure SBS.

On the other hand, the composition between 30/70 to 70/30 of SBS/PS shows that mechanical properties change linearly with composition which may suggest following the rule of mixtures[18,23].

In general the mechanical behavior of heterogeneous systems in different situations such as stiff phase dispersed in soft matrix, or soft
dispersed in stiff matrix as in the case of these blends depend on their composition.

4.3.1.2 Impact test

The Izod impact test was performed on Static Impact Testing Machine equipped with Izod pendulum and specimen holder. The test calculates the energy required to break a specimen when the pendulum hits the specimen on impact. The impact tests were carried at room temperature of 25 °C, and their results are presented in Fig (4.8).

The results recorded for this test show for pure PS the value of impact resistance is (20.2) J/m, and this value increases to (24.7, 38.8,39.7, 82.6 ,142.5 ,184.2 ,201.1) J/m with increasing proportion of SBS in the blend ratios (90/10 ,80/20 ,70/30 ,60/40) respectively. The results of the Izod impact testing shows same behavior as shown by tensile test, thus these results follow the rule of mixtures.

![Fig (4.8): Effect of SBS content on Impact resistance](image-url)
4.3.2 DSC Test Results and Discussion for PS/SBS

The DSC test in this work was carried out mainly to investigate the effect of PS/SBS blend, extruded with different compositions, on the value of glass transition temperature. The results for pure polymer and blends with different compositions are shown in Figs (4.9, a, b, c, d, e, f and g).

Fig (4.9, a): glass transition temperature for pure polystyrene.

Fig (4.9, b): glass transition temperature for pure SBS.
Fig (4.9, c): glass transition temperature for sample of (90/10) PS/SBS blends.

Fig (4.9, d): glass transition temperature for sample of (80/20) PS/SBS blends.
Fig (4.9, e): glass transition temperature for sample of (60/40) PS/SBS blends.

Fig (4.9, f): glass transition temperature for sample of (40/60) PS/SBS blends.
Fig (4.9, g): glass transition temperature for sample of (20/80) PS/SBS blends.

- The DSC thermogram of pure SBS shows two glass transitions, one for soft elastomer phase of PB block at -64 °C and the other for hard plastic phase of PS block at 78.7 °C.

- Pure PS exhibits only one glass transition temperature at 116 °C which is higher than that of the SBS block copolymer.

- The PS/SBS blends with different compositions show also two Tg’s; one at negative temperature that is indicated due to soft phase PB block of SBS Tg₁ which increases slightly with increasing amount of SBS in the blends except for composition (20/80) PS/SBS is -66 °C. The other glass transition temperature Tg₂ which is indicated due to the hard phase PS shows a significant shift with decreasing PS in the blend i.e from 112.5 to 90 °C for 90/10 to 20/80 respectively. This
may suggest that the monomers of pure PS in the blend are combined with the monomers of PS block which exist in the SBS block copolymer then gave only one Tg. The shift in the two Tg’s becomes smaller with decreasing PS proportions.

4.3.3 **SEM Results and Discussion for PS/SBS**

Scanning electron micrographs for internal morphological studies of the melt mixing pure polymers and blends of PS/SBS with different compositions of (90/10, 80/20, 70/30, 50/50, 30/70, 20/80) are shown in Figs (4.10, a,b,c,d,e,f,g and h) respectively.

The scanning electron microscopy for PS Fig (4.10,a) shows a homogeneous particle distribution with average particle size of 2 µm. Fig (4.10,b) for pure SBS shows a very wide distribution and coarse particles, which belong to the 30% of PS block in the tri-block copolymer of styrene-butadiene-styrene.

The 10% SBS blend micrograph shows dispersed matrix phase morphology, where elastomer domains are dispersed in the continuous PS matrix phase as shown in Fig (4.10,c).

The increase of SBS proportion to 20% as shown in Fig (4.10,d) indicates that the particle size increases considerably, but this pure phase is still isolated from the matrix phase. For 30% SBS blend, the phases start to percolate forming large domains of complicated shapes and a tendency of initiating interconnection and no more isolated particles are observed, as appear very clearly in Fig (4.10, e). For the same magnification as shown in Fig (4.10, f), co-continuous phases are observed very clearly with fiber connections between each phase for 50% SBS composition. When the SBS
constituents are increased to 70%, the micrograph shows an intermediate co-
continuous between phases and PS-phase dispersed in the continuous SBS
matrix phase as shown in Fig (4.10, g). Previously, the mechanical
properties for the 30% to 70% SBS blends were found to follow the rule of
mixture. This may reflect the influence of co-continuous phases on
mechanical properties of the blends.

Furthermore, as in Fig (4.10, h), the micrograph for 80% SBS shows
PS domain is dispersed in the continuous elastomer matrix phase. Similar
behavior of two-phase morphology has been reported for PS/PB blends by
Susan Joseph et.al.[13].
Fig (4.8): SEM photomicrographs for: (a) PURE PS (b) PURE SBS (c) PS/SBS [90/10]% (d) PS/SBS [80/20]% (e) PS/SBS [70/30]% (f) PS/SBS [50/50]% (g) PS/SBS [30/70] (h) PS/SBS [20/80]%.
Conclusions

In the present work, attempts are made to develop a polymer with desirable properties; by mixing the hard and brittle PS with two different types of rubber. Mechanical studies, thermal studies and microscopy of a new blend containing PS with ABS and SBS have been carried out in order to elucidate the morphology and characteristics of these blends.

From the result of these investigations, the following conclusions can be drawn:
1. Addition of ABS to PS between 30 to 50% is found to improve the mechanical properties in comparison with the ABS or PS for extruded samples.
2. For morphological studies by optical microscope and SEM, the following findings are observed. The polymer blend having low proportions of ABS shows morphology of spheres embedded in the PS matrix, in the case of films cast from solution. While extruded samples show that their structure is basically long fibrils running along the extrusion direction. For ABS proportions between 30-50%, they show a co-continuous morphology.
3. The DSC results for blend of PS/ABS averment the state of miscibility by recording one glass-transition temperature located between the values of the pure polymers; its value decreases with increasing ABS proportions.
4. The mechanical properties for blend system of PS/SBS indicate the possibility to control the product property by controlling the blend ratios, i.e. the strength and elasticity of the product depend on the content of each material, which suggests the rule of mixture is obeyed.

5. The SEM results for blend system of PS/SBS at low proportions of SBS or PS show that the minor phase is dispersed in the continuous matrix phase, while for intermediate proportions show co-continuous phases.

6. The DSC results for blend system of PS/SBS yield good indications of improvement in state of partial miscibility.

7. In general the morphological behaviors of polymer blends depend strongly on blend ratios and method of preparation. To satisfy the goal of blend formulation to achieve additive behavior, a machine of high mixing quality must be used.

8. The FTIR results for PS/ABS blend system show that the PB phase in pure ABS shows a cis configuration and these configurations change from cis to trans for all blend ratios.
**Suggestions for future work**

From the present study, the following fields could be suggested for future work.

1. Study the effect of environment and thermal history on the mechanical and physical properties of different compositions of PS/ABS and PS/SBS.
2. Addition of silicate foam and carbon black as a binder for blend system of PS/SBS to study thermal conductivity.
3. Study the effect of blend ratios of ABS/SBS on the creep behavior, thermal properties and morphology.
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB</td>
<td>Polybutadiene</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
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<tr>
<td>PP</td>
<td>Polypropylene</td>
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<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
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<td>Polyethylene terphthalate</td>
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<td>Polyurethane</td>
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<td>HIPS</td>
<td>High impact Polystyrene</td>
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<td>PS</td>
<td>Polystyrene</td>
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<td>SBS</td>
<td>Styrene-Butadiene-Styrene</td>
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<td>EVA</td>
<td>Ethylene Vinyl Acetate Copolymer</td>
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<td>PPS</td>
<td>Poly phenylene sulfide</td>
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<td>Styrene/acrylonitrile copolymer</td>
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<td>Scanning Electron Microscopy</td>
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<td>FT-IR</td>
<td>Fourier Transform Infrared</td>
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### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>unit</th>
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<tbody>
<tr>
<td>$A$</td>
<td>Area</td>
<td>$\text{mm}^2$</td>
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<tr>
<td>I.S</td>
<td>Impact Strength</td>
<td>$\text{KJ/m}^2$</td>
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<tr>
<td>UCS</td>
<td>Ultimate Compressive Strength</td>
<td>MPa</td>
</tr>
<tr>
<td>$t$</td>
<td>Thickness</td>
<td>mm</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
<td>($\text{m}^2/\text{sec}$)</td>
</tr>
<tr>
<td>$E$</td>
<td>Young's modulus</td>
<td>MPa</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>volume fraction</td>
<td>%</td>
</tr>
<tr>
<td>$r$</td>
<td>degree of polymerization</td>
<td>%</td>
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<tr>
<td>$\rho$</td>
<td>Density</td>
<td>$\text{g/cm}^3$</td>
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<tr>
<td>$\tau$</td>
<td>Shear stress</td>
<td>MPa</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Tensile strength</td>
<td>MPa</td>
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<tr>
<td>$p$</td>
<td>Load</td>
<td>N</td>
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<tr>
<td>$\Delta L$</td>
<td>Elongation</td>
<td>mm</td>
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<tr>
<td>$\varepsilon$</td>
<td>Failure strain</td>
<td>%</td>
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Appendix

Fig (1): FTIR results for pure PS

Fig (2): FTIR results for 60/40 PS/ABS
Appendix

Fig (3): FTIR results for 50/50 PS/ABS

Fig (4): FTIR results for 40/60 PS/ABS
Appendix

Fig (5): FTIR results for 20/80 PS/ABS

Fig (6): FTIR results for pure ABS
Appendix

Fig (7): stress-strain curve for 90/10 PS/SBS

Fig (8): stress-strain curve for 80/20 PS/SBS
Appendix

Fig (9): stress-strain curve for 70/30 PS/SBS

Fig (10): stress-strain curve for 60/40 PS/SBS
Appendix

Fig (11): stress-strain curve for 50/50 PS/SBS

Fig (12): stress-strain curve for 40/60 PS/SBS
Appendix

Fig (13): stress-strain curve for 30/70 PS/SBS

Fig (14): stress-strain curve for 20/80 PS/SBS
Fig (15): stress-strain curve for 10/90 PS/SBS

Fig (16): stress-strain curve for pure SBS
Appendix

Fig (17): Single screw Extruder machine

Fig (18): Haake PolyDrive extruder.
Appendix

Fig (19): Tensile testing machine.

Fig (20): Impact test machine.
Appendix

Fig (21): (A) DSC-6, (B) DSC 60
Appendix

Fig (22): FTIR Instrument.

Fig (23): Optical Microscope Instrument.
Appendix

Fig (24): SEM instrument.
References


