Thermal stability, mechanical properties, impact strength, and uniaxial extensional rheology of reactive blends of PS and SBS polymers

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Abstract Polystyrene (PS) has low impact strength and also shows poor strain hardening. In this work, poly(styrene-butadiene-styrene) triblock copolymer (SBS) was solution- and melt-blended with PS in the presence of a free-radical polymerization initiator, dicumyl peroxide (DCP), to enhance PS's thermo-mechanical properties, impact resistance, and strain hardening. The solution blended PS/SBS containing 0.1% DCP annealed at 180 °C showed strong strain hardening but the melt blended PS/SBS annealed at the same temperature and time showed poor strain hardening. The changing of the blending temperature, DCP concentration, and PS to SBS ratio had minimal effect on the strain hardening of PS. The tensile strength increased with an increase in the concentration of DCP up to 0.1%, beyond that the tensile strength started decreasing. The impact resistance considerably improved with an increase in the SBS loading in the PS matrix and the enhancement was more than double of the impact resistance shown by the neat PS.

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Introduction

Polymer blending is extensively practiced in polymer processing to enhance the performance of a polymer to widen its application, i.e. to convert a low performing polymer into a high performing polymer. For example, the grafting of PS onto high-density polyethylene (HDPE) improves the tensile strength and decreases its hygroscopic expansion [1].

PS is used for the manufacturing of toys, Petri dishes, test tubes, foam packaging, etc. It is relatively resistant to degradation compared to polylactide used in packaging but because of its low impact strength, for some applications, it needs to be toughened [2]. High impact polystyrenes are made by bulk polymerization of styrene in the presence of rubber particles, and these rubber particles toughen PS and enhance its impact strength. A range of polymers and inorganic nanoparticles, such as polybutadiene (PB), polybutadiene-grafted-polystyrene, a copolymer of butyl acrylate, methyl methacrylate and styrene, and calcium carbonate micro/nanoparticle, have been investigated for the improvement of the impact strength of PS [3–6]. The addition of a small quantity of silica nanoparticles to PP/EPDM composites largely improved their toughness [7]. The addition of a small percentage of polyurethane elastomer to PLA in the melt blending improved its toughness, impact strength and tensile strength [8, 9]. It was reported that the blending small weight % of UHMW-PP to PP increased its transient uniaxial extensional viscosity and showed strong strain hardening [10]. Fowler and Baker melt blended carboxylic group-containing acrylonitrile-butadiene rubber with a copolymer of styrene and vinyl oxazoline, which was added to PS by melt blending to enhance its impact strength [11]. The latex particles act as stress concentrators and produce more extensive matrix deformation by crazing or shear yielding [12]. Depending on the intrinsic brittleness of the matrix polymer, they toughen the matrix polymer by introducing multiple crazing, especially in the case of PS [13].

On the other hand, the rheological properties under uniaxial extensional flow have been recognized to be very important for the processing of thermoplastic polymers by various processing methods including film extrusion, and foaming [14, 15]. Molten thermoplastic polymers show non-Newtonian flow and their viscosity decreases with an increase in the shear rate [14]. For homogeneous polymeric systems, the extensional viscosity initially gradually increases with time but then suddenly the viscosity steeply increases and goes above the linear viscoelastic envelope. This phenomenon is known as ‘strain hardening’, which is present in both planar and uniaxial flows but is more pronounced in the latter [16]. It is achieved when the strain rate is larger than the reciprocal value of the maximum relaxation time. As the strain hardening of polymer exhibits strong resistance against fast stretching of molten polymer, the polymer processing becomes easier to control.

Lentzakis et al. reported that the larger the number of entanglements of the segments between branches, the stronger the strain hardening and the smaller the characteristic rate for its onset [17]. Therefore, until now, numerous studies have been carried out in the area of the uniaxial extensional rheology of various polymer melts [18–21]. The uniaxial extensional rheology of various polymers including PS, polyethylene (PE), polypropylene (PP), PS/ultra-high molecular weight PS (UHMW-PS), and polycarbonate/polytetrafluoroethylene has been studied [17–23]. It was reported that the introduction of a small amount of long chain branching in the polymer causes strain hardening [24, 25]. The modification of PP with an electron beam or with peroxide provided a significant improvement in its strain hardening [26, 27]. It was found that ultraviolet, and electron beam irradiations, and polymeric grafting introduce few ultra-high molecular weight (UHMW) short or long chain branches in the polymer backbone [24, 28, 29]. Takahashi et al. reported that in the case of miscible and homogeneous blends, the addition of 1.5 weight % UHMW polymethyl methacrylate (PMMA) to an ordinary PMMA by melt blending considerably increased its strain hardening property but for immiscible blends, no strain hardening was observed [30]. The UHMW chains are stretched when they are entangled with surrounding polymers, which causes strain hardening. It was also reported that the strain hardening behavior of a polymer is dependent on the strain rate and the diverse branching structures [15, 31]. It was explained that under extensional deformation the strain hardening is caused by the restricted stretching of the backbone between two branch points. Minegishi et al reported strain hardening of a miscible and homogeneous blend of PS and UHMW-PS [22]. At the frequency lower than 0.001 rad/s, the enhancement of G′ was observed by the incorporation of 1.5% UHMW-PS and the degree of enhancement was in the order of molecular weight of UHMW PS and its concentration. The melt rheology, mechanical properties and impact resistance of reactive melt-blended PS/SBS have been rarely reported.

In this work, SBS was solution- and melt-blended with PS in the presence of DCP to enhance PS’s thermal stability, mechanical properties, impact resistance, and strain hardening behavior. The uniaxial extensional rheology, impact strength, thermal properties, and mechanical properties of the melt blended PS/SBS were compared with the uniaxial extensional rheology and impact strength of the solution-blended PS in the presence of 0.1% DCP and annealed at 180 °C for 10 min.

Experimental section

Materials

The PS pellets used were general purpose atactic PS (Type HF77, M_n = 220,000, polydispersity = 2.0, melt flow index = 7.5 g/10 min) supplied by A&M Styrene Co Ltd. (Japan). SBS pellets (Tufrene, M_n = 80,000, polydispersity = 1.3, S:B:S = 20:60:20), was supplied by Asahi Chemical Industry Co. Ltd. (Japan). Tetrahydrofuran (THF) and DCP of 99% purity were purchased from Sigma-Aldrich Chemicals (USA) and Arkema Peroxide Ltd. (France), respectively.

Blending of SBS with PS

The blending conditions are presented in Table 1. PS and SBS pellets were dried at 80 °C for 24 h under vacuum to remove the absorbed moisture before carrying out the melt or solution blending. The melt blending of PS and SBS was carried out by using a static mixer (Labo Plastomil, Model 655, Toyo Seiki Seisaku-sho, Inc., Japan). The blending of PS/SBS was carried out at three different ratios, 80/20, 90/10, and 95/5 at different doses of DCP (0.1, 0.2, 0.3, 0.4 and 0.7% on the weight of polymer) at various temperatures for 10 min under the flow of nitrogen. The torque vs time data showed that 10 min blending was enough to get a homogeneous blending of PS and SBS without considerable degradation. For the comparison of the uniaxial extensional rheology of the melt blended PS/SBS with solution blended SBS, PS/SBS mixed with SBS at 20/20 ratio and 0.1% DCP was dissolved in THF and then the solvent was evaporated by placing them in a tray in a fume hood.

Measurement of Uniaxial Elongation Rheology

The melt blended PS and SBS prepared at different processing conditions were converted into rectangular shaped plates of size 8 × 15 × 50 mm by compression molding using a Toyo-Seiki Mini Hot Press at 160 °C (otherwise stated) and at 10 MPa pressure for 10 min. The heater of the molding machine was switched off and the samples were cooled by using a fan by maintaining 10 MPa load. The solution blended PS/SBS was also annealed at 180 °C for 10 min at 10 MPa load and then slowly cooled.

The uniaxial extensional rheology of PS/SBS was measured at 140 °C (except the solution blended PS/SBS, which was measured at 180 °C) at 0.5, 0.2, 0.1 and 0.05/s strain rates by a Meissner type uniaxial extensional rheometer (Model: RME, Rheometric Scientific, USA). A rectangular-shaped three-dimensional polymer sample is extended by two sets of oppositely driven belt clamps and the sample is held by a flow of hot nitrogen, which is passed through the fritted metallic base situated just under the sample. The belt clamps are housed in an electrically heated oven. The belt clamps inside the oven are driven by a motor in a counter-rotating fashion. Metallic belts are attached to the clamp grips that extend the polymer sample. The force required to extend the sample is measured by a transducer connected to the right-hand side belt clamps by a leaf spring. A rectangularly shaped sample was placed between the two sets of belts of the rheometer and allowed to melt. The sample was heated for 5 min to remove heat memory and then the upper belt clamps were lowered and the force was set to zero. Two pins with a diameter greater than the sample thickness by 0.5 mm were placed near both ends of the sample over the lower belts as a spacer between the upper and lower belts to prevent from the premature squeezing of the sample by the upper belts prior to extension. When the sample reached the test temperature, the upper belts were lowered and the test was started and the transient uniaxial extensional viscosity was measured.

Thermal stability and mechanical properties

Thermo-gravimetric (TG) analysis was carried out on a Seiko DSC/TG Analyzer (Model SSC 5000, Seiko Corporation, Japan) from room temperature to 600 °C at a heating rate of 5 °C/min under the nitrogen gas environment. A high purity oxygen-free nitrogen gas was used as an inert gas to purge air from the pyrolysis zone to prevent oxidation of polymer samples. A constant flow of nitrogen was fed at a rate of 100 ml/min to the system from a point just below the samples. The TG curves were recorded simultaneously along with the temperature rise.

For the measurement of tensile strength, samples of various PS/SBS blends of 100 × 10 × 1.5 mm size were prepared by compression molding at 160 °C for 10 min at 10 MPa pressure and then slowly cooled. Tensile tests were performed to examine tensile strength and elongation according to the ASTM standard test method D638-03. The tensile strength and the elongation at break were measured by Instron Universal Testing Systems (Model 4400, Instron Inc., Norwood, USA). The gauge length was 40 mm and the crosshead speed was 10 mm/min. An extensometer was employed to determine the elongation of the samples. Tests were carried out in an environmentally conditioned room maintained at 20±1 °C and 65±1% RH and the samples were previously conditioned at the mentioned conditions for 48 h. The 12 identical samples of neat PS and each PS/SBS blends were measured and the average values are reported here. The Charpy impact strength of the notched PS and PS/SBS blends was determined on a Charpy XCJ-500 impact tester made by Chengde Precession Testing machine Co. (China) at 20±2 °C. For each type, 10 samples were tested and the average impact strength is reported.

Attenuated Total Reflectance (ATR) - Fourier transform infrared (FTIR) spectroscopy

The ATR-FTIR spectra of neat PS and its blends with SBS were recorded on a Perkin Elmer System 2000 FT-IR spectrometer using a ZnSe crystal. The pellets of neat PS and various PS/SBS blends were converted to films by compression molding and they were then scanned on an FTIR at a resolution of 4 cm^{-1} at room temperature and a minimum of 64 scans was signal-averaged.

Water absorption and hygroscopic expansion

The water absorption by PS and its blends with SBS at various ratios was carried out using 50 × 25 × 1.5 cm size samples according to the ASTM D570 method. The samples were immersed in 200 ml of distilled water at room temperature. After which they were removed from the water at 24 h intervals, wiped by tissue paper and weighed. The samples were again immersed in water after each measurement and the measurement was continued up to seven days. The weight of the samples was measured to a precision of 1 mg. Finally, the water absorption was calculated according to the following equation:

$$Water\ absorption\ ratio, W_a(t) = \frac{W_t - W_o}{W_o} \times 100 \qquad [1]$$

where $W_a(t)$ is the water absorption at time t, W_o is the original weight of the sample and W_t is the weight of the sample at a given immersion time t.

The hygroscopic expansion was measured by placing 50 × 25 × 1.5 mm size samples in 200 ml distilled water and the length of the samples was measured after a predetermined time by a digital slide caliper (Mitutoyo Corporation, Japan) at 24 h intervals up to seven days.

The hygroscopic expansion was calculated as the length difference before and after immersion in water and expressed as a percentage.

Scanning electron microscopy

Plate samples of size 25 × 25 × 5 cm were made by compression molding. The samples were immersed in a liquid nitrogen bath for 30 min and fractured by the impact. The fractured surfaces were scanned on JEOL field emission scanning electron microscope (Model: JSM-7000F, JEOL Corporation, Japan) equipped with an energy dispersive X-ray spectrometer without any conductive coating using a backscatter mode. The accelerating voltage was 15 kV for all the samples.

Results and discussion

Uniaxial extensional rheology

Melt and solution blended PS/SBS

Fig. 1 shows the transient uniaxial extensional viscosity curve of the 80/20 mixture of the solution and melt-blended PS/SBS measured at 0.5, 0.2, 0.1 and 0.05/s strain rates. The viscosity of the solution-blended PS/SBS was measured at 180 °C but the viscosity of the melt-blended samples was measured at 140 °C since the melt blended PS/SBS samples were disintegrating at temperatures higher than 140 °C. The time-dependent transient uniaxial extensional viscosity curves of 80/20 mixture of solution-blended PS/SBS shows strong strain hardening at all the strain rates investigated. On the other hand, the melt blended PS/SBS showed poor strain hardening at all the strain rates. As the solution-blending process is highly expensive because of the high cost of THF and also it is not an environmentally friendly solvent, our effort continued whether we can achieve similar strain hardening by melt blending by changing various processing parameters, i.e. by changing blending temperatures, PS to SBS ratios and the DCP concentrations.

Melt blended PS/SBS at high temperatures without DCP

It was expected that the increase in the temperature would reduce the viscosity of the polymer melts allowing homogenous mixing. Therefore PS/SBS were melt-blended and annealed at 180, 220, 240, and 260 °C for 10 min without the addition of DCP. Fig. 2 shows the time-dependent transient uniaxial extensional viscosity curves of the 80/20 mixture of PS/SBS measured at 140 °C at 0.5, 0.2, 0.1 and 0.05/s strain rates. The solid line shows the three times of linear viscosity at different time intervals. For the control PS, the transient uniaxial elongation viscosity curves deviated from the linear extensional viscosity curve and went upward, especially at 0.5 and 0.2/s strain rates, indicating some levels of strain hardening behavior. It is evident that the increase in the melt-blending and annealing temperature had almost no beneficial effect on the transient uniaxial extensional viscosity up to 220 °C, after which the transient uniaxial elongation viscosity decreased with further increase of the temperature. Only the sample prepared and annealed at 180 °C showed marginally higher transient uniaxial extensional viscosity at 0.2 and 0.1/s strain rates but at 0.05 strain rate, the viscosity was lower compared to the control PS. For other temperatures, the transient uniaxial extensional viscosity decreased with an increase in the processing and annealing temperatures. However, the strain hardening achieved by melt blending at high temperatures was not comparable to the strong strain hardening achieved by solution blending. We then investigated whether the increase in the DCP concentration can increase the strain hardening behavior of PS/SBS blends.

Melt blended PS/SBS with various DCP concentrations

Fig. 3 shows the transient uniaxial extensional viscosity curves of neat PS and 80/20 blends of PS/SBS. It can be seen that only for the DCP concentration of 0.1%, a marginal improvement in the strain hardening was observed for the PS/SBS blend at 05, 0.2 and 0.1/s strain rates but at 0.05/s strain rates, the viscosity decreased compared to the control PS. However, increasing the DCP concentration to 0.2 and 0.4% had no effect on the strain hardening behavior of PS/SBS blends but for the concentrations higher than 0.4%, instead of showing a positive effect on the strain hardening of PS, actually the viscosity decreased. As the increase in the DCP concentration failed to improve the strain hardening, we investigated the effect of weight% of SBS in the PS/SBS blends on the strain hardening effect.

PS/SBS melt blended at various PS/SBS ratios with DCP

Fig. 4 shows uniaxial extensional rheology of 95/05, 90/10 and 80/20 blends of melt- blended PS/SBS at various strain rates. It is evident that the transient uniaxial extensional viscosity increased only marginally with an increase in the weight% of SBS in the PS/SBS blends but the level of improvement in strain hardening is not at all comparable to the strain hardening shown by the solution blended PS/SBS.

Long-chain branched, moderately cross-linked or highly branched polymers were found to show strong melt elasticity expressed by the first normal stress difference and storage modulus, and strong strain hardening under extensional flow [32]. A peroxide initiator has been used to promote free-radical grafting of functional monomers onto polymer molecules in melt blending. Several researchers used this technique to produce graft-copolymers. For example, the reactive processing of PP and SBS in the presence of DCP produced SBS-grafted-PP [32]. Reactive processing of PS and PB in the presence of DCP produced interpenetrating polymer networks [33]. Similarly, trimethylolpropane trimethacrylate and 1,6-hexane dioldicrylate added with PP in the presence of DCP produced long chain branched PP [34, 35]. Münstedt et al. found that bimodal PS with a distinct high-molecular-weight component showed strong strain hardening [36]. Sugimoto et al. showed that PP containing 1% or less ultra-high-molecular-weight polyethylene showed strong strain hardening [5].

The solution blended PS/SBS containing 0.1% DCP produced strong strain hardening but when the same PS/SBS was melt-blended in the presence of various concentrations of DCP, did not show better strain hardening than the control PS. The reason could be that the temperature at which the blending was carried out, DCP decomposed very quickly and did not get enough time for molecular level mixing. On the other hand, in the case of solution blending, the SBS and DCP both are properly mixed together with the PS and branching occurred in the PS molecular chains resulting in an increase in the strain hardening. Therefore, we can conclude that it is not possible to increase the strain hardening behavior of PS by melt blending with the addition of SBS in the presence of DCP. The strain hardening is only observed when the branching of SBS to the molecular chain of PS occurs at the molecular level.

Mechanical properties

Fig. 5(a) shows the tensile strength of neat PS, and PS/SBS blends with various weight% of SBS prepared by melt blending at 180 °C in the presence of 0.1% DCP. The average tensile strength shown by the neat PS was 2.8 MPa. It is evident that the addition of SBS to PS increased the tensile strength of PS as the tensile strength increased to 3.22 MPa at 5 weight% of SBS, which is 15% increase in tensile strength, but after which the tensile strength decreased marginally with further increase in the weight% of SBS. However, all the

PS/SBS blends showed higher tensile strength than the neat PS. The increase in tensile strength indicates that SBS bonded to the PS matrix polymer.

Fig. 5(b) shows the tensile strength of 80/20 blends of PS/SBS prepared at 180 °C by melt blending in the presence of various concentrations of DCP. It can be seen that the tensile strength increased at lower concentrations of DCP up to 0.1% but beyond that concentration, the tensile strength started decreasing with an increase in the concentration of DCP. The lowest tensile strength was shown by the blend prepared in the presence of 0.7% DCP, which was considerably lower than the tensile strength shown by the neat PS/SBS blend. The increased concentration of DCP probably increased the degradation of polymer causing a decrease in the molecular weight and thereby decreasing tensile strength. Several published literature also shows that the crystallinity of the polymer decreases with an increase in the DCP concentration [37, 38]. We observed that the color of the blend turned to yellow with an increase in the concentration of DCP, which indicates that probably degradation of PB of the SBS took place at high DCP concentrations producing hydroperoxide and oxidation products as well as chain scission and disaggregation of the styrene units [39, 40]. Therefore, we can conclude that 5% SBS loading and 0.1% DCP concentration are the optimum and beyond that level, the tensile strength decreased.

Zhu et al. studied the properties of miscible blends of PS and SBS. They found that the tensile strength decreased from 16.01 MPa for the neat PS to 12.26 MPa for the PS/SBS blend with 60% SBS loading but the impact strength and the elongation at break increased with an increase in the SBS loading [41]. Thomann et al found that in the case of SBS/PS blend, SBS with a substantial ‘PS softening’ effect was found to preferentially form elongated PB lamellar morphologies, which lead to increasing ductility [42]. On the other hand, several researchers reported that grafting of PS onto macromolecular chains of HDPE and polyurethane (PU) copolymer increased the tensile strength of HDPE and PU respectively [1, 43]. It was also reported that the addition of a small amount of PP to LDPE in the presence of DCP increased the tensile strength of LDPE [44]. It was observed that in the case of reactive blending of PS and SBS, the tensile strength of PS increased when blending was carried out in the presence of 0.1% DCP and the SBS loading was 5%. The results indicate that some levels of branching in the PS occurred and therefore the tensile strength increased.

Impact strength

Fig. 6 shows the impact strength of melt and solution blended PS/SBS with various SBS loadings. It is evident that the addition of SBS had a positive effect on the impact strength of PS. The impact resistance dramatically increased with an increase in the SBS loading. It is known that the addition of rubber particles to a glassy polymer, such as PS, improves the impact strength of the glassy polymer. However, for immiscible glassy polymer and rubber blends, the addition of rubber may show poor toughening as debonding between matrix glass polymer and the toughening rubber may occur. It is possible that partial cross-linking of PB component of SBS with PS took place, which created a balance between miscibility/immiscibility thereby improving impact toughening of these blends. The notched Charpy impact strength shown by the control PS was only 1.9 kJ/m^2. In the case of melt blending, the notched Charpy impact strength increased to 5 kJ/m^2 for the PS with 20% SBS loading, which is 163% increase in impact strength. The solution blended PS/SBS showed slightly higher impact strength compared to the impact strength showed by the melt blended PS/SBS. The high increase in the impact resistance shows that SBS and PS blends are miscible.

Thermal stability

The TGA curves of neat PS and 90/10 blends of PS/SBS melt blended in the presence of 0.1 and 0.4% DCP are shown in Fig. 7. The melting temperature of PB is 80 °C, much lower than the softening point of polystyrene. Therefore, PB segments of SBS degrade much earlier than the PS segments [45]. It can be seen that the thermal stability and the ash content of PS increased with an increase in the concentration of DCP up to 0.1% after which, the thermal stability started to decrease but still was better than the thermal stability shown by the neat PS indicating that branching of PS with SBS increased its thermal stability. The ash content of neat PS was 0.60%, which increased to 4.65% for the PS blended with 10% SBS in the presence of 0.1% initiator. However, the increase in the initiator concentration decreased the ash content to 0.29%. Probably the increase in the concentration of DCP increased degradation of PB of SBS during the melt blending of PS/SBS resulting in quicker degradation of PB in the TGA test and therefore the ash content decreased with an increase in the DCP concentrations. The differential thermal analysis (DTA) curves of neat PS and PS melt blended with 10% SBS in the presence of 0.1 and 0.4% DCP are shown in Fig. 7. The peak degradation temperature for the neat PS is 432.0 °C, which increased to 436.6 °C for the PS sample melt blended with 10 weight% SBS in the presence of 0.1% DCP but decreased to 432.4 °C when the concentration of DCP was increased to 0.4%. It can be seen that 0.1% DCP is the optimum concentration to improve the thermal stability of PS reactive blended with SBS.

Surface morphologies

The PS/SBS miscible blends prepared with various SBS loadings were characterized in terms of phase morphology by the scanning electron microscopic technique. Fig. 8 represents SEM micrographs of impact-fractured surfaces of neat PS, and melt-blended PS/SBS with various SBS loadings prepared at 180 °C in the presence of 0.1% DCP and annealed at 160 °C for 10 min. The SEM micrographs for each PS/SBS blends are shown at two different magnifications (20 and 100 µm). In the case of neat PS, the white stress stripes visible in Fig. 8(a) are the traces of stress in a propagating process and there is no longitudinal projection of the stripes are visible indicating the brittle nature of the neat PS. In the case of PS/SBS blends, SBS homogeneously mixed with the PS matrix for all the SBS loadings investigated in this work. None of the blends shows any delamination or porous structure. In the case of 5% SBS loading, the glassy nature of PS only slightly reduced as no longitudinal projection of stress stripes are visible. However, the formation longitudinally projected stripes of the fractured surface are visible for the SBS loading 10 and 20% [Figs. 8(c)-8(d)] indicating that the glassy nature of PS diminished with an increase in the SBS loading and the PS/SBS blends started to show elastomeric nature. Therefore, the impact strength increased with an increase in the SBS loading.

ATR - FTIR spectroscopy

The ATR-FTIR spectra of 80/20 mixtures PS/SBS containing 0, 1, 3 and 7% DCP are shown in Fig. 9. The spectrum of PS/SBS blend without DCP shows IR bands at 695, 748, 841, 906, 965, 1028, 1069, 1155, 1182, 1373, 1452, 1492, 1601, 2850, 2924, and 3025 cm^{-1}. The bands at 694, 748, and 841 cm^{-1} are related to out of plane bending of the C–H groups in the aromatic ring of styrene, deformation vibration of the C-H groups in the aromatic ring, vibration, and –CH$_2$ rocking [45]. The IR bands at 906, 964, and 1028 cm^{-1} are related to out-of-plane vibration of the benzene ring, and –CH_2 twisting respectively. The IR bands at 1069, 1155, and 1182 all are associated with PS. The IR bands at 1373, 1452 and 1492 cm^{-1} are related to the –CH_3 anti-symmetric bending, the *vinyl*-PB d(CH) in CH_2=CH–, and stretching vibrations of the carbons in the aromatic ring respectively [45, 46]. The band at 1601 cm^{-1} could be assigned to the stretching vibration of the carbons in the aromatic ring of PS. The IR bands at 2850, 2924 and 3025 cm^{-1} could be attributed to the stretching vibrations of the CH_2 groups in PB-units n(CH_2), asymmetrical stretching vibrations of the CH_2 groups in PB-units n(CH_2), and to the stretching vibrations of the CH_2 groups in PB units and CH groups in the aromatic ring respectively.

On the other hand, PS/SBS blends treated with various concentrations of DCP showed a small new band at 1716 cm^{-1}, which is related to stretching vibration of the polar carboxyl groups (–C=O) and this band is absent in the spectrum of neat PS/SBS blend. The intensity of the carboxyl band increased with an increase in the concentration of DCP indicating the production of hydrophilic degradation products. It is also evident that the intensity of the bands at 911 and 965 cm^{-1} decreased with an increase in the concentration of DCP suggesting degradation of PB of SBS and other bands suggest some levels of crosslinking [46].

Water absorption and hygroscopic expansion

The water absorption by polymers is related to their dimensional stability as the absorption of water will result in extending the length and width of the polymeric products. The water absorption by neat PS and PS melt blended with SBS at various initiator concentrations was monitored over seven days. The results of the water absorption tests are shown in Fig. 10(a). It can be seen that neat PS showed a very low level of water absorption and after five days of the test, the water absorption (%) became virtually zero. On the other hand, for the reactive blends of PS/SBS, water absorption increased with an increase in the initiator concentrations and also with time. However, overall absorption of water was still very low as the highest water absorption for the 0.7% DCP was only 0.7%. Fig. 10(b) shows hygroscopic expansion of neat PS and PS blended with SBS with various concentrations of DCP. It is evident that the hygroscopic expansion data are consistent with the water absorption (%) data shown in Fig. 10(b). The neat PS merely showed any change in the hygroscopic expansion and even after 7 days of immersion in water, no change in the expansion was observed. On the other hand, in the case of DCP-treated blends, the hygroscopic expansion increased over the time of test and also with an increase in its concentration. The increase in water absorption (%) and the expansion of PS/SBS blend along with a decrease in uniaxial extensional viscosity with an increase in the DCP concentrations beyond 0.1% indicate the production of hydrophilic degradation products of PB of SBS. The FTIR spectra of the blends treated with various concentrations of DCP do not show any hydroxyl band. However, the spectra showed the band of polar carboxyl groups at 1714 cm^{-1} responsible for the water absorption by PS/SBS treated with high concentrations of DCP. However, the increase in the water absorption observed is quite significant as the water absorption increased from 0.14% for the 0% DCP to 0.35% for the 0.4% DCP suggesting quite high degradation of PB took place.

Conclusions

We demonstrated that the solution blended PS/SBS in the presence of 0.1% DCP annealed at 180 °C showed strong strain hardening but the PS and SBS at the same ratio melt blended in the presence of 0.1% DCP failed to provide strong strain hardening. The increase in the ratio of SBS to PS and DCP concentration had little effect on the strain hardening improvement. For the melt blending of PS/SBS without the incorporation DCP, the increase in the blending and annealing temperature did not produce better strain hardening compared to the neat PS and the strain hardening actually worsened for the samples processed at temperatures higher than 220 °C. However, the addition of SBS to PS in the presence of 0.1% DCP improved the thermal stability and tensile strength of PS but beyond that concentration not only the thermal stability and tensile strength was negatively affected but the hygroscopic expansion and water absorption properties also increased. The reactive blending of PS with SBS increased the impact strength of PS, which increased with an increase in the SBS loading. The maximum increase in the impact strength was provided by PS/SBS blend containing the maximum SBS loading investigated. The SEM micrographs of the fractured surface of neat PS was quite smooth, which is the typical feature of fracture of glassy materials. For the PS/SBS blends, the formation of widespread stress stripes shows the sign of fracture of toughened materials. The reactive melt blending of PS/SBS could be used in industry to enhance the impact and tensile strength of PS but solution blending could be useful for increasing its transient uniaxial extensional viscosity.

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References

1. Hassan MM, Koyama K (2015) Thermal, physicomechanical, and morphological properties of HDPE graft-copolymerized with polystyrene. Polym Adv Technol 26:1285–1293.

2. Sukhareva LA, Legonkova OA, Yakovlev VS (2008) Polymers for Packaging and containers in Food Industry, CRC Press, Boca Raton, USA, 455–490
3. Piorkowska E, Argon AS, Cohen RE (1993) Izod impact strength of polystyrene-based blends containing low molecular weight polybutadiene. Polymer, 34, 4435-4444.
4. Zhou C, Wu S, Yang B, Gao Y-X., Wu G-F., Zhang H-X (2015) Toughening polystyrene by core-shell rubber particles: analysis of the internal structure and properties. Polym Polym Compos 23:317–324.
5. Guo TY, Tang GL, Hao GJ, Song MD, Zhang BH (2003) Toughening modification of PS with n-BA/MMA/styrene core–shell structured copolymer from emulsifier-free emulsion polymerization. J Appl Polym Sci 90:1290–1297.
6. Wu DY, Svazas Y (2006) Micro- and Nano-Sized Calcium Carbonate Toughened Polystyrene. J Nanosci Nanotechnol 6:3919–3922.
7. Yang H, Zhang X, Qu C, Li B, Zhang L, Zhang Q, Fu Q (2007) Largely improved toughness of PP/EPDM blends by adding nano-SiO2 particles. Polymer 48:860–869.
8. Han J-J, Huang H-X (2011) Preparation and characterization of biodegradable polylactide/thermoplastic polyurethane elastomer blends. J Appl Polym Sci 120:3217–3223.
9. Feng F, Zhao X-W, Ye L (2011) Structure and properties of ultradrawn polylactide/thermoplastic polyurethane elastomer blends. J Macromol Sci B 50:1500–1507.
10. Sugimoto M, Masubuchi M, Takimoto J, Koyama K (2001) Melt rheology of polypropylene containing small amounts of high-molecular-weight chain. 2. Uniaxial and biaxial extensional flow. Macromolecules 34:6056–6063.
11. Fowler MW, Baker WE (1988) Rubber toughening of polystyrene through reactive blending. Polym Eng Sci 28:1427–1433.
12. Schneider M, Pith T, Lambla M (1997) Toughening of polystyrene by natural rubber-based composite particles: Part I Impact reinforcement by PMMA and PS grafted core-shell particles. J Mater Sci 32:6331–6342.
13. Michler GH (1990) Formation of crazes in polymer blends. Macromol Chem: Macromol Sympos 38:195–204.

14. Doufas AK, Rice L, Thurston W (2011) Shear and extensional rheology of polypropylene melts: Experimental and modeling studies. J Rheol 55:95–126.
15. Wang J, James DF, Park CB (2010) Planar extensional flow resistance of a foaming plastic. J Rheol 54:95–116.
16. Takahashi M, Isaki T, Takigawa T, Masuda T (1993) Measurement of biaxial and uniaxial extensional flow behavior of polymer melts at constant strain rates. Journal of Rheology, 37, 827–846.
17. Lentzakis H, Vlassopoulos V, Read DJ, Lee H, Chang T, Driva P, Hadjichristidis N (2013) Uniaxial extensional rheology of well-characterized comb polymers. J Rheol 57:605–625.
18. Ahirwal D, Filipe S, Neuhaus I, Busch M, Schlatter G, Wilhelm M (2014) Large amplitude oscillatory shear and uniaxial extensional rheology of blends from linear and long-chain branched polyethylene and polypropylene. J Rheol 58:635–658.
19. Huang Q, Magnus M, Alvarez NJ, Koopmans R, Hassager O (2016) A new look at extensional rheology of low-density polyethylene. Rheol Acta 55:343–350.
20. Sugimoto M, Suzuki Y, Hyun K, Ahn KH, Ushioda T, Nishioka A, Taniguchi T, Koyama K (2006) Melt rheology of long-chain-branched polypropylenes. Rheol Acta 46:33–46.
21. Stange J, Munstedt H (2006) Rheological properties and foaming behavior of polypropylenes with different molecular structures. J Rheol 50:907–927.
22. Minegishi A, Nishioka A, Takahashi T, Masubuchi Y, Takimoto J, Koyama K (2001) Uniaxial elongational viscosity of PS/ a small amount of UHMW-PS blends. Rheol Acta 40:329–338.
23. Kurose T, Takahashi T, Sugimoto M, Koyama K (2005) Uniaxial elongational viscosity of PC/a small amount of PTFE blend. Nihon Reoroji Gakkaishi 33:173–182.
24. Liu J, Lou L, Yu W, Liao R, Li R, Zhou C (2010) Long chain branching polylactide: Structures and properties. Polymer 51:5186–5197.
25. Li S, He G, Liao X, Park CB, Yang Q, Li G (2017) Introduction of a long-chain branching structure by ultraviolet-induced reactive extrusion to improve cell morphology and processing properties of polylactide foam. RSC Adv 7:6266–6277.
26. Sugimoto M, Tanaka T, Masubuchi Y, Takimoto J, Koyama K (1999) Effect of chain structure on the melt rheology of modified polypropylene. J Appl Polym Sci 73:1493–1500.

27. Kurzbeck S, Oster F, Munstedt H (1999) Rheological properties of two polypropylenes with different molecular structure. J Rheol 43:359–374.
28. Auhl D, Stange J, Münstedt H, Krause B, Voigt D, Lederer A, Lappan U, Lunkwitz K (2004) Long-chain branched polypropylenes by electron beam irradiation and their rheological properties. Macromolecules 37;9465–9472.
29. Li S, Xiao M, Wei D, Xiao H, Hu F, Zheng, A (2009) The melt grafting preparation and rheological characterization of long chain branching polypropylene. Polymer 50:6121–6128.
30. Takahashi T, Takimoto J–I, Koyama K (1999) Elongational viscosity for miscible and immiscible polymer blends. II. Blends with a small amount of UHMW polymer. J Appl Polym Sci 72:961–969.
31. Wagner MH, Bastian H, Hachmann P, Meissner J, Kurzbeck S, Munstedt H, Langouche F (2000) The strain-hardening behavior of linear and long-chain-branched polyolefin melts in extensional flows. Rheol Acta 39:97–109.
32. Yang L, Huang J, Lu X, Jia S, Zhang H, Jin G, Qu J (2015) Influences of dicumyl peroxide on morphology and mechanical properties of polypropylene/poly(styrene-b-butadiene-b-styrene) blends via vane-extruder. J Appl Polym Sci 132:41543.
33. Ghosh P, Ray P (1991) Studies on polybutadiene rubber (PBR)-polystyrene (PS) interpenetrating polymer network. J Mater Sci 26:6004–6012.
34. Jehani Y, Ghetmiri M, Vaseghi MR (2015) Polypropylene and chain extension of poly(ethylene terephthalate) on the thermal behavior, rheology and morphology of their blends. RSC Adv 5:21620–21628.
35. Su F–H, Huang H–X (2010) Rheology and melt strength of long chain branching polypropylene prepared by reactive extrusion with various peroxides. Polym Eng Sci 50:342–351.
36. Münstedt H (1980) Dependence of elongational behavior of polystyrene melts on molecular weight and molecular weight distribution. J Rheol 24:847.
37. Krupa I, Luyt AS (2001) Mechanical properties of uncrosslinked and crosslinked linear low-density polyethylene/wax blends. J Appl Polym Sci 81:973–980.
38. Ha CS, Kim SC (1989) Tensile properties and morphology of the dynamically cured EPDM and PP/HDPE ternary blends. J Appl Polym Sci 37:317–334.

39. Lungulescu EM, Zaharescu T (2016) Stabilization of polymers against photodegradation. In: Dan R, Visakh PM (Ed), Photochemical Behavior of Multicomponent Polymeric-based Materials, Springer International Publishing, Switzerland, p. 187.
40. Munteanu SB, Brebu M, Vasile C (2005) Thermal and thermo-oxidative behavior of butadiene-styrene copolymers with different architectures. Poly. Degrad Stab 89:501–512.
41. Zhou J, Du X-H, Yue W (2017) Study on the blend of SBS and polystyrene, and properties of their mixture. Adv Eng Res 112:27–30.
42. Thomann Y, Thomann R, Hasenhindl A, Mülhaupt R (2009) Gradient interfaces in SBS and SBS/PS blends and their influence on morphology development and material properties. Macromolecules 42:5684–5699.
43. Chung Y-C, Lee BH, Jo SH, Chun BC (2015) Preparation and characterization of polyurethane copolymer grafted with polystyrene side chains. Polym Plastic Technol Eng 54:1066–1076.
44. Andreopoulos AG, Tarantili PA, Anastassakis P (2007) Compatibilizers for low-density polyethylene/polypropylene blends, Novel determination of the crystallinity of syndiotactic polystyrene using FTIR spectrum. J Macromol Sci A 36:1113–1122.
45. Masson J-F, Pelletier L, Collins P (2001) Rapid FTIR method for quantification of styrene-butadiene type copolymers in bitumen, J Appl Polym Sci 79:1034–1041.
46. Wang S-M, Chang J-R, Tsiang RC-C (1996) Infrared studies of thermal oxidative degradation of polystyrene-block polybutadiene-block polystyrene thermoplastic elastomers. Polym Degrad Stab 52:51–57.

Captions of Figures

Fig. 1. The time-dependent transient uniaxial extensional rheology of 80/20 mixture of PS/SBS prepared in the presence of 0.1% DCP by melt (a) and solution (b) blending.

Fig. 2. The transient uniaxial extensional viscosity of neat PS (a) and 80/20 blends of PS/SBS blended and annealed at 180 (b), 220 (c), 240 (d) and 260 °C (e).

Fig. 3. The transient uniaxial extensional viscosity of neat PS (a), and also 80/20 blends of PS/SBS prepared in the presence of 0.1 (b), 0.2 (c), 0.4 (d), 0.6 (e), and 0.8% (f) of DCP.

Fig. 4. The time-dependent transient uniaxial extensional viscosity of 95/05 (a), 90/10 (b), and 80/20 blends of PS/SBS.

Fig. 5. The effects of SBS loading (a) and DCP concentrations (b) on the tensile the strength of melt blended PS/SBS. In the case of SBS loading, the concentration of DCP was 0.1% but for the different concentrations of DCP, the blending ratio of PS and SBS was 80/20.

Fig. 6. Effect of SBS loading on the on the impact resistance of melt and solution-blended PS/SBS.

Fig. 7. TGA and DTA curves of neat PS (a), and 90/10 blends of PS/SBS prepared by melt blending in the presence of 0.1% (b) and 0.2% (c) DCP.

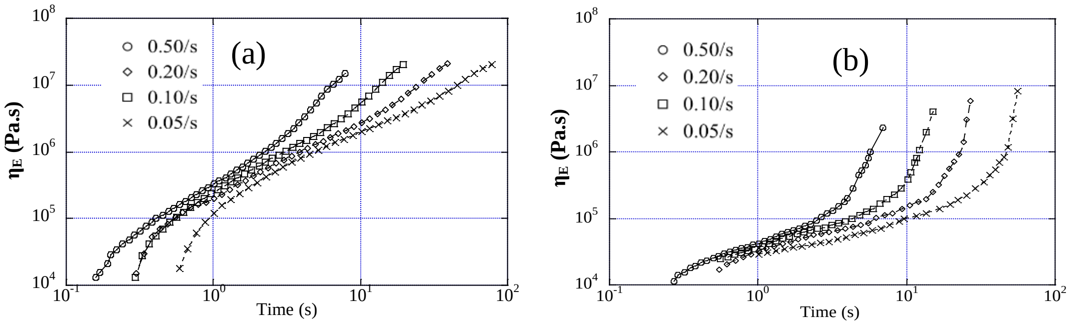
Fig. 8. SEM micrographs of neat PS (a), and also PS/SBS blends with 5 (b), 10 (c), and 20% (d) SBS loading.

Fig. 9. ATR-FTIR spectra of neat PS and also PS with 5, 10 and 20% SBS loading prepared in the presence of 0.1% DCP.

Fig. 10. The effect of DCP concentration of DCP on the water absorption (a) and hygroscopic expansion (b) of 80/20 blends of PS and SBS.

Captions of Tables

Table 1. The blending conditions and mechanical properties of neat PS, and PS/SBS blends with various SBS loading.



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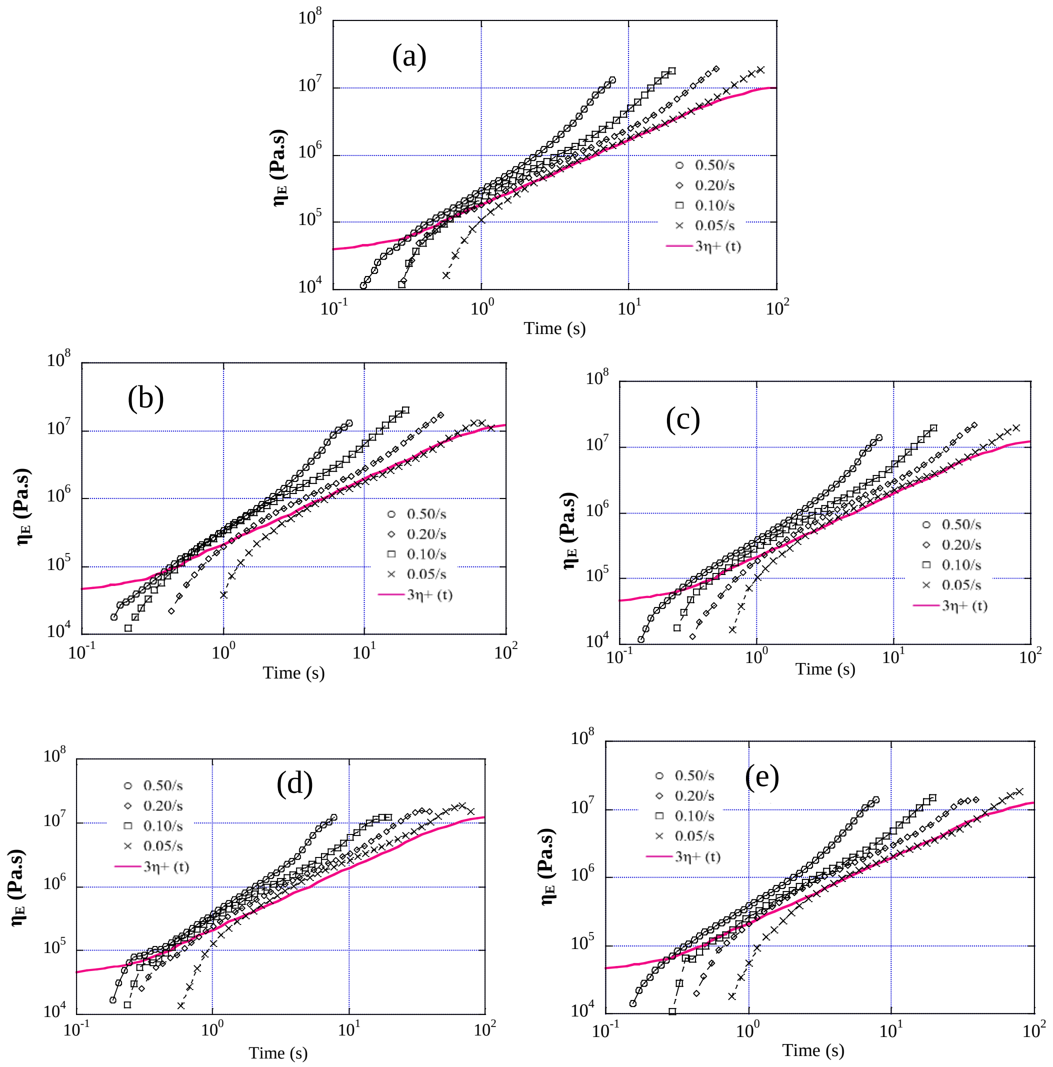

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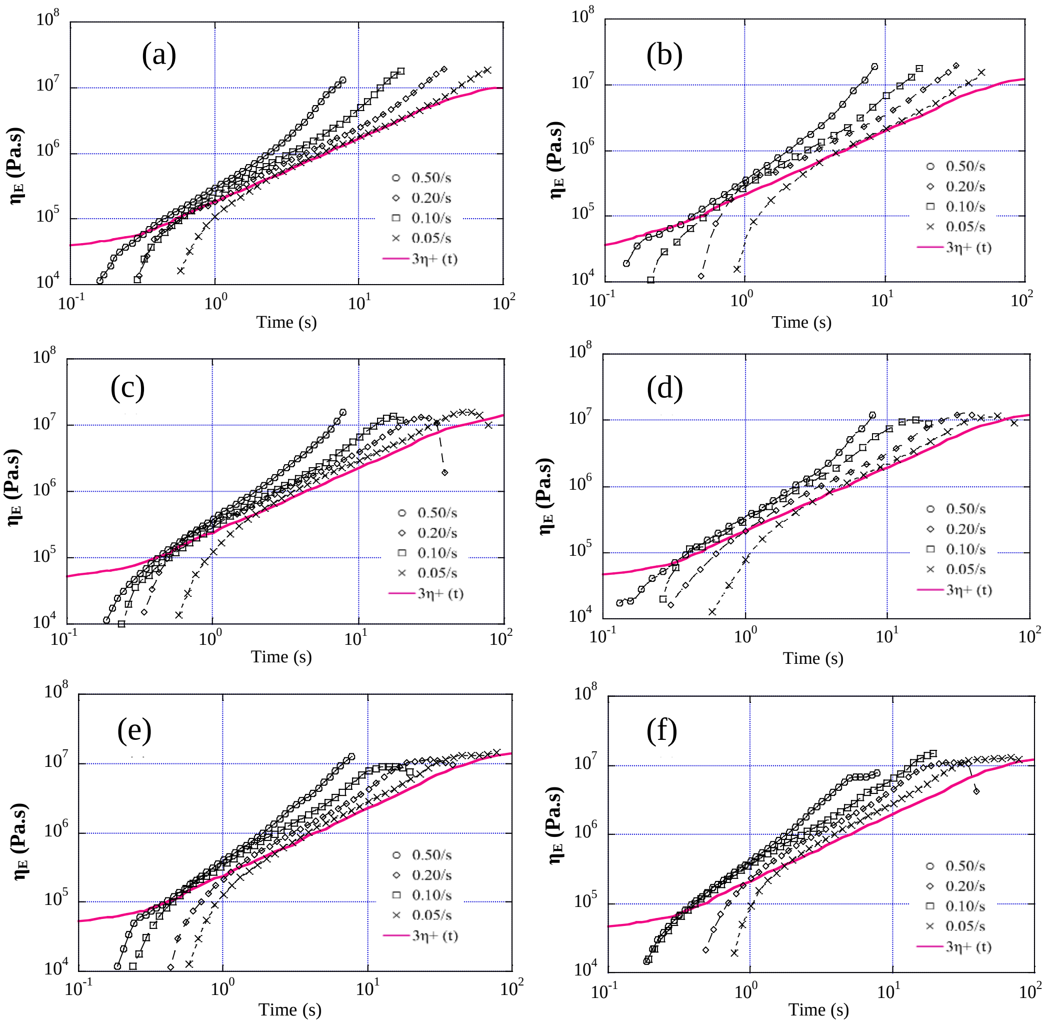

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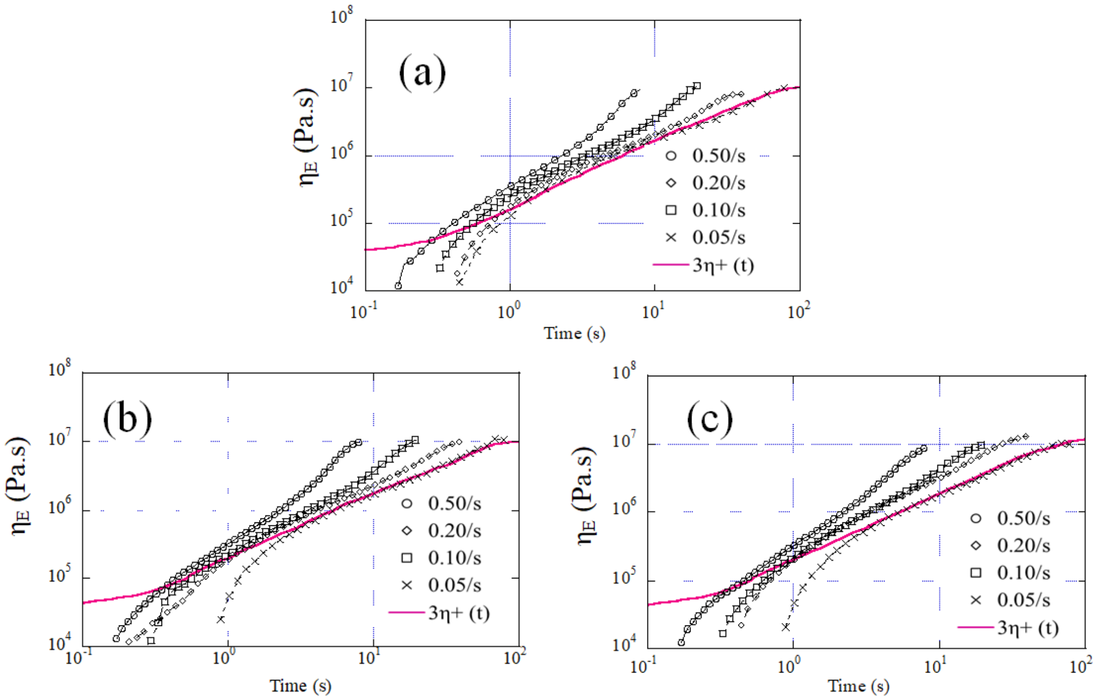


Fig. 4. The time-dependent transient uniaxial extensional viscosity of 95/05 (a), 90/10 (b), and 80/20 blends of PS/SBS prepared at 180 °C using DCP concentration of 0.1%.

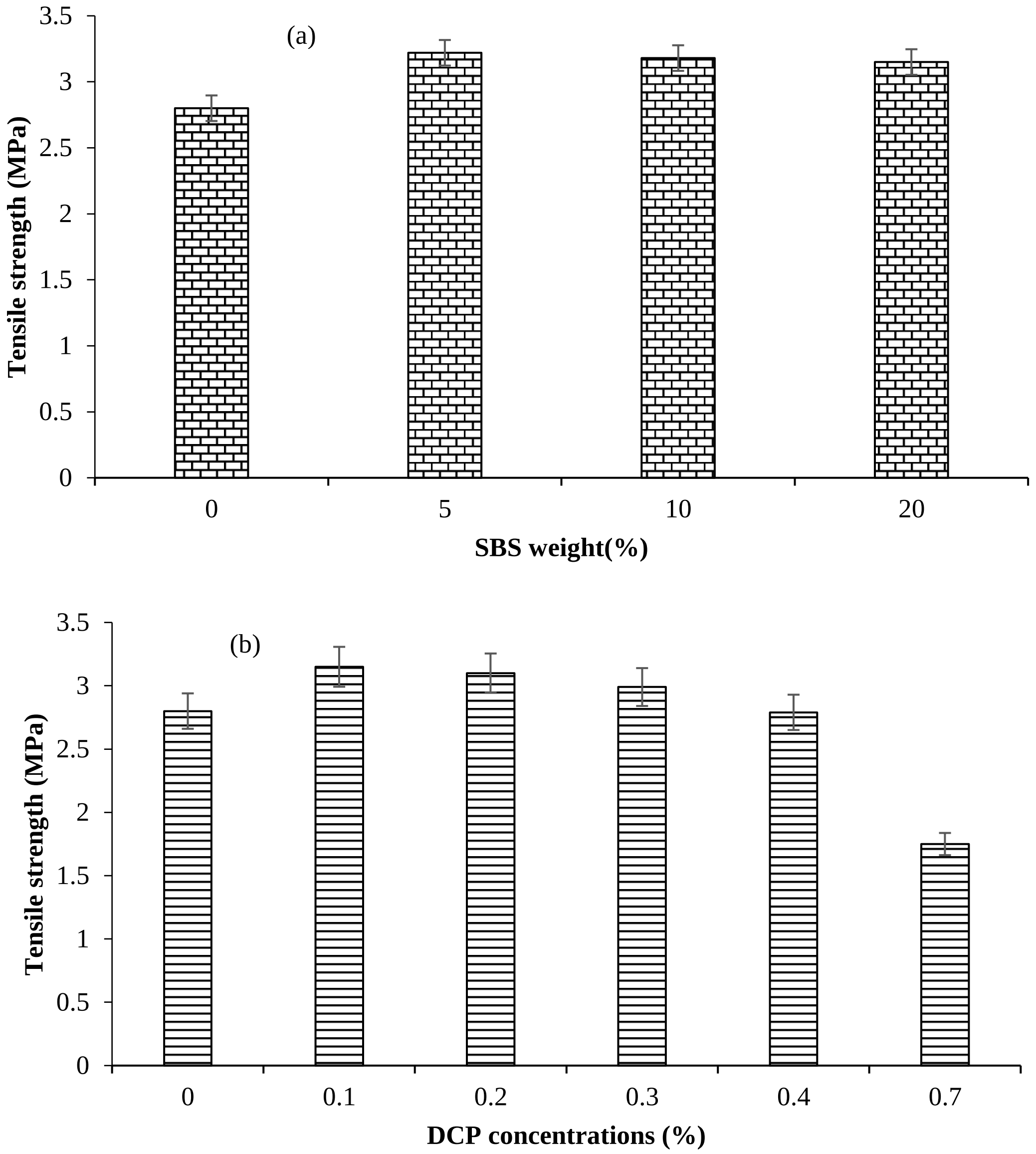
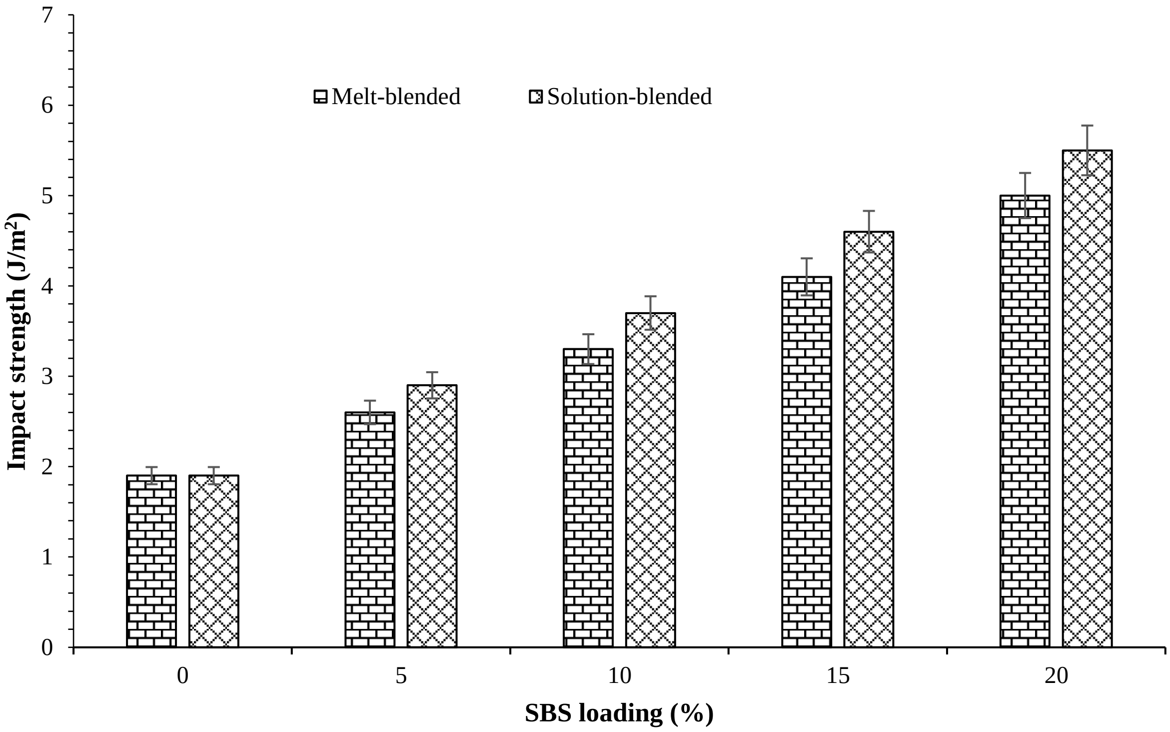


Fig. 5. The effects of SBS loading (a) and DCP concentrations (b) on the tensile the strength of melt blended PS/SBS. In the case of SBS loading, the concentration of DCP was 0.1% but for the different concentrations of DCP, the SBS was 20%.



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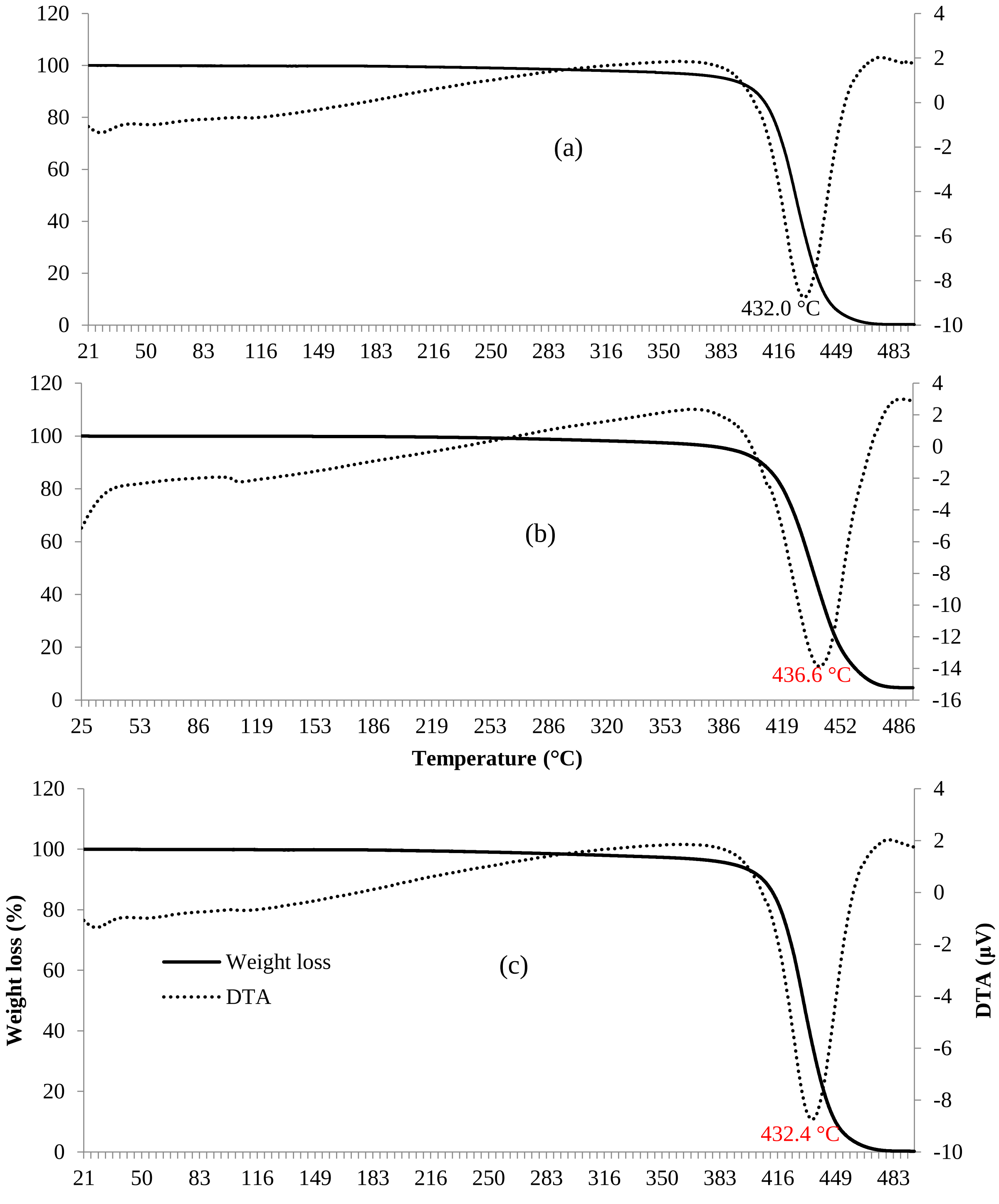

Fig. 7. TGA and DTA curves of neat PS (a), and 90/10 blends of PS/SBS prepared by melt blending in the presence of 0.1% (b) and 0.4% (c) DCP.

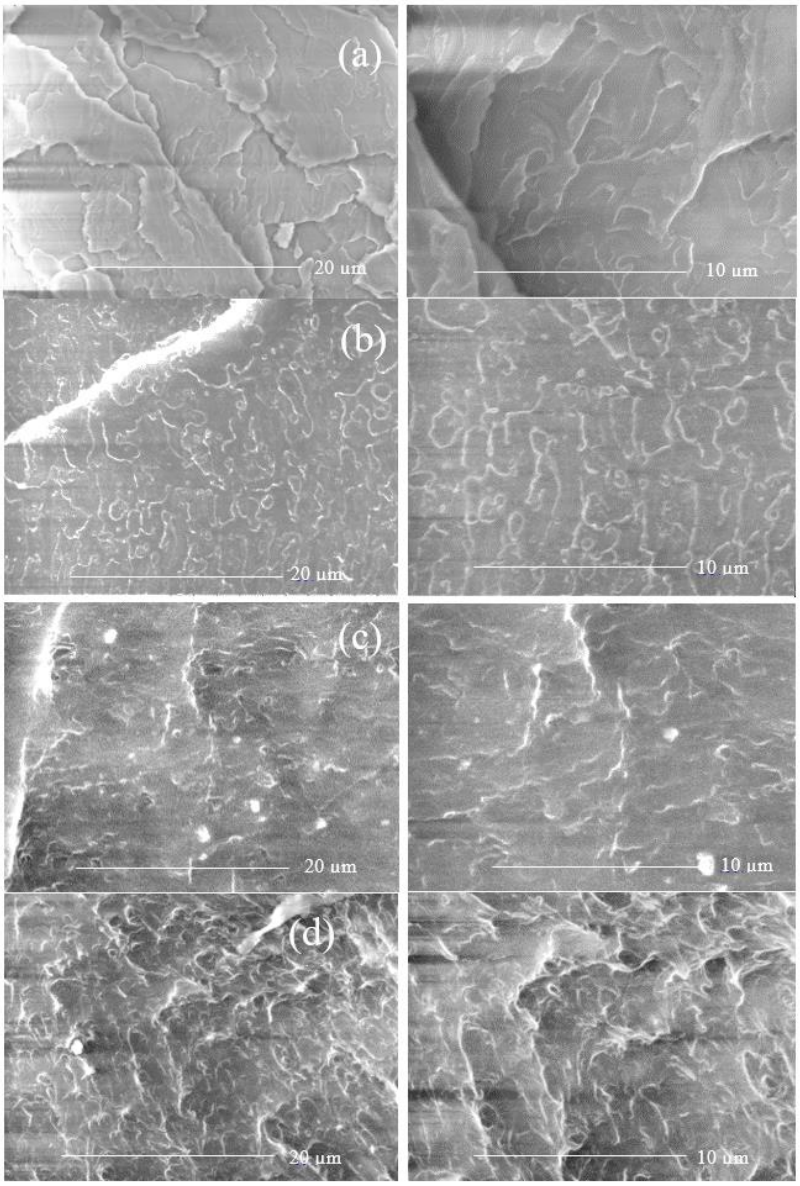

Fig. 8. SEM micrographs of neat PS (a), and also PS/SBS blends with 5 (b), 10 (c), and 20% (d) SBS loading.

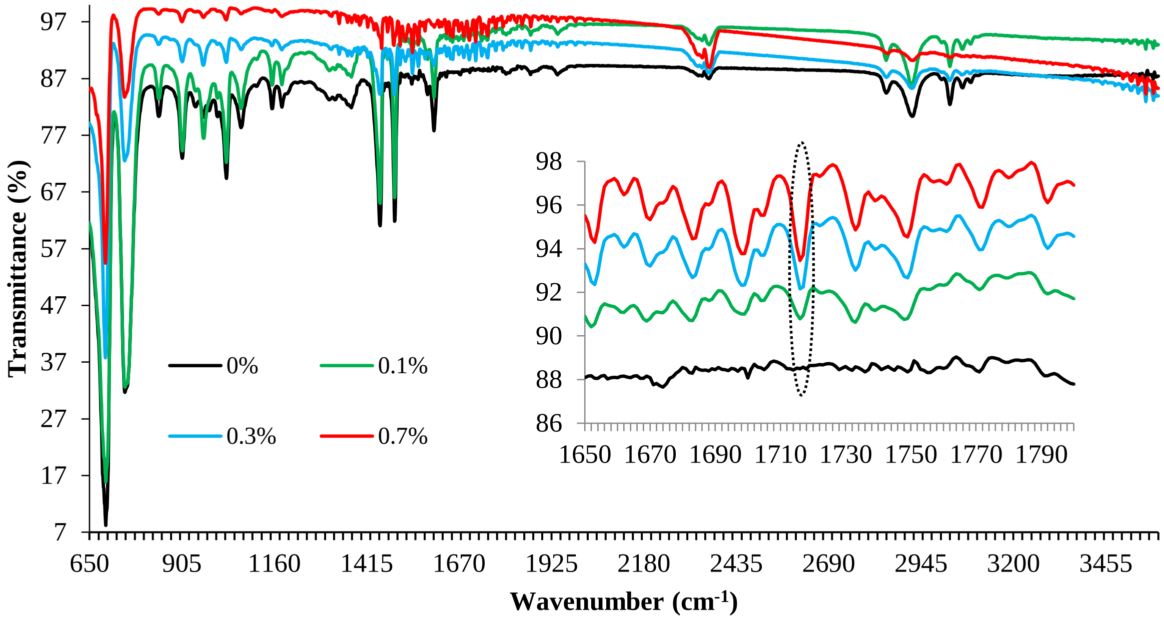

Fig. 9. ATR-FTIR spectra of 80/20 mixture of PS/SBS treated with 0, 0.1, 0.3 and 0.7% DCP.

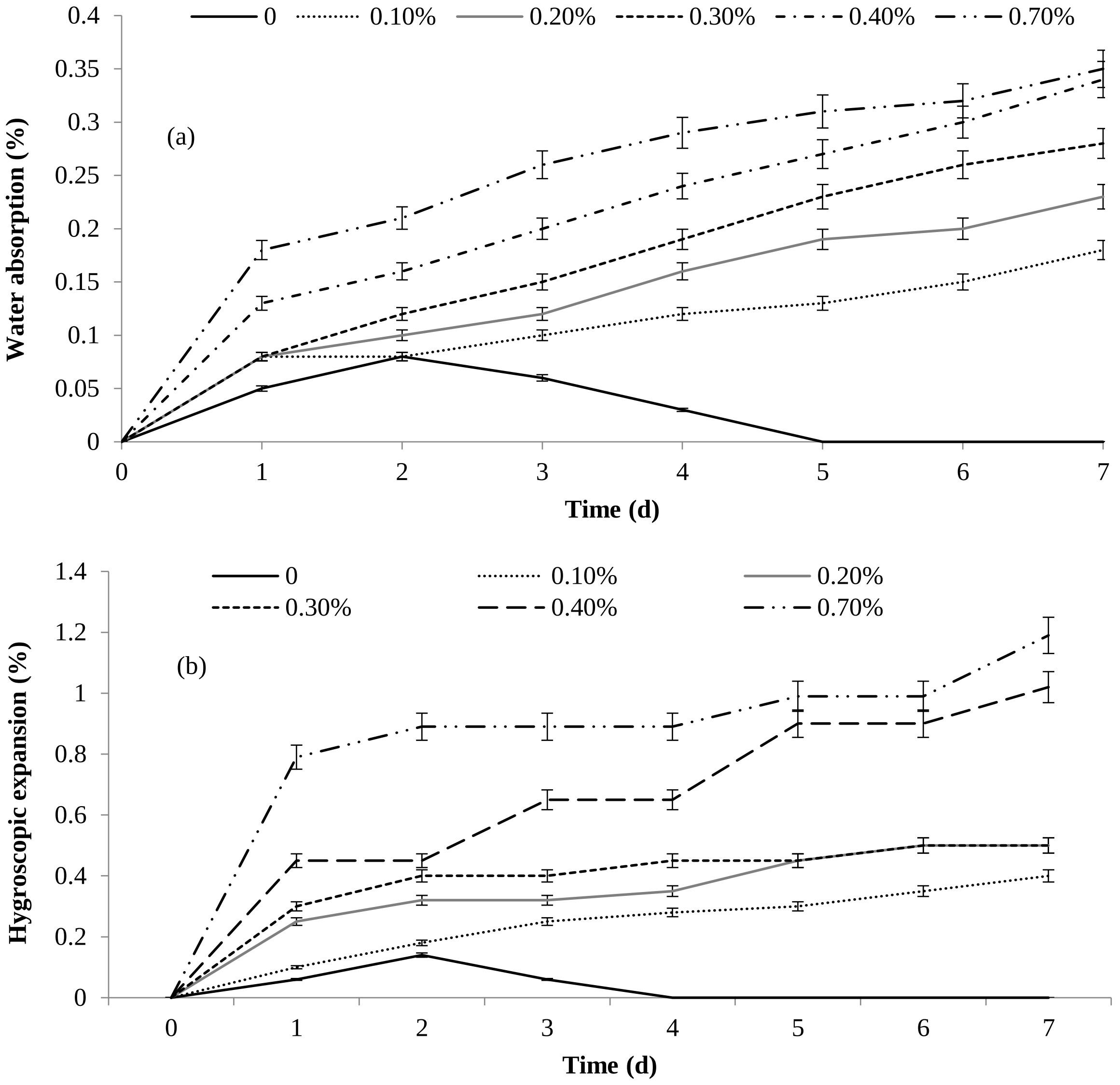

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Table 1. The blending conditions and mechanical properties of neat PS, and PS/SBS blends with various SBS loading.

Sample Id.	PS/SBS (wt./wt.)	Blending conditions			Molding conditions		Tensile strength (MPa)	Elongation at break (%)
		DCP conc. (%)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)		
Neat PS	100/0	-	180	10	160	10	3.05±0.2	1.69±0.53
PS/SBS melt blended at various PS to SBS ratios								
C1	95/05	-	180	10	160	10	2.94±0.17	1.83±0.35
A1	95/05	0.1	180	10	160	10	3.38±0.15	1.98±0.46
A2	90/10	0.1	180	10	160	10	3.25±0.10	2.15±0.43
A3	80/20	0.1	180	10	160	10	3.15±0.18	2.30±0.78
PS/SBS melt blended at various DCP concentrations								
C2	80/20	-	180	10	160	10	2.80±0.35	2.05±0.56
X1	80/20	0.1	180	10	160	10	3.15±0.14	2.32±0.85
X2	80/20	0.2	180	10	160	10	3.10±0.18	2.65±0.63
X3	80/20	0.3	180	10	160	10	2.99±0.08	3.02±0.97
X4	80/20	0.4	180	10	160	10	2.79±0.13	3.20±0.83
X7	80/20	0.7	180	10	160	10	1.75±0.25	3.43±1.34
PS/SBS solution blended at 80/20 PS to SBS ratio								
Y1	80/20	0.1	-	-	180	10	-	-