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Compatibilising action of random and triblock copolymers of poly(styrene–butadiene) in polystyrene/polybutadiene blends: A study by electron microscopy, solid state NMR spectroscopy and mechanical measurements

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Abstract

Scanning electron microscopy, solid-state proton NMR spectroscopy and static mechanical analysis have been performed in order to evaluate the compatibilising action of random copolymers of polystyrene and polybutadiene and triblock copolymers of poly(styrene–butadiene–styrene) in incompatible polystyrene/polybutadiene (PS/PB) blends. Scanning electron microscopic examination of the cryofractured and etched surfaces showed high degree of compatibilising action of the triblock copolymers as evidenced by the very sharp decrease of the domain size of the dispersed phase followed by an increase at higher concentrations. This is a clear indication of interfacial saturation. These results were in agreement with the theoretical predictions of Noolandi and Hong. The random copolymer was not effective in compatibilising the system. Solid-state proton NMR experiments were performed on the uncompatibilised and compatibilised blends. The proton spin–lattice relaxation times in the laboratory frame, $T_1(H)$, and in the rotating frame, $T_{1\rho}(H)$, and spin–spin relaxation times, $T_2(H)$, were carefully measured for the systems. Significant changes were observed for the systems compatibilised with triblock copolymers due to the preferential localisation of the copolymers at the PS/PB interface. However, the random copolymer did not have any compositional drift and is not an effective interface modifier in agreement with microscopy study. The static mechanical properties of the blends have also been analysed. The addition of triblock copolymers increased the mechanical properties of the blends. Finally, attempts have been made to correlate the NMR results with the microstructure and mechanical properties of the blends.

Keywords: Polymer blends; Compatibilisation; Polybutadiene

1. Introduction

Polymer blends are very often found to be multiphase systems on account of the very small value of the entropy of mixing. Most of the multiphase polymer blends show poor mechanical properties as a result of the weak adhesion between the phases. The properties of multiphase systems depend on the spatial organisation of each phase and the characteristics of the interface. Different strategies such as physical compatibilisation and reactive compatibilisation are being used to control and stabilise the morphologies of immiscible polymer blends. In the physical compatibilisation process, a third component (block copolymer, graft copolymer, random copolymer or even a homopolymer) can be added into polymer/polymer interface. In the case of copolymers, they nicely organise at the interface and modify the properties of the heterogeneous systems. In the reactive compatibilisation technique, chemical reactions take place during mixing leading to the formation of an in situ compatibiliser. Both techniques have been applied to many polymer/polymer blend systems.

A large number of techniques have been used to characterise the morphology and interface of polymer

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blends containing copolymers. Each technique analyses [1] the domain size in the material under study with its own spatial scale. For example, Riess and co-workers [1] in a pioneering work used the transparency of films cast from solutions as a criterion to evaluate the efficiency of the compatibilising agents. In transparent materials the domain size must be of the order of or smaller than the visible wavelength, i.e. in the range of a few hundred nanometres. If the domain size is larger, the films will be opaque. Both optical and electron microscopy have been extensively used for the observation of phase size reduction for many compatibilised blends. Differential scanning calorimetry (DSC), dielectric spectroscopy, dynamic mechanical analysis and techniques, which detect the glass transition temperature of polymers, can investigate polymer/polymer interactions at a spatial scale of 10–20 nm. Anastasiadis and co-workers [2] measured the lowering of the interfacial tension on the addition of compatibilisers for the understanding of the interfacial activity of the copolymer. Small-angle X-ray scattering measurements have been employed for the characterisation of the interfacial thickness in PS/PB blends in the presence and absence of compatibilisers by Perrin and Prud'homme [3]. Neutron reflectometry has been used by Fernandez and Higgins [4] and Anastasiadis and co-workers [2] for the characterisation of interfacial thickness in PS/PMMA containing diblock copolymers.

Solid-state NMR is a very powerful technique to investigate the heterogeneity of polymer blends. As with many other applications of NMR, the enormous freedom and flexibility of NMR experiments has resulted in many different approaches, each approach employing specific solid-state NMR experiments. Carbon-13 chemical shifts, intermolecular cross polarisation, spin diffusion and dynamic nuclear polarisation can be used for analysing the interactions in polymer blends. The ^{13}C line widths have been reported to be sensitive for the characterisation of chain mobility in IPNs by Brachais and co-workers [5]. Proton spin–lattice relaxation times in the laboratory frame, $T_1(H)$, and in the rotating frame, $T_{1\rho}(H)$, can be used to estimate the microstructure of heterogeneous systems at a spatial scale of the order of 100 and 10 Å, respectively. In a miscible blend, all protons relax at about the same rate via spin diffusion. However, when the domains are larger than 100 Å, different proton relaxation times $T_1(H)$ and $T_{1\rho}(H)$ may be observed. Therefore, separate $T_1(H)$s, $T_{1\rho}(H)$s have often been used as proof for lack of miscibility at these very small spatial scales. Besides, $T_1(H)$ and $T_{1\rho}(H)$ values have also been shown to depend on the size of the domains in heterogeneous systems. Asano et al. [6] reported the miscibility of polymethyl methacrylate/polyvinyl acetate (PMMA/PVAc) blends at various mixing ratios by both ^{1}H spin–lattice relaxation times in the laboratory $T_1(H)$ and the rotating $T_{1\rho}(H)$ frames. The molecular motion of both polymers was investigated by the ^{13}C spin–lattice relaxation time in the laboratory frame, $T_1(H)$. They observed that PMMA/PVAc blends are homogenous on a scale of 20–50 nm. Serrano et al. [7] established the morphology of alternating poly(ester amide based on 1,4-butylene) by ^{13}C NMR relaxation measurements. Yu et al. [8] studied the microphase structure and the interface of a few poly(styrene–butadiene–styrene) triblock copolymers by solid state NMR spectroscopy. Yi and Goh [9] studied the miscibility and interactions in poly(methyl thiomethyl methacrylate)/poly(vinyl alcohol) PMTMA/PVA blends, by NMR spectroscopy. The measurements of proton spin–lattice relaxation time revealed PMTMA and PVA do not mix intimately on a scale of 1–3 nm, but are miscible on a scale of 20–30 nm.

The main purpose of the present study is to analyse the morphology and mechanical properties of polystyrene (PS) /polybutadiene (PB) blends in the presence and absence of random and triblock copolymers of PS and PB. Blends of PB and PS are highly incompatible, which show macrophase separation. Addition of the copolymer is expected to decrease the phase separation and reduce the size of the dispersed phase. In the present paper, scanning electron microscopy has been used to characterise the dimensions of the dispersed phase upon the addition of the copolymers. NMR measurements have been made use of to get more information on the dependence of the blend structure upon the addition of the copolymers. Finally, static mechanical properties of these blends have been evaluated in the presence and absence of copolymers.

2. Experimental

2.1. Materials

Polystyrene (PS) was supplied by Poly Chem India Ltd, Mumbai. *cis*-1,4 Polybutadiene (PB) was obtained from IPCL Vadodara, India. The glass transition temperatures of neat PB and neat PS are of −101 and 100 °C, respectively. A random copolymer of styrene and butadiene (SBR) having 30% of polystyrene content, $M_w = 311{,}792$, $M_w/M_n = 2.94$, T_g (−40 °C) and a triblock copolymer of styrene–butadiene–styrene (SBS) having 30% of PS were used as compatibilisers. SBR was obtained from Synthetics and Chemicals Ltd, Bareilly, UP, India. SBS was purchased from Shell chemicals, UK. The characteristics of the materials are given in Table 1.

2.2. Preparation of the blends

Blends of PS and PB were prepared by melt mixing in a Haake Rheocord. Polystyrene was melted for 2 min and then PB was added. The temperature, rotor speed and mixing time were 180 °C, 60 rpm and 8 min, respectively. The melt mixed samples are denoted as S_{00}, S_{30}, S_{50}, S_{70} and S_{100}, where 'S' stands for PS and the subscripts indicate content of PS in the blend. In compatibilised blends, compatibiliser was added prior to the addition of PB phase.

Table 1
Characteristics of the materials

Material	Density (g cm^{-3})	Molecular weight (M_w)
PS(atactic)	1.04	3.51×10^5
PB(*cis*1,4)	0.94	1.25×10^6
SBR	0.97	3.11×10^5
SBS	0.95	2.24×10^5

The compatibilised blends are denoted by SB_{3001}, $SB_{3002.5}$ and SR_{3001}, $SR_{3002.5}$, respectively, where the letters B and R denote the block and random copolymers, respectively, and additional subscripts correspond to the weight percentage of SBR or SBS added with respect to the minor phase of the blends.

2.3. Morphology of the blends

The morphology of the blends have been analysed by scanning electron microscopy (SEM). For SEM both cryo fractured and etched surfaces were used. The preferential etching of the phases was carried out using selective solvents. The diameter of the dispersed phase has been evaluated by image analysis. The photographs were quantitatively analysed for number-average domain diameter [10] according to the equation,

$$\bar{D}_n = \frac{\sum N_i D_i}{\sum N_i} \tag{1}$$

2.4. Static mechanical properties

The static mechanical properties of the blends and homopolymers were studied on a universal testing machine at 25±2 °C according to the ASTM standard D638-81 test method with dumb-bell shaped test specimens at cross-head speed of 50 mm/min using a universal testing machine model TNE 5T.

2.5. Solid-state nuclear magnetic resonance spectroscopy studies

The NMR measurements were made on a Bruker ASX-300 spectrometer operating at 300 MHz for ^{1}H. The proton spin–lattice relaxation times in the laboratory frame and the rotating frame were measured using an inversion-recovery pulse sequence and spin-lock pulse sequence, respectively. The solid echo pulse sequence was used to observe the very first points of the free induction decay (FID) of the rigid protons in the sample. The Hahn echo pulse sequence was used to determine the spin–spin relaxation times of the mobile protons. The duration of the $\pi/2$ pulse was 3 μs, which corresponds to a H_1 intensity of 83 kHz. The intensity of the H_1 field used for the spin-lock period was 45 kHz.

3. Results and discussion

3.1. Effect of copolymer addition on dispersed phase size

Morphology of the dispersed phase was followed by increasing the copolymer concentration. Scanning electron micrographs of 70/30 PB/PS blend with and without addition of block copolymer were studied (Fig. 1). The uncompatibilised blend shows a dispersed matrix phase morphology in, which PS is dispersed in the continuous PB matrix (Fig. 1(a)). The morphology of the compatibilised blends shows that the addition of the block copolymer results in a considerable reduction in the domain size and size distribution. The average domain size of the uncompatibilised blend is 2.40 μm. It is seen from the micrographs that for SBS compatibilised blends, addition of 1% SBS causes a reduction in domain size of 33%. Further addition of SBS of 2.5% loading reduces the domain size considerably and a reduction in domain size of 42% occurs. With further addition of copolymer, there is no more reduction in domain size at all. Thus, it is important to note that there is a sharp decrease in dispersed phase with the small amount of the compatibiliser followed by a leveling off, as the copolymer content is increased above the equilibrium concentration. The scanning electron micrographs of PB/PS (70/30) blend with the addition of 2.5% of random copolymer show no compatibilising action for this copolymer due to its random structure. The morphology is very coarse and the distribution is very wide (Fig. 2).

The plot of average domain diameter versus compatibiliser loading (Fig. 3) shows that the statistical copolymer is not able to localise at the interface due to its random structure. Therefore, it is unable to compatibilise the blend effectively. Kramer and co-workers [11,12] studied on the effect of composition drift on the effectiveness of random copolymer as an interface modifier in polymer/polymer interfaces. In fact the effectiveness arises from the non-homogeneous nature of the random copolymer on account of the compositional inhomogeneities. The non-homogeneity associated with the so-called ‘composition drift’ as explained by Kramer and group [11], arises from the difference in the reactivity ratio of the monomers for the copolymer preparation. This difference in reactivity ratio results in the preferred addition of one monomer in the early stages of the reaction and depletion of that monomer in the later stages. This leads to the generation of non-homogeneous copolymers. Such copolymers are effective as interfacial modifiers in polymer/polymer interfaces. It is very important to note that the so-called non-homogeneous copolymers produced by composition drift becomes effective only at 50/50 composition of the two monomers, i.e. $f=0.5$. In this paper they have compared the effectiveness of random copolymers without composition drift and with composition drift. They have shown that the effect becomes predominant only at 50/50 composition of the copolymer. Let us now examine the present study on the

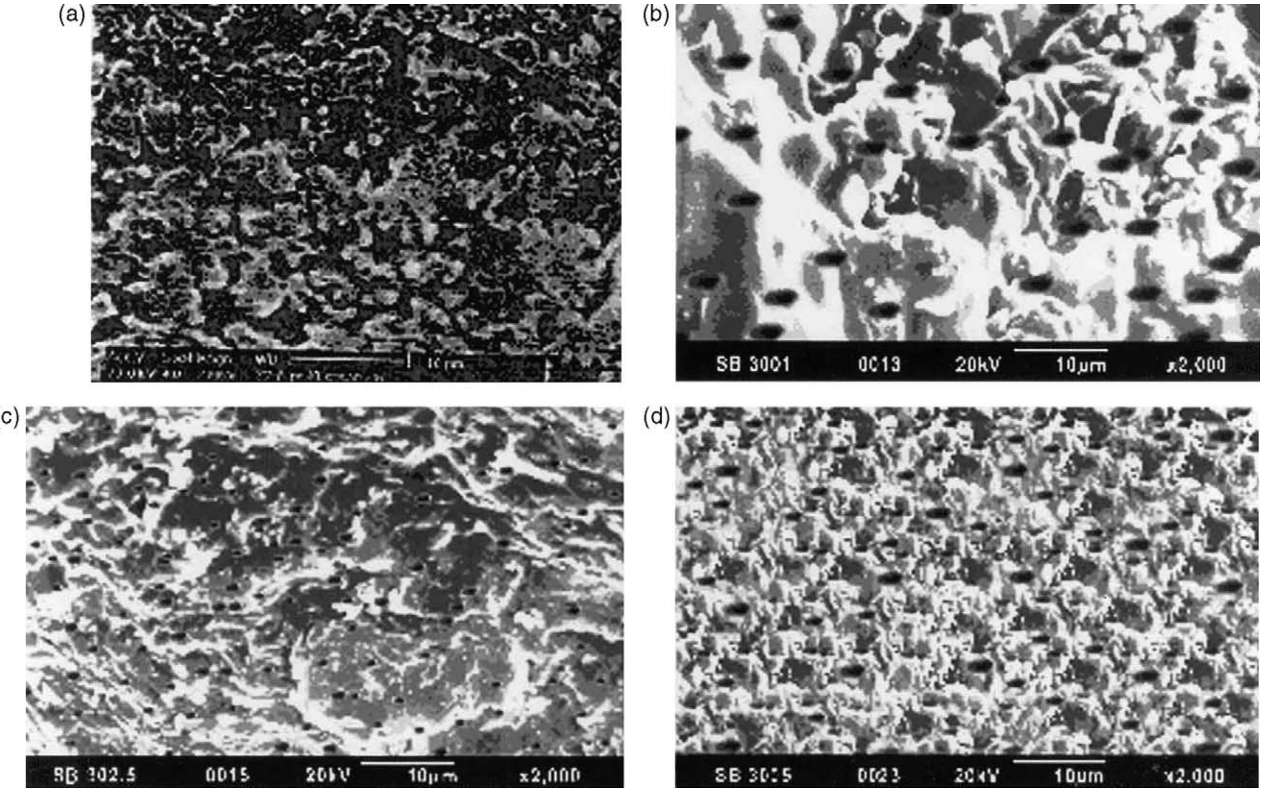

Fig. 1. Scanning electron micrographs of the 70/30 PB/PS blends compatibilised with (a) 0% (b) 1% (c) 2.5% (d) 5% (e) 10 wt% block polymer.

light of papers of Kramer and group. Since, the random copolymer used in the present study is an asymmetrical random copolymer having a composition of 0.70:0.30, butadiene:styrene, no improvement in interfacial strength could be achieved in agreement to Kramer's [11] analysis. The random copolymer used in the present does not have any compositional drift as evidenced by the T_g analysis and is homogeneous in nature. In the case of triblock copolymers, the dispersed phase size decreases sharply followed by an increase at higher concentration. The equilibrium at, which levelling off is observed is known as critical micelle concentration (CMC). The CMC values are estimated from intersection of straight line (Fig. 3) and the levelling off line at higher concentration. This is the concentration at, which micellar formation occurs. In this context, we would like to add that generally CMC is estimated from the plot of interfacial tension versus copolymer concentration. Since, the interfacial tension is directly proportional to the domain size, the estimation of CMC from the plot of domain sizes versus copolymer concentration is justified. Noolandi and Hong [13] pointed out that the reduction in interfacial tension with increasing copolymer concentration is due to reduction in interaction energy of the block copolymers at the interface, taking into consideration the associated entropy loss of the localised chains. The CMC indicates the critical amount of compatibiliser required to saturate unit volume of interface. The percentage of SBS required to saturate the interface is

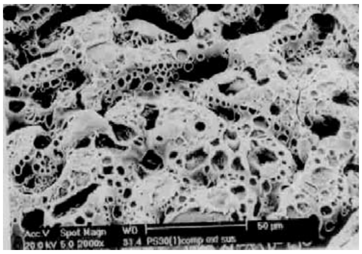

Fig. 2. Scanning electron micrographs of 70/30 PB/PS blend with addition of 2.5% random copolymer.

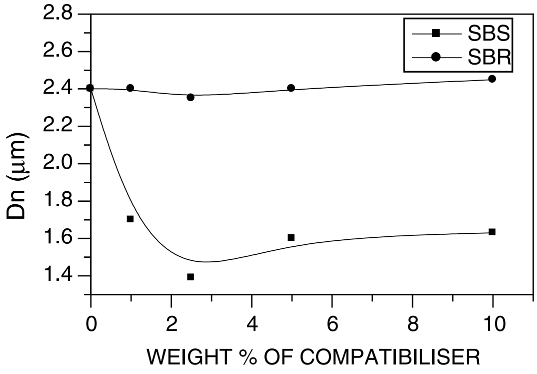

Fig. 3. The average domain sizes as a function of compatibiliser concentration for block and random copolymers.

found to be 2.5%. For concentrations below the critical value, the particle size reduction is drastic with copolymer volume fraction (Fig. 3). The reduction in particle size with the addition of block copolymers is due to the stabilisation of phase morphology formed during melt-mixing. The copolymers diffuse into the interface formed between the homopolymers and they form shells around the dispersed drops, thus, reducing the interfacial tension and coalescence behaviour.

The action of triblock and random copolymer is shown schematically in Fig. 4, where the triblock copolymer nicely organises at the interface. This leads to a large reduction in interfacial tension and domain size and an increase in interfacial thickness. In contrast, the random copolymer is unable to localise at the blend interface, but rather dispersed in the homopolymer phases. The leveling off of dispersed phase dimension at high block copolymer concentration is an indication of clear interfacial saturation. The incorporation of more copolymer may be wasteful since, it does not modify the interfacial zone but rather produces copolymer micelles in homopolymer phases. Other blend compositions also showed similar behaviour upon the addition of the compatibiliser. Taylor's theory can satisfactorily explain the interfacial saturation point. The analysis of Taylor [14] considers how the balance of applied shear forces and counteracting interfacial forces affects drop dimensions and stability. The results were expressed in terms of Weber number according to

$$(W_e)_c = \frac{\eta_m D_n \dot{\gamma}}{2\Gamma} \tag{2}$$

where $\dot{\gamma}$ is the shear rate, η_m is the matrix phase viscosity, D_n is the dispersed phase size, and Γ is the interfacial tension. On addition of compatibilizer, W_e decreases and a reduction in dispersed particle size occurs. According to Taylor's [14] analysis, deformation of the droplet is enhanced by large shear rates, a high matrix viscosity, large droplet size and small interfacial tension. From this equation, it is evident that there is a critical value of capillary number below, which there is no particle deformation and as a result critical particle size. At this particular point, compatibiliser attains maximum possible interfacial area and, therefore, critical amount of compatibiliser is required to saturate the interface.

The mechanism of copolymer action at the interface is believed to be due to: (i) A reduction in the average size of the dispersed phase due to the suppression of coalescence and the decrease of interfacial tension, (ii) an increase in the break-up of the largest particles in the size distribution of the dispersed phase, (iii) a substantial narrowing of the size distribution of the dispersed phase and (iv) a decrease of the mobility of the interface, which slows down the coalescence

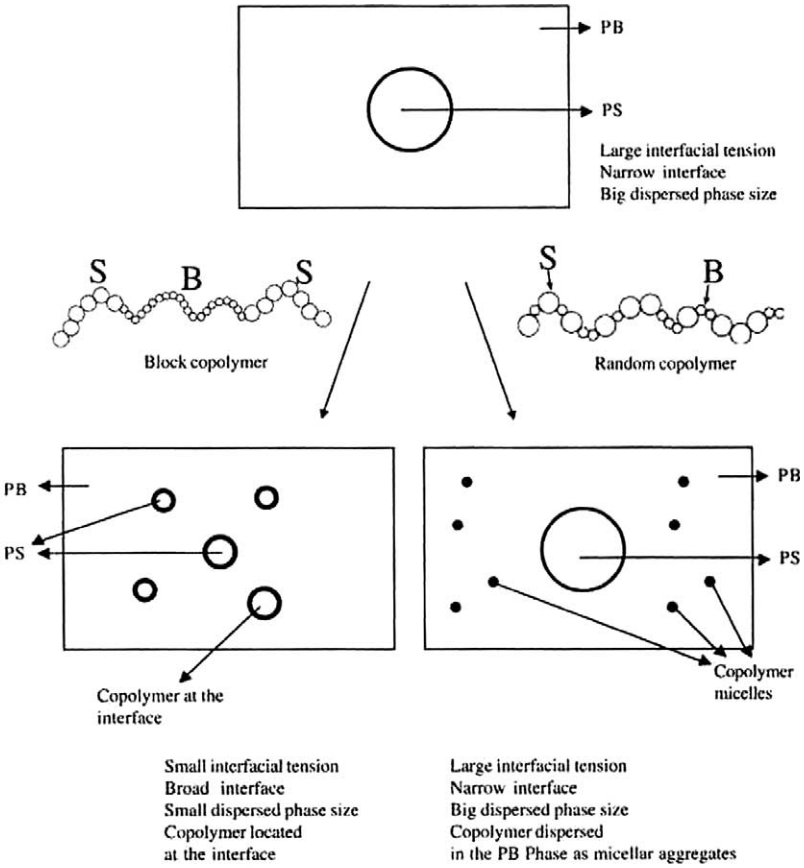

Fig. 4. Schematic representation of the conformation of the copolymer at the interface.

rate. The interfacial saturation by the addition of compatibilisers has been reported in various polymer/polymer blend systems. For example, Fayt, Jerome and Teyssie [15] reported on the equilibration of the dispersed phase size with increasing copolymer content in blends of PE/PS. The interface was saturated by the incorporation of 2-wt% of poly (butadiene-*b*-styrene) as compatibiliser. Anastasiadis and co-workers [2] reported on the sharp decrease in interfacial tension by the incorporation of 1.5 wt% of PS-*b*-PB in PS/PB blends. The interfacial tension levelled off at higher copolymer concentration. The CMC was evaluated from the plot of interfacial tension versus block copolymer concentration. Further addition of the copolymer did not modify the interface any more. The studies of Thomas and co-workers [16–21] also indicated the interfacial saturation by the incorporation of compatibilisers.

According to the equation proposed by Tang and Huang [22] for the average radius (R) of the dispersed phase,

$$R = (R_0 - R_s)e^{-KC} + R_s \tag{3}$$

In this equation, R_0 and R_S are the average radii of dispersed domains at compatibiliser concentration zero and at saturation, respectively, and C is the concentration of the compatibiliser. The equation is based on the assumption that the change in the interfacial tension with the concentration of compatibiliser is according to

$$-\frac{d\gamma}{dC} = K(\gamma - \gamma_S) \tag{4}$$

where γ is the interfacial tension at a compatibiliser concentration C, γ_S is the interfacial tension at the saturation concentration and K is a constant. The changes of average radii of domains with compatibiliser concentration were substituted in Eq. (3). The values obtained for K are given in Table 2. The K values are found to decrease with the level of compatibilisation in the blend [22,23]. The value of K at 2.5% copolymer concentration is the lowest, which is in good agreement with interfacial saturation point. The K value is increased beyond the CMC due to micellar aggregation.

3.2. Comparison with theory

The thermodynamic theories concerning the emulsification of the copolymer in heterogeneous polymer blends have been proposed by Leibler [24], Noolandi and Hong [25]. Leibler [24] developed a mean field formalism to study the interfacial properties of nearly compatible systems. According to this, the reduction in interfacial tension is due to the adsorption of copolymers at the interface. The free energy was expressed in terms of monomer concentration correlation functions that were calculated in a self-consistent way within the random phase approximation. The theory of Leibler is applicable to nearly compatible systems, which suggests that presence of copolymer molecules dissolved in the bulk homopolymer phases causes the compatibility behaviour. The theories of Noolandi and Hong [25] can be applied to incompatible systems like PS/PB for concentrations less than CMC. According to them, the compatibiliser added to a heterogeneous blend locates at the interface and reduces the interfacial energy by broadening the interfacial area. The consequent reduction in interfacial tension [13,25] ($\Delta\gamma$) in a heterogeneous binary blend A/B upon the addition of a divalent copolymer, A-*b*-B is according to

$$\Delta\gamma = d\phi_c\left[\frac{1}{2}\chi + \frac{1}{Z_c} - \frac{1}{Z_2}\exp Z_c\frac{\chi}{2}\right] \tag{5}$$

where d is the width at half height of the copolymer profile reduced by Kuhn statistical segment length, ϕ_c is the bulk copolymer volume fraction in the system, χ is the Flory Huggin's interaction parameter and Z_c is the degree of polymerisation of copolymer. This theory is applicable to completely incompatible systems having concentration less than the CMC. However, beyond CMC, $\Delta\gamma$ levels off with ϕ_c. According to this equation, the plot of interfacial tension reduction versus ϕ_c should yield a straight line. In fact the surface activity of the block copolymer chains causes the interfacial tension reduction. The exponential dependence of the interfacial tension reduction of the block copolymer on molecular weight, and total homopolymer volume fraction, predicts the effectiveness of using large molecular weight diblock as surfactants for immiscible homopolymers. Noolandi and Hong [25] also pointed out that both copolymer concentration and molecular weight are equally important in reducing the interfacial tension. However, it is noted that the theoretical treatment is applicable only for concentrations well below the critical micelle concentration. Above the critical concentration, the compatibiliser may not surface any more, but forms compatibiliser micelle in the major continuous phase. The theory says that localisation of some of the block copolymers at the interface results in a lowering of the interaction energy between the two immiscible homopolymers, broadening of interface between the homopolymers and decrease in free energy. The localisation of the copolymer also results in a decrease in entropy and ultimately limits the amount of copolymer required at the interface. The separation of the two blocks into corresponding homopolymer phases leads to a decrease in the interaction energy of the oriented block with the homopolymers and a small decrease in entropy. Since,

Table 2
The K parameter defined by Eq. (3) substituted to number-average radii (R) of dispersed domains in PB/PS (70/30) blend

wt% of SBS in PS/PB 30/70 blend	K value
0	0
1	0.191
2.5	0.025
5	0.654
10	1.107

interfacial tension reduction is directly proportional to the particle size reduction [26,27], it can be argued that,

$$\Delta D = Kd\phi_c\left[\frac{1}{2}\chi + \frac{1}{Z_c} - \frac{1}{Z_c}\exp Z_c\frac{\chi}{2}\right] \tag{6}$$

where ΔD is the particle size reduction or increment upon the addition of compatibiliser and K is the proportionality constant. The plot of particle size reduction (Δd) versus volume fraction of compatibiliser (ϕ_c) is given in Fig. 5. It can be seen from the figure that the domain size reduced with copolymer content at low concentration followed by a levelling off at higher concentration. This is in agreement with the predictions of Noolandi and Hong.

3.3. Conformation of the copolymer at the interface

The conformation of the compatibiliser at the interface can be predicted based on the interfacial area occupied by the copolymer at the blend interface. There are reports regarding different physical models illustrating the conformation of the copolymer at the interface [28,29]. The physical models representing the conformation of copolymer at the interface reported in literature are (a) fully extended model (b) completely flat model and (c) intermediate model (Fig. 6(a)–(c)). In the fully extended model, the segments are extending into the corresponding homopolymer phases. In such a case, the occupied area at the interface is two times the cross-sectional area of the extended copolymer molecule. In the case of poly(styrene–butadiene–styrene), the theoretical average cross-sectional area of the extended copolymer molecule and, hence, the area it occupies at the interface is ~1 nm^2. In the completely flat model, the occupied copolymer lies almost completely flat at the interface, in which case the occupied area is the lateral surface area of the entire copolymer molecule. Using the experimental values of the root mean square radius of gyration of PS reported in the literature and considering the styrene and butadiene segments of the copolymer as a spherical random coil, the lateral surface area of the SBS copolymer was estimated to be approximately 106 nm^2. Let us now estimate the interfacial area occupied the copolymer at the blend interface. For a binary blend AB, if ϕ_A is the volume fraction of A with spherical domains of radius R in a matrix B, the total interfacial area per unit volume [30] of the original blend is $3\phi_A/R$. If each copolymer molecule occupies an area Σ at the interface, the amount of copolymer (m) required to saturate unit volume of the blend is given by:

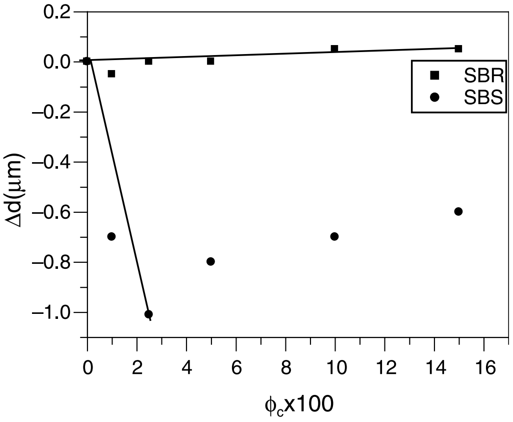

Fig. 5. The reduction in domain diameter as a function of compatibiliser concentration for block and random copolymers.

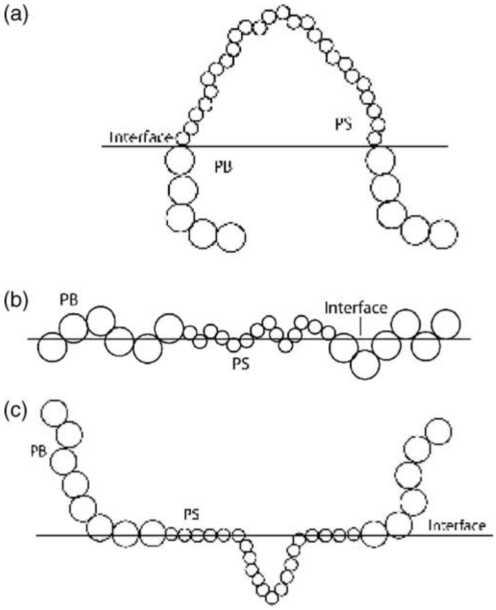

Fig. 6. Speculative model representing the compatibilising action of block and random copolymers (a) fully extended model (b) completely flat model and (c) intermediate model.

$$\Sigma = \frac{3\phi_A M}{mrN} \tag{7}$$

where ϕ_A is the volume fraction of polymer A, M is the molecular weight of the copolymer, r is the radius of the dispersed particle of A in a matrix B, N is the Avogadro number and m the mass of the copolymer required to saturate unit volume of the blend interface at (CMC). The experimental Σ value is 12.97 for the blends. This value is intermediate between those values obtained from the two models (1 and 106 nm^2). This suggests that the completely flat and fully extended models do not represent the actual situation. The actual behaviour is intermediate to those between the two models. The most realistic conformation of a block copolymer at the interface is such that part of the segments lie at the interface and the rest penetrates into the homopolymer phases (Fig. 6(c)).

Molecular weight of the copolymer is one other important factor contributing to penetration of segments into homopolymer phases. According to Gaylord [31], for high molecular weight copolymers where the molecular weight is >150,000, macromolecular interactions such as chain entanglements hinder the complete penetration of each segment into the corresponding homopolymer phases and, therefore, it could be argued that part of the copolymer stays at the interface and the rest penetrates into the homopolymer phases. Earlier Anastiadiasis et al. [2] in polystyrene/1,2-polybuadiene blends compatibilised by poly(styrene-*b*-butadiene) copolymer showed that a 24% of contour length of the copolymer chains (degree of polymerization 261 repeat units) is located at the interface and this corresponds to a length of 38 nm. This is in agreement with the model given in Fig. 6(c).

3.4. The solid-state ^{1}H NMR spectroscopy studies

3.4.1. PS/PB incompatible blends

The ^{1}H magnetization decays, determined at room temperature for neat PB and neat PS, in a $T_1(H)$ or $T_{1\rho}(H)$ experiment, are exponential functions of time, *t*. The corresponding spin–lattice relaxation times in the laboratory frame, $T_1(H)$, in the rotating frame, $T_{1\rho}(H)$ and spin–spin relaxation time $T_2(H)$, are given in Table 3. The values listed in Table 3 are in reasonable agreement with data reported in the literature [32]. For both homopolymers, the ^{1}H magnetization decay in a FID experiment at room temperature can be expressed as a function of time as:

$$M(t) = M_0 \exp - \left(\frac{t}{T_2}\right)^a \tag{8}$$

where a is equal to 2 for PS and 1.66 for PB. The corresponding T_2 values for PS and PB are 16.5 and 265 ms, respectively. The differences in the time dependence and $T_2(H)$ values can be readily explained by the fact that, at room temperature, PS is in the glassy state and behaves like a solid whereas PB is much above its glass transition and exhibits the classical NMR behaviour of an elastomer. The $T_1(H)$, $T_{1\rho}(H)$ and $T_2(H)$ values determined for the PB/PS blends in the absence of compatibilisers are given in Table 3. Whereas the magnetization shows a mono-exponential decay as a function of time in the $T_1(H)$ experiment, it exhibits a bi-exponential decay in the $T_{1\rho}(H)$ determination as seen in Fig. 7. In the temperature range investigated from 26 to 100 °C, the ^{1}H free induction decay (FID) of the blend is well described by the sum of an exponential and a Gaussian function:

$$M(t) = \mathrm{A} \exp\left(-\frac{t}{T_{2\mathrm{rigid}}}\right)^2 + \mathrm{B} \exp\left(-\frac{t}{T_{2\mathrm{mobile}}}\right)^a \tag{9}$$

where a is between 1 and 2.

The $T_{1\rho}(H)$ bi-exponential decay is a clear indication of a phase separation in the incompatible PB/PS blends. It indicates that the domains are too large for an efficient averaging of the ^{1}H relaxation by spin-diffusion. Whatever the blend composition, the shorter $T_{1\rho}(H)$ value determined in the PB/PS blend is very close to the $T_{1\rho}(H)$ measured in neat PS. It can, therefore, be assigned to a PS-rich phase. The longer $T_{1\rho}(H)$ value corresponds to the PB-rich domains. It is a decreasing function of the PS content in the blend. These results tend to indicate that the phases are separated but that there is some communication between the spins of the two components.

The Gaussian decay observed at short times in the FID corresponds to the rigid protons contained in the PS-rich phase. The longer exponential decay can be assigned to the mobile protons contained in the PB-rich domains of the blend. The sensitivity of the FID is not sufficient to observe the protons in the interfacial regions between the PS-rich and PB-rich domains. The $T_2(H)$ values of the rigid protons are unaffected by the blending with PB (Table 3). The percent of rigid protons increases with increasing PS concentration. As indicated in Table 3, it is important to mention that the percents of mobile protons in the PB-rich phase and of rigid protons in the PS-rich phase obtained from the NMR analysis at room temperature are very close to the percents of PB and PS protons introduced in the blends. The influence of temperature on the percent of mobile and rigid protons of the 50/50 PB/PS blend is given in Table 4. The $T_2(H)$ of the PB-rich phase increases with increase of temperature and mobility of the elastomeric regions. It is interesting to note that, on increasing temperature, the percent of rigid protons of the PS-rich phase decreases. This result can be interpreted in terms of a PS/PB interface where PS protons have a glass transition temperature which is lower than the glass transition temperature of bulk PS.

3.4.2. Effect of compatibilisation by the addition of block and random copolymers

The compatibilising action of the SBS triblock copolymer and SBR random copolymer has been studied for the

Table 3
The spin–lattice relaxation time and spin–spin relaxation time of homopolymers and the incompatible PB/PS blends

Sample	Neat PS	PB/PS 30/70	PB/PS 50/50	PB/PS 70/30	Neat PB
$T_1(H)$ (ms)	450	657	626	521	1660
$T_{1\rho}(H)$ 1 (ms)	6.2	3.3	5.2	4.5	
$T_{1\rho}(H)$ 2 (ms)		80	92	112	128
T_2 (H) rigid (μs)	16.5	16.5	16.5	16.5	
% ^{1}H rigid	100	56	38	21	
$T_2(H)$ mobile (μs)		328	309	337	265
% ^{1}H mobile		44	62	79	100
a	2	1.77	1.66	1.8	1.66

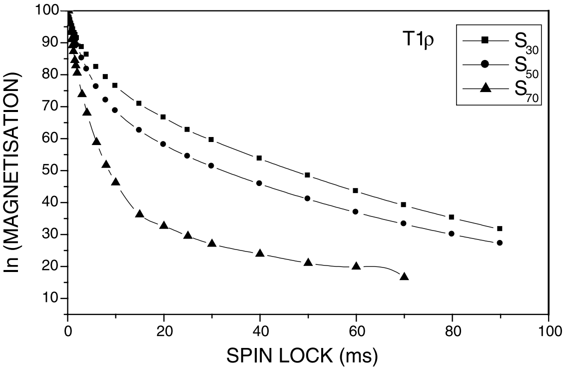

Fig. 7. The relaxation behaviour of different PB/PS blends.

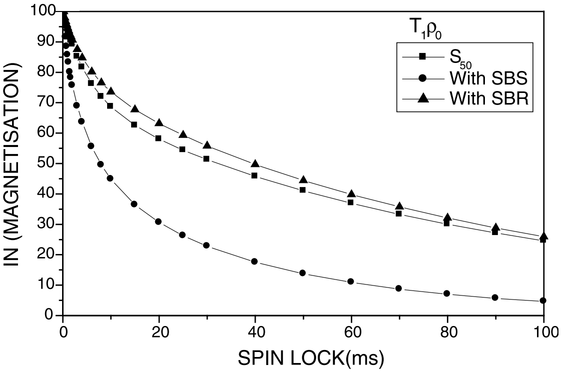

Fig. 8. The relaxation behaviour of uncompatibilised, random and block copolymer compatibilised PB/PS blends.

50/50 and 70/30 PB/PS blends by solid-state ^{1}H NMR spectroscopy. The results are presented in Tables 5 and 6, respectively. $T_1(H)$ values are not significantly modified on the addition of the triblock and random copolymers to the PB/PS blends. All the compatibilised blends show a bi-exponential $T_{1\rho}(H)$ magnetization decay as a function of time, (Fig. 8) indicating that the blends are still heterogeneous at the scale of a few nanometres, even in the presence of copolymers, in agreement with microscopy data. Interestingly, the addition of the random copolymer has no effect on the $T_{1\rho}(H)$ values. On the opposite, the longer $T_{1\rho}(H)$ value shows a dramatic change with the incorporation of 2.5% SBS triblock copolymer. For example, in the 50/50 blend, the $T_{1\rho}(H)$ of the PB-rich phase decreases from 92 ms in the absence of copolymer to 35 ms on the addition of 2.5% SBS triblock copolymer. A similar behaviour is observed for the 70/30 PB/PS blends with a strong decrease of the longer $T_{1\rho}(H)$ for an addition of 2.5% SBS triblock copolymer. This decrease in $T_{1\rho}(H)$ can be related to the decrease of the size of the dispersed phase due to the fact that, as explained in the previous sections, the copolymer decreases the interfacial tension and suppresses the coalescence. The localisation of the triblock copolymer at the interface decreases the interaction energy between the PS and PB phases so that the PB and PS chains interact more favourably and, as a consequence, a high degree of interpenetration of PS and PB chains takes place at the blend interface. In contrast with the behaviour induced by the presence of the SBS triblock copolymer, the relaxation behaviour of the 50/50 and 70/30 blends with the random SBR copolymer is very similar to that of the PB/PS blend without copolymer. This result is readily explained by the random microstructure of the SBR copolymer, which cannot localise at the blend interface. The whole set of NMR results is in full agreement with conclusions derived from the microscopy study.

In order to understand the effect of the concentration of the copolymers on the relaxation behaviour, we have analysed the relaxation behaviour of the 70/30 PB/PS blend with varying copolymer concentration (Table 6). At the optimum concentration of the SBS triblock copolymer, i.e. at 2.5 wt%, the longer $T_{1\rho}$ value, associated with the PB-rich domains, decreases dramatically. On the addition of the excess copolymer beyond 2.5%, the longer $T_{1\rho}(H)$ value increases. This result tends to indicate that the compatibilising effect decreases when excess copolymer is incorporated, in agreement with the microscopy data. The morphological investigations clearly showed that the interface is saturated at 2.5% copolymer. Above this critical copolymer concentration, the copolymer undergoes micellar aggregation. Besides, some copolymer units, which were already located at the interface, may leave the interfacial region and join the micellar aggregation. This process, which leads to the coalescence of some of the domains, competes with the spontaneous localisation of the copolymer at the interface

Table 4
The influence of temperature on the percent of mobile and rigid protons of 50/50 PB/PS blends

Temperature	Mobile protons			Rigid protons	
	$T_2(H)$ mobile	% ^{1}H mobile	a	$T_2(H)$ rigid	% ^{1}H rigid
26 °C	309	62	1.66	16.5	38
30 °C	313	62	1.59	16.1	38
40 °C	322	64	1.51	16.3	37
50 °C	310	64	1.66	17.0	36
60 °C	385	68	1.16	16.5	32
70 °C	358	69	1.26	16.9	32
80 °C	346	69	1.32	17.5	31
90 °C	380	72	1.10	17.8	28
373 K/100 °C	352	75	1.14	18.9	25

Table 5
The compatibilising action of SBS triblock copolymers and SBR random copolymers for the 50/50 PB/PS blends

Sample	Block copolymer 2.5%	Random copolymer 2.5%	Without compatibilizer
$T_1(H)$ (ms)	590	527	626
$T_{1\rho}(H)$ 1 (ms)	3.1	5.1	5.2
$T_{1\rho}(H)$ 2 (ms)	35	89	92
T_2 (H) rigid (μs)	16.5	16.5	16.5
% ^{1}H rigid	20	17	38
T_2 (H) mobile (μs)	302	335	305
% ^{1}H mobile	80	83	63
a	1.6	1.6	1.6

Table 6
The compatibilising action of SBS triblock copolymers and SBR random copolymers for the 70/30 PB/PS blends

	Block copolymer			Random copolymer			Without compatibilizer
	2.5%	5%	20%	2.5%	5%	20%	
$T_1(H)$ (ms)	442	446	440	446	449	441	521
$T_{1\rho}(H)$ 1 (ms)	1.6	2.6	3.7	6.6	6.0	5.1	4.5
$T_{1\rho}(H)$ 2 (ms)	29	100	98	90	98	102	112
T_2 (H) rigid (μs)	17.2	16.7	16.7	16.4	16.9	16.7	16.6
% ^{1}H rigid	23	18	19	20	18	18	21
T_2 (H) mobile (μs)	291	339	356	337	331	335	337
% ^{1}H mobile	77	83	81	80	82	82	79
a	1.51	1.88	1.88	1.62	1.72	1.74	1.80

and prevents the copolymer from covering the entire surface. In order to underline the correlation between NMR and microscopy data, the $T_{1\rho}(H)$ values of the PB-rich phase are plotted as a function of the average domain size in the blends on Fig. 9 $T_{1\rho}(H)$ values show a progressive decrease with the decrease in the average domain diameter, in agreement with the above interpretation of the $T_{1\rho}(H)$ variations in terms of domain sizes.

3.5. Effect of copolymer addition on mechanical properties

Variations of the tensile strength of the 70/30 PB/PS blend as a function of the wt% of the two compatibilisers, SBS and SBR were studied (Fig. 10). The uncompatibilised 70/30 PB/PS blend has a very low tensile strength. The mechanical behaviour of the blend with the random copolymer is almost similar to that of the uncompatibilised system, in agreement with the fact that the random SBR copolymer cannot localise at the blend interface. In contrast, there is a considerable improvement in tensile strength up on the addition of SBS as a compatibiliser. The optimum tensile strength is observed with 2.5% of compatibiliser. On further addition of compatibiliser, the tensile strength decreases and tends to a limiting value on further addition. This increase in tensile strength with the addition of SBS is due to the increase in the interfacial adhesion between PS and PB phases. The highest tensile strength at 2.5% compatibiliser loading corresponds to the higher surface covering. In agreement with NMR and microscopy data, the leveling off of tensile strength at higher concentration of

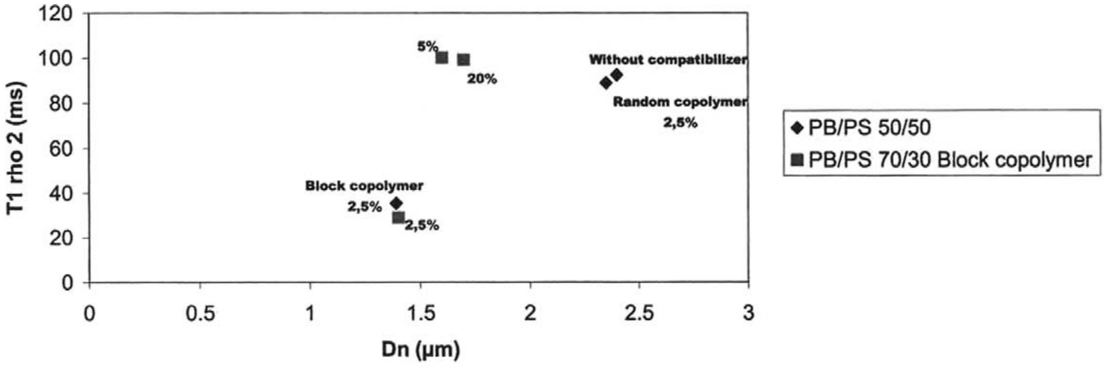

Fig. 9. Spin–lattice relaxation time versus average domain sizes for the blends.

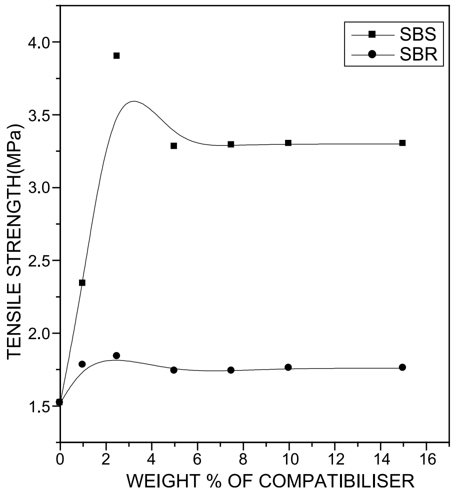

Fig. 10. Variation of the tensile strength of 70/30 PB/PS blend with weight percent of SBS and SBR.

compatibiliser can be related to the formation of compatibiliser micelles in the continuous PS matrix.

4. Conclusion

A combination of three different techniques such as electron microscopy, solid-state proton NMR spectroscopy and static mechanical analysis have been used in order to compare the interface modification of random copolymers of polystyrene and polybutadiene and triblock copolymers of poly(styrene–butadiene–styrene) in incompatible (PS)/(PB) blends. The addition of the triblock copolymers reduced the domain size of the dispersed phase followed by increase at higher copolymer concentration. The equilibrium concentration of the copolymer was estimated and was related to the critical micelle concentration. The decrease in domain size was accounted with two major effects (i) decrease of interfacial tension (ii) suppression of coalescence. The experimental compatibilisation results were in agreement with the predictions of Noolandi and Hong. The random copolymer being asymmetric, and having no compositional drift, no improvement in interfacial strength could be achieved. The conformation of the copolymer at the interface was evaluated by characterising the area occupied by the copolymer at the blend interface. The experimental results showed that part of the triblock copolymer lies flat at the interface and the rest penetrates into the homopolymer phases. The conclusions derived from the solid-state NMR studies are in agreement with the microscopy observations. All the incompatible blends showed two $T_{1\rho}(H)$ values indicating that the blends are phase separated. The addition of triblock copolymers reduced the $T_{1\rho}(H)$ value of the PB-rich phase, indicating the localisation of the copolymer at the interface, which is in agreement with the microscopy data. NMR study further indicated the existence of a critical concentration of copolymer as revealed by microscopy. A correlation was obtained between domain size and $T_{1\rho}$ values. Finally the static mechanical properties also showed a linear increase of the tensile strength up on the addition of triblock copolymer followed by decrease indicating the existence of critical concentration as revealed by solid state NMR and microscopy studies.

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