Influence of Geometrical Parameters of Screw Melt Mixing on Visco-Elastic Properties of PC/ABS Blends

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ABSTRACT: In the present article, we describe an experimental study of blends of polycarbonate (PC) with acrylonitrile-butadiene-styrene graft copolymer (ABS) melt mixed in two types of single screw (varying in compression ratio) and twin screw (counter and co-rotational) extruders. The effect of screw design variation is qualified via storage and loss moduli differences obtained for particular screw geometries. Rotational rheometer with parallel-plates geometry was used to determine dynamic viscoelastic properties at a strain of 1% selected as the value representative of the linear viscoelasticity. Measurements were carried out at 220, 240, and 260°C and angular frequencies in the range from 0.1 to 100 rad/s. Regardless of the dependences variation with blend compositions, mixing performed on the extruder with counter rotating twin screws resulted in the lowest viscoelastic response in the whole range investigated. The rheological observations were confirmed by the results of SEM analysis. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2847–2853, 2010

Key words: immiscible blend; screw extrusion; viscoelasticity

INTRODUCTION

Screw extruders are the most often used equipment for preparation of polymer blends in industry.[1] Majority of studies on polymer blending has been focused on elementary processes such as drop formation, thread break-up, and coalescence, and recently, morphology development during mixing.

As already pointed out in 1975 by Han et al.,[2] moderately different modes of dispersion can give rise to pronounced differences in the rheological response of the blends in the molten state, since the rheological variables depend strongly on the size, size distributions, and the shape of the discrete phase droplets dispersed in the continuous phase. Thus, rheological properties might be considered as a powerful tool to distinguish efficiency of various types of compounding.

Influences of components' rheology, blend composition and processing variables on morphology evolution have been recently reported by several authors. Lee et al.[1] demonstrated on five binary immiscible blends (including PS/PC) mixed in twin screw extruder that their morphology depends on the melt blending temperature relative to the melting temperature of crystalline polymer and critical flow temperature (50°C above glass transition) of amorphous polymer, the screw speed, residence time, viscosity ratio, and blends composition. They showed that the flow of two immiscible polymers forming co-continuous or dispersed morphology during mixing in a twin screw extruder cannot be regarded as being equal to the flow of a homogenous polymer as it is often considered when modeling the process.

Chuai et al.[3] compared the morphology evolution of PC/PS blends for three blending methods of industrial relevance. The composition, where the phase inversion occurs, was obtained from both experimental data and theoretical predictions through semi-empirical models,[4,5] which are based on rheological properties of pure components. Thus, morphology of polymer blends is directly related to the viscoelastic properties of their individual components. However, a failure of these predictions for PC/PS has been found in the mentioned work as well as in Ref. 6 although for other blends investigated they were in a good accordance.

Very important result of paper[3] is the significant modification of the morphology with radial position obtained for the first extruded strands. Vanoene[7] has shown that in a capillary flow there are two main modes of dispersion: stratification or droplet formation. These morphologies were shown to be controlled by the particle size, interfacial tension, and the variations in viscoelastic response of the two

phases. Tsebrenko et al.[8] suggested that the main factor governing structure formation process is the ratio of the melt viscosities. Based on this proposal Chuai et al.[3] observed that the fiber formation is the most pronounced if melt viscosity ratio approaches unity. Further, the results obtained clearly demonstrated that the presence of fiber or rod-like structures is favored by higher shear rates (close to the die wall).

Very recently, Russo et al.[9] compared single and twin screw extruders used for remixing of nylon 6 nanocomposites prepared by melt compounding. Single screw extrusion resulted in a modification of initial morphology since the reaglomeration of silicate layers could occur. On the other hand, a better nanodispersion attributed to the additional mechanical stresses was produced with two screws. Furthermore, enhanced shear stresses caused significant chain scission of the matrix polymer.

Generally, it is observed that fast morphology change and rapid decrease of phase dimensions occur in the initial stages of mixing.[10] In Willemse et al.[11] traditional approach to predict phase size (break-up of isolated droplets in a matrix flow field governed by the Capillary number (Ca) is compared to the prediction based on "sheeting" mechanism. From this work, it seems that "sheeting" mechanism occurs in a single screw extruder, while in a static mixer it appears only when the number of mixing elements is smaller than seven (higher number resulted in dispersed droplets). It has been shown that independent of Ca, the phase dimensions do not significantly decrease any further after sheet break-up, whether or not the blend passed through a static mixer or neutral elements. However, the type of morphology obtained depends on Ca, since it governs stability of the structures formed after sheet break-up. The type of final morphology then depends on the stability of the fibers formed after the sheet break up. If the capillary number is higher than one, fiber/matrix morphology is obtained, for lower Ca break up occurs and droplet matrix morphology is gained.

Literature survey concerning PC/ABS blends in the last decade comprises rheological, mechanical, and morphological investigations (for the earlier works there is an excellent review by Greco and Sorrentino[12]). Khan et al.[13] performed rheological study of various PC/ABS blends compositions demonstrating improvement of PC processability by addition of ABS. Mechanical properties in terms of tensile tests (obeying a mixing rule) as well as impact strength indicated broadening of a processing window of PC by adding ABS. Sohn et al.[14] reported enhancement in tensile strength and, on the other hand, lower impact strength of PC/ABS blends upon adding reactive flame retardant (brominated epoxy resin).

It is widely accepted that PC/ABS blends can be used without compatibilizers due to the strong interactions between PC and styrene-acrylonitrile. Rubber content in ABS, on the opposite, reduces compatibility of PC/ABS blends as shown recently by Nigam et al.[15]

However, compatibilizer can play a positive role in reduction of phase coarsening and stabilizing morphology as shown by Yang et al.[16] and Kang et al.[17] when utilizing PMMA, or maleic anhydride grafted ABS as in case of the study by Balakrishnan et al.[18] The changes in the interfacial properties of PC and SAN due to a presence of compatibilizers is described in detail by Kim and Kim.[19]

Yang et al.[16] examined the morphology evolution of PC/ABS blends along a twin screw extruder and found out that the size of minor phase domains was reduced toward the die of the extruder.

Although the type of mixing has been stated as one of the important variables influencing the final properties of the PC/ABS blends,[12] there seems to be no systematic study taking it into account. Therefore, the task of our investigation is to determine the effect of the screw design variation on the blending efficiency via comparison of viscoelastic properties. PC/ABS blends have been selected for the study because of their high interfacial tension resulting in a mixing with certain difficulties.

EXPERIMENTAL

Materials, blends, and samples preparation

In this work, commercially produced polycarbonate (PC) - Makrolon® 2600 supplied from Bayer, and acrylonitrile-butadiene-styrene graft copolymer (ABS) - Lustran® 440 from Monsanto were used as components for preparation of blends. Gel permeation chromatography (GPC) was used for determination of the molecular characteristics of PC. The GPC was equipped with set of water columns Styragel® HR 0.5, 1, 4 and water guard column Styragel®. Tetrahydrofuran with flow rate of 1 mL/min was used as a mobile phase. It was calibrated with polystyrene standards with MW 486, 947, 2980, 9580, 17,500 and 188,000 g/mol. Weight, number, and Z-averages of the molecular weight of PC were obtained as follows: $\overline{M}_w = 46{,}009$, $\overline{M}_n = 20{,}584$, $\overline{M}_z = 77{,}022$; polydispersity index 2.24. The internal composition of ABS was obtained from ^{1}H-NMR spectra measured in solution: 31, 5, and 64 wt % of acrylonitrile, butadiene, and styrene, respectively.

The blends were prepared in compositions of 0, 20, 40, 50, 60, 80, and 100 wt % of ABS. The abbreviation for individual PC/ABS blends consists two digits number: first stands for content of PC and second for content of ABS (e.g., blend containing

TABLE I
Extruders and Their Characteristics

Screw	Diameter D (mm)	Length L (mm)	Speed (rpm)	Details
Abbreviation				S1: BX-18, PSE, Axon AB, Plastic Machinery
Single	15 (18)	600 (540)	30	Compression 3.7 : 1
Abbreviation				S2: Extrusiograph, Type 30/25D, Brabender
Single	29.85	746.25	30	Conical core, compression 2 : 1
Abbreviation				T1: Rheocord 300p, Haake
Twin	15	400	90	Co-rotational
Abbreviation				T2: Twin screw compounder TSC 42/6, Brabender
Twin	41.8	250.8	20	Counter-rotate, axial grooves

40 wt % of PC and 60 wt % of ABS is denoted as blend 46).

Both components in the form of pellets were dried in an air oven for about 5 h, PC at 120°C and ABS at 100°C, followed by dry-blending. Then, the components were melt-mixed on two types of single screw (S1,S2) and two types of twin screw (T1,T2) extruders. Characteristics of extruders are depicted in Table I, and their geometries are schematically shown in Figure 1. The temperatures in the metering zones were as follows: 220°C (entrance), 240°C (mixing), and 250°C (terminal zone) for both twin screw extruders, and accordingly entrance zone for single screw extruders (S1,S2) was 245°C, mixing zone 250°C, and terminal zone 260°C. Extruded blends in a form of string were cut into pellets, and dried for 5 h at 100°C prior to preparation of test samples. The required testing specimens were obtained by compression molding at 260°C and cut from molded sheets.

Measurements of rheological properties

Rotational rheometer (Rheometric Dynamic Analyzer ARES) with a parallel-plate geometry (plate diameter 25 mm, gap between plates 1 mm) equipped with RSI Orchestrator™ software, was used to determine dynamic viscoelastic properties, i.e., storage (G') and loss (G'') moduli. Nitrogen atmosphere prevented degradation during measurements.

Strain sweep test in the strain (γ_o) range from 0.01% to 100% for three angular frequencies (ω) 0.1, 1, and 10 rad/s was carried out to determine linear
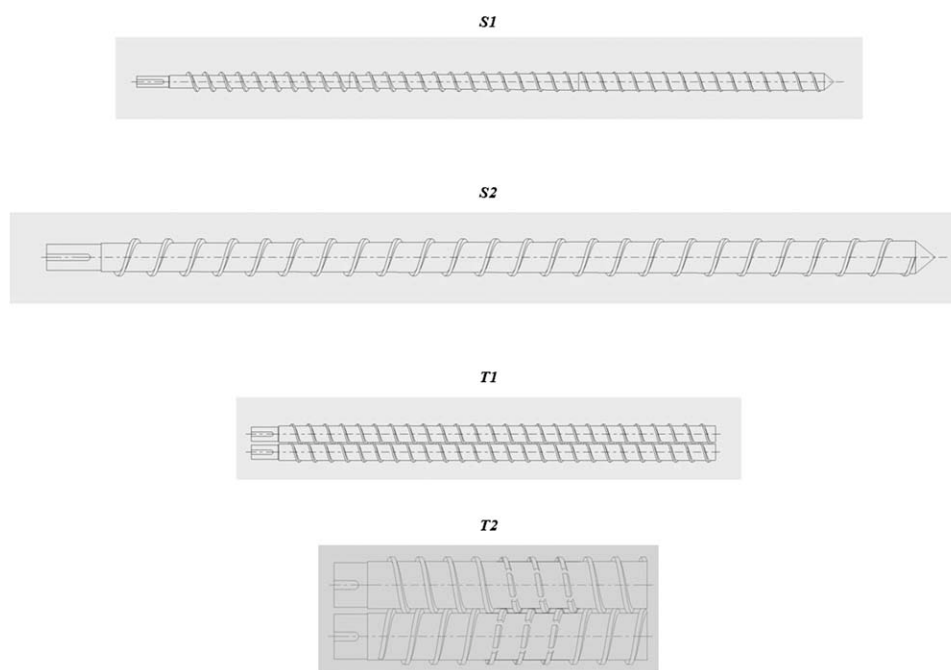

S1

S2

T1

T2

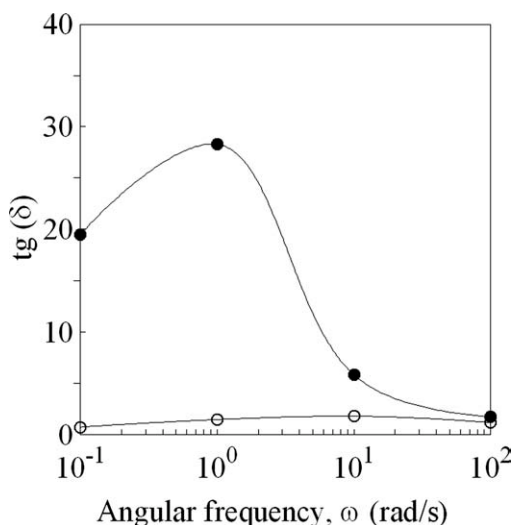**Figure 1** Scheme of the screw extruder geometries.

Figure 2 Contribution of elastic and viscous responses to viscoelastic behavior: PC (●), ABS (○).

viscoelastic region. Strain of 1% was selected as the value representative of the linear viscoelasticity.[20] Measurements were carried out at 220, 240, and 260°C and angular frequencies in the range from 0.1 to 100 rad/s.

SEM analysis

The influence of mixing methods on the structural arrangement was studied with scanning electron microscopy (SEM) on blends 46 and 64.

Specimen surfaces were achieved by breaking samples (specimens with dimensions 80 mm × 10 mm × 4 mm) during Charpy impact test. Obtained fracture surfaces were etched as followed.

The etching liquid used was prepared from 0.35 g of grinded potassium permanganate dissolved in a mixture of 10 mL of sulphuric acid and 10 mL of phosphoric acid. Samples were etched for 20 sec, and then the etching liquid was washed with water for 60 min.

After the above treatment, samples were coated with a thin gold/palladium (SC7620 Mini Sputter Coater) film and examined in a scanning electron microscope Vega LMU (Tescan, Czech Republic).

RESULTS AND DISCUSSION

Viscoelastic properties of pure PC and ABS in terms of loss tangent tan δ as a function of angular frequency ω are shown in Figure 2. Similar values of both moduli obtained for pure ABS results in tan δ being close to 1, pointing out an equal contribution of elastic and viscous responses in the whole measured range of ω. On the other hand, tan δ of PC exhibits maximum at 1 rad/s, and then it approaches 1 at high frequency region.

Regardless of the mixing setup employed, storage modulus G' of PC/ABS blends generally show a slight positive deviation from log additivity rule at lower angular frequencies (0.1 and 1 rad/s), however at higher shearing the deviations are negative, Figure 3. The latter is valid for the loss modulus G'' regardless of the angular frequency tested.

As demonstrated in Figure 4, T2 twin screw blending resulted in the lowest G' and G'' moduli among the used methods through the whole range of blends' compositions employed in the study. To quantify the distinctions in the blending methods,
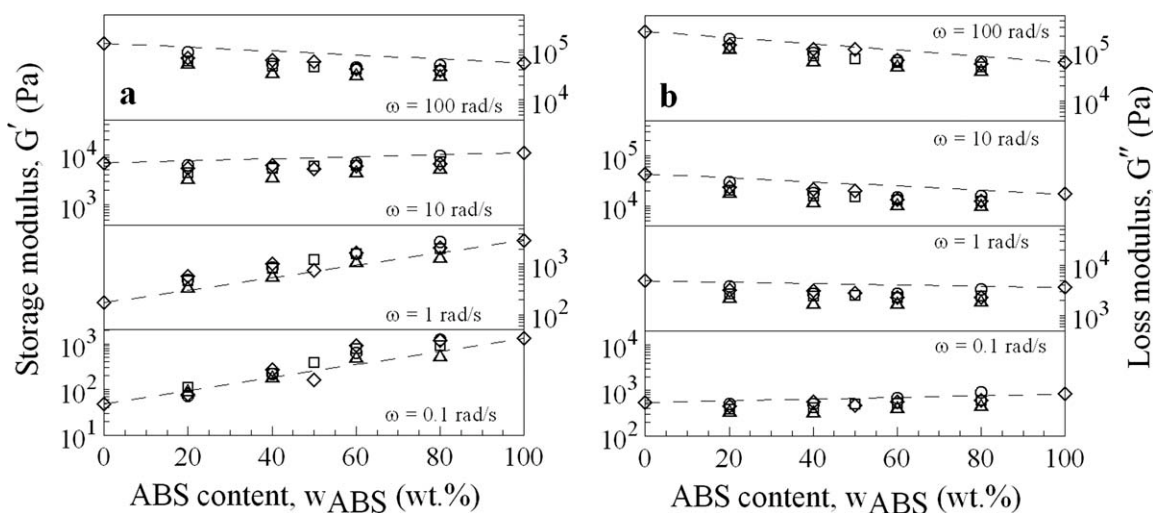

Figure 3 Viscoelastic properties of pure components (PC and ABS) and their blends determined at angular frequencies 0.1, 1, 10, and 100 rad/s after melt-mixing in single (S1 ◇, S2 ○) and twin (T1 □, T2 △) screw extruders.
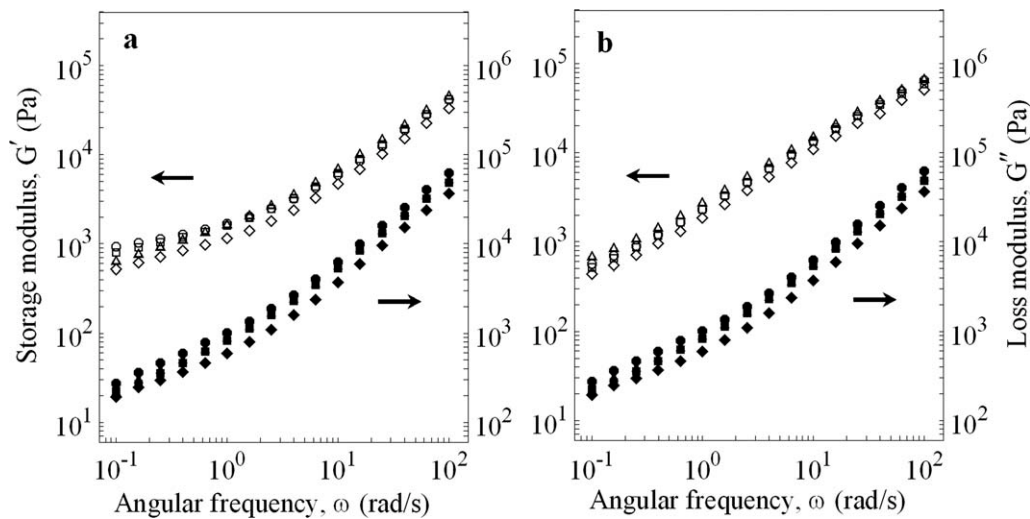
Figure 4 Storage (a) and loss (b) moduli as functions of angular frequency for the PC/ABS 46 (open symbols) and 64 (full symbols) blends: single (S1 ○, S2 △) and twin (T1 □, T2 ◇) screw extruders.

the difference D (in %) of G' and G'' between S1 (S2, T1) and T2 is calculated as described

$$D = \frac{G_X - G_{T2}}{G_X} \times 100 \qquad (1)$$

where G_X denotes modulus (storage or loss) of blends melt-mixed with S1 or S2 or T1 and G_{T2} modulus of blends melt-mixed with T2.

The calculated differences D for storage and loss moduli are shown in Figures 5 and 6, respectively. The smallest discrepancies for both G' and G'' were found between twin screw extruders T1 and T2. In case of elastic response characterized by storage modulus the trends in D vs. ω can hardly be distinguished as shown in Figure 5. On the opposite, the cause of loss modulus differences between T1 and T2 is similar regardless of blends composition, exhibiting maximum at about 0.3 s^{-1}, Figure 6(c). In

the case of single screw extruders [Fig. 6(a,b)] the differences in G'' between blends 46 and 64 were almost independent of angular frequency, while 28 and 82 exhibited minima/maxima.

These particular blends compositions (46 and 64) have been qualified as the most favorable in our previous study[21] based on classification of polymer blends in the view of log-additivity rule. Since the positive deviation implies formation of interactions between blend components, especially PC/ABS 60/40 and 40/60 seem to be favorable materials when considering essential immiscibility of PC and ABS. The elimination of this phenomenon at higher ω, where almost all compositions followed the mixing rule or exhibited even negative deviations, suggests breakage of the structure resisting only if less deformation was applied.

To support the results of the rheological study, the blends were additionally analyzed with SEM. Figure
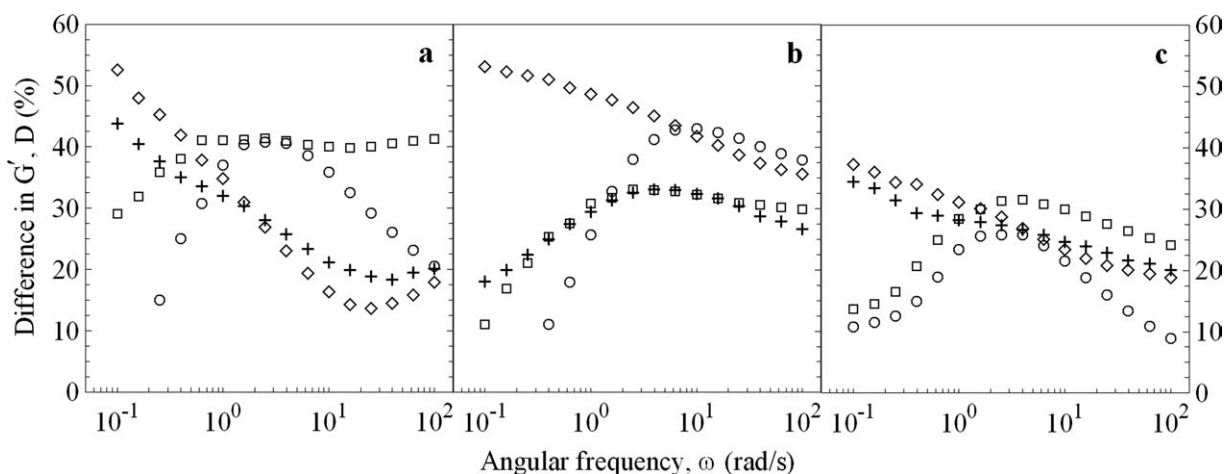

Figure 5 Storage modulus differences between S1 − T2 (a), S2 − T2 (b), and T1 − T2 (c) mixing of PC/ABS blends 28 (◇), 46 (+), 64 (□), and 82 (○).
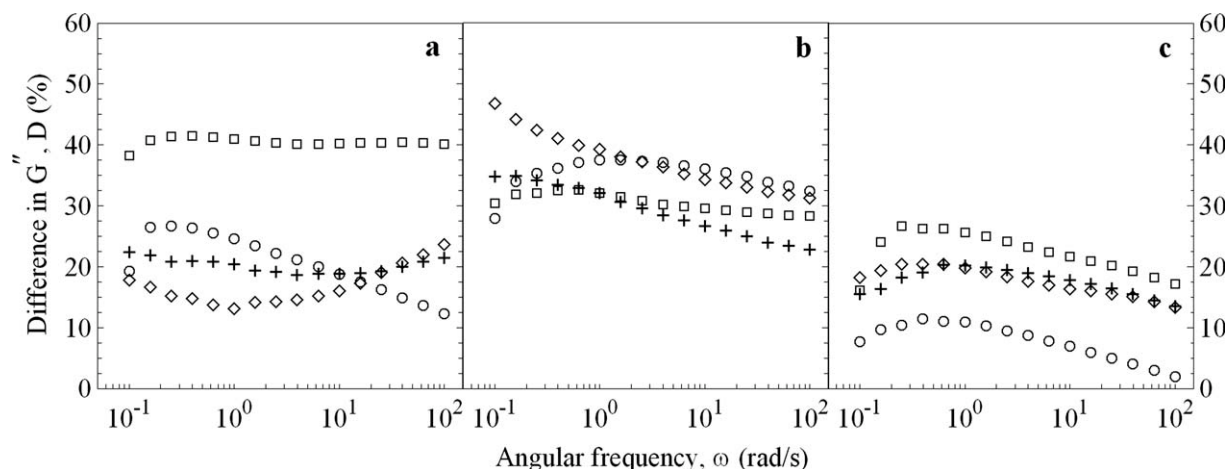
Figure 6 Loss modulus differences between S1 − T2 (a), S2 − T2 (b), and T1 − T2 (c) mixing of PC/ABS blends 28 (◇), 46 (+), 64 (□), and 82 (○).

7 demonstrates rather coarse structure obtained with single screw extruders in contrast to fine morphology of PC/ABS mixed on twin screw extruder T2. PC and butadiene were removed by etching leaving acrylonitrile and styrene appearing as brighter regions in the micrographs; small dark voids in acrylonitrile-styrene regions respond to butadiene.

Finally, the mixing efficiency was examined from $\log G'$ versus $\log G''$ plots. Vanoene[7] argued already in 1974 that the second normal stress difference (N_2) is important factor in determining morphology, and consequently mechanical properties of immiscible polymer blends. Since N_2 is difficult to obtain, according to Han[22–24] elastic properties might be evaluated from $\log G'$ versus $\log G''$ plots.

Based on molecular viscoelasticity theory Lee and Han[25] found this type of plot independent of temperature for monodisperse homopolymers. From the observation that elasticity ratio remained constant regardless mixing temperature, while viscosity ratio was strongly temperature dependent, they stated that the morphological state of blend depends on viscosity ratio, while elasticity plays a little role. At the same time the authors believe that fluid elasticity is important for determining the size of the dispersed phase via droplet break-up and/or coalescence during processing.

The plots of $\log G'$ versus $\log G''$ for the PC/ABS were also found temperature independent as shown in Figure 8 for S2, T1, and T2 extrusions represented by blends 46 and 64 (S1 not shown, similar to S2). The only exception were ABS-rich blends (in Fig. 8 represented by blend 46) slightly departuring from the master curve at the lowest temperature for twin screw extruders. The deviation might come from the behavior of pure components shown in Figure 9, where PC was almost independent of temperature for all tested mixing methods, while ABS gave temperature independent curves only for higher storage

and loss moduli regions. Butadiene component of ABS is thought to be responsible for this discrepancy. The plateau regions characteristic for both twin screw extruded PC (Fig. 9) were also present at mixing of blends [Fig. 8(b)]. The $\log G'$ versus $\log G''$ plots for the PC/ABS blends occurred between the curves obtained for the pure components.

CONCLUSIONS

The effect of the screw design variation on the blending efficiency via comparison of blends' viscoelastic properties was investigated. The viscoelastic moduli of the PC/ABS blends prepared using counter
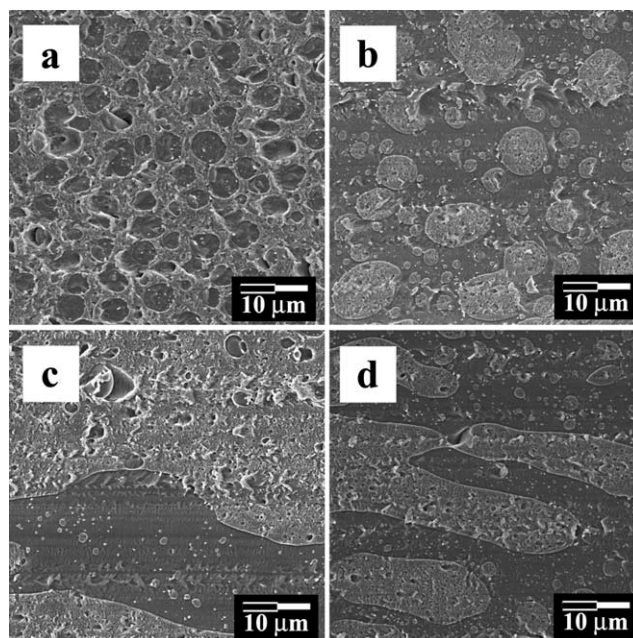

Figure 7 SEM pictures of PC/ABS blends 46 (a, c) and 64 (b, d) prepared with T2 twin screw (a, b) and S2 single screw (c, d) extruders.

rotating twin screw extruder differed from those obtained with single screw extruders as well as co-rotation twin screw blending. The counter rotating screw extruder has been found to reveal the lowest viscoelastic functions for all PC/ABS blends investigated. This observation is further sustained with SEM analysis provided. Further, it has been shown that plots of storage versus loss moduli, representing elastic properties, can be employed to intercept the differences in the structure formed during mixing on screw extruders of various geometrical arrangements. The
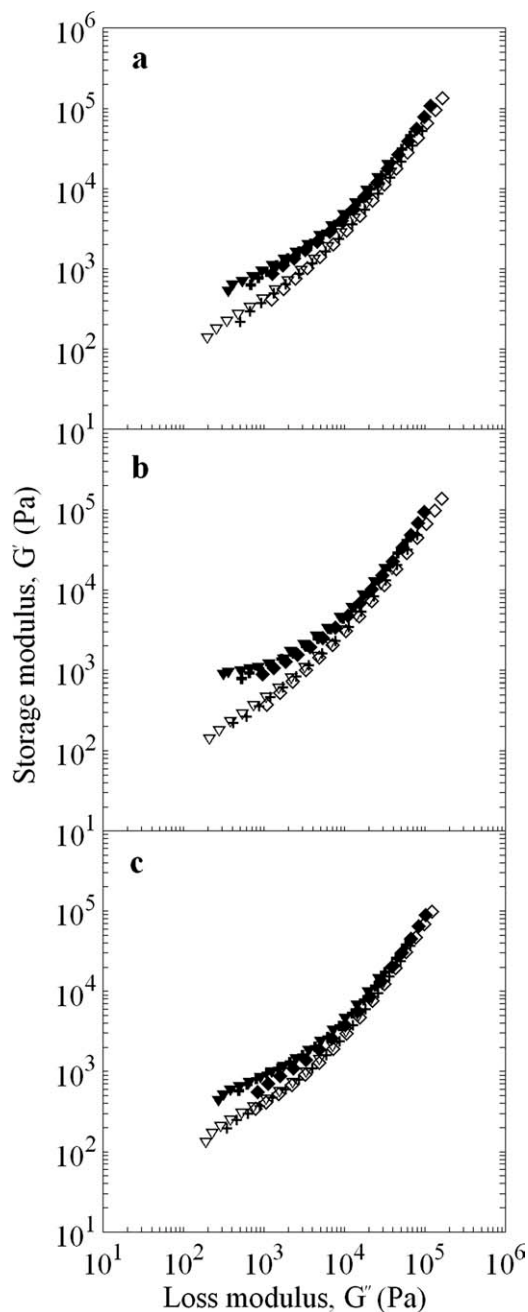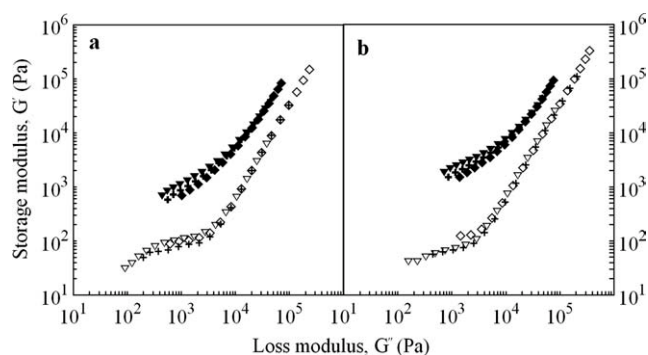

Figure 9 Storage versus loss moduli plots for pure PC (open symbols) and ABS (full symbols) prepared with T2 (a) and T1 (b) twin screw extruders at 220 ($\diamond$), 240 ($+$), and 260°C ($\triangledown$).

morphology designed with various mixing elements can lead to the desired properties.

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Figure 8 Storage versus loss moduli plots for PC/ABS blends 46 (full symbols) and 64 (open symbols) prepared with S2 (a), T1 (b), and T2 (c) screw extruders at 220 ($\diamond$), 240 ($+$), and 260°C ($\triangledown$).