Linear Viscoelastic and Morphological Description of Multiphase Systems Affected by Processing Parameters

Vanda Kuthanová,[1] Berenika Hausnerová,[1] Takeshi Kitano,[1] Monika Lapčíková,[2] Petr Sáha[1]

[1]Polymer Centre, Tomas Bata University in Zlín, T. G. M. 275, CZ 762 72, Zlín, Czech Republic
[2]Institute of Macromolecular Chemistry AS CR, v.v. i., Heyrovského nám. 2, CZ 162 06, Praha 6—Břevnov, Czech Republic

ABSTRACT: Influence of processing methods, in terms of comparing compression and injection moldings, on the rheological behavior of polycarbonate (PC)/acrylonitrile-butadiene-styrene (ABS) blends and PC/ABS/glass fibers composites is presented. Blend compositions and fiber content are considered as material variables. For blends, the effect of the processing route on the viscoelastic functions is evident only for low shearing frequencies. Injection molding created morphology with cocontinuous character, while compression molded blends have "relaxed" structure, where dispersed phase domains are several times larger than in injection molded ones. The glass fiber reinforcement led to the significant differences in viscoelastic properties of composites processed by injection and compression molding. Injected composites have both moduli always higher than compression molded. Also, fiber lengths are reduced more for compressing molding. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 989–999, 2011

Key words: polymer composites; injection molding; compression molding; morphology; viscoelastic properties

INTRODUCTION

Majority of polymer mixtures are thermodynamically immiscible, and thus, heterogeneous structure, two glass transition temperatures[1] (with no shift through compositions)[2] as well as mechanical and rheological properties below the "log-additivity rule," are attributes mostly observed.[3] From industrial point of view, blending is generally considered as mixing process with presence of an appropriate compatibilization method.

Most prevalent methods to achieve compatible blends include addition of a compatibilizer (block or graft copolymer), *in situ* grafting and/or polymerization by reactive blending. Although these routes are available to improve the compatibility, introducing the third component brings some limitations to practical implementation due to the lack of adequate chemical routes and high expenses. An alternative might be the irradiation treatment as we have shown in our previous papers,[4,5] or even finding certain concentration, where the blends posses required properties without any treatment.[6]

Polycarbonate (PC)/acrylonitrile-butadiene-styrene (ABS) blends are generally considered as immiscible pair. In a compatibilized form, they offer mechanical properties of PC together with reasonable processability and price of ABS. They have been commercially known for some time in automotive industry (interior body panels), office equipment, and appliance housing.[7–9] Their physical, and consequently, utility properties are governed not only by the features of the individual components (viscosity, molecular weight, molecular weight distribution) and components composition but also by the mixing of components in melt followed by final processing. All mentioned factors affect the blends morphology, which in turn influence blends properties. The results from several authors, which draw the ground of direction for presented PC/ABS blends, are summarized below.

First aspect, effecting thermal, flow, and consequently mechanical properties of PC/ABS blends is the presence of low molecular weight (LMW) species, for example, monomers, oligomers, or additives in the commercially produced copolymers. Influence of LMW species contained in SAN or ABS was firstly reported in 1989.[10] It was proposed that presence of LMW species affects components similarly as a plasticizer, therefore change of viscosity ratios between components can be expected, which in turn

influences development of blend morphology. Similar result was later confirmed for PC/ABS blends[11] with the suggestion that LMW species, initially present in the ABS, migrate during melt-mixing toward PC domains. Subtraction of LMW species seems to enhance the chemical affinity between PC and SAN domains at the interface. This in turn decreases the interfacial tension and particles dimensions.

Second aspect is the content of particular components in copolymer. It was observed[12] that the adhesion between PC and SAN passes a sharp maximum for 25–27 wt % of acrylonitrile (AN) in copolymer. In the case of PC/ABS, both negative and positive deviations were obtained for 20 and 22 wt % content of AN.[13] It was suggested[14] that synergistic effect, obtained at certain PC/ABS composition with 22 wt % of AN, can be broadened by lowering of butadiene (B) content from 29 to 18 wt %. Further, hypothesis of the interlayer zones situated at the interphase boundary was pronounced and confirmed irrespective of the ABS internal composition.[15,16]

Positive deviations from the "log-additivity rule" were observed for ABS-rich blends[17] from commercially produced components, where AN and B contents in ABS were 24 and 16.5%,[18] on the opposite to the reported negative deviations of apparent viscosity for blends containing maleic anhydride-grafted ABS. However, microstructure of the unmodified PC/ABS was coarse and irregular; the microstructure of modified samples (due to reactive blending process) was fine with lamellar morphology oriented along the flow direction of injection molding.

Further, two ABS with AN/B/S contents of 22/19/59 and 18–22/32/40–50 were compared,[19] and positive deviations of tensile strength for the first ABS type were found at 50 and 70 wt % of PC in the blend, whereas blends containing the second type of ABS showed no positive deviations at all. Partial miscibility over the entire blend composition, even in case that AN was in as broad range as 23–70 wt %, was reported by Mendelson[20] for blends of polystyrene-co-acrylonitrile and PC.

Further aspects, which should be taken into account, are conditions of mixing and sample preparation. Conventional twin-screw extruder and injection molding machine were used by Kurauchi and Ohta[13] to mix and mold, respectively, PC with SAN and two kinds of ABS differing in AN/B ratio. Positive deviations of impact strength at 70 and 90 wt % of PC were observed for PC/SAN and PC/ABS blends containing 22AN/29B.

Similar treatment, compounding in twin screw extruder with consequent injection molding, was done for 50/50 PC/ABS blend.[21] Interphase adhesion between PC and ABS was investigated by testing strength of weldlines. Weldline strength of the blend was dramatically lowered when compared with the pure PC. Although AN content in ABS did not appear to influence the weldline strength, it was improved by increasing rubber content.

In the paper of Guest and Daly,[22] PC/SAN blends in the whole composition range underwent treatment analogous to usual processing. Polymers were melt-blended using cokneader compounding machine followed by either injection molding (IM) or compression molding (CM). It has been attempted to illustrate investigation of microstructural characteristics via dynamic mechanical properties. Significant differences between the dynamic mechanical properties of IM and CM samples showed IM as a better molding technique resulting in a fine, laminar, oriented structure of IM samples. For compression-molded samples, a coarse "relaxed" uniform morphology was observed.

In the work of Quintens et al.,[23] shape of relaxation modulus on temperature curve was not typical for an immiscible PC/SAN two phase system, with AN content of 24 wt %, melt mixed similarly. Both transitions seemed to approach each other, thereby shifting from the zones of the pure components and could be interpreted as an evidence of miscibility. On the other hand, the annealed samples (4 MPa at 200°C, 3 min) showed two transition regions with plateau in-between, which was interpreted as immiscibility.

McLaughlin[24] demonstrated the difference resulting from various processing conditions on the dynamic mechanical behavior of PC/SAN blends. Complex modulus and loss tangent of the blends containing 40–80 wt % of PC in temperature range of 120–160°C differed for IM and CM.

Commercially supplied PC and two SAN (content of AN 5.5 and 30 wt %) were mixed at twin-screw extruder, and subsequently injection molded. The small shifts of blends T_g in comparison to T_g of pure components corresponded to a very small miscibility of SAN and PC.[25]

PC/ABS as well as PC/SAN prepared by solution casting and extrusion were studied through the whole composition range by Kim and Burns.[26] Morphology and T_g revealed that phase separation between the PC-rich and SAN-rich phases was more pronounced in the case of PC-rich compositions. Further, compatibility increased more in the regions of SAN-rich composition. From the specific heat increment, it was concluded that SAN dissolved more in PC-rich phase than PC in SAN-rich phase. The extrudate swell passed maximum in the middle of composition range, which was presented as behavior typical of incompatible blends.

The control of the phase structure created during processing is another assumption for successful tailoring of polymer blends, that is, development of materials with desirable performance.[27] Chaudhry et

al.[28] focused on relationship between processing conditions and morphology of 55PC/45ABS (23% of AN). Compounding was performed on the torque rheometer, under various mixing times, temperatures, and rotor speeds, followed by pressing of samples. Well-defined PC dispersed (PC domains were rather spherically shaped) in ABS phase was obtained for the short times (1 and 2 min) or for low temperature (230°C). Increase of mixing time (5, 7, 10 min) or temperature (250, 270°C) led to elongation of both the phases and to the formation of "quasi" cocontinuous morphology. In addition, morphology did not alter with mixing speed.

Influence of processing conditions, involving extrusion followed by injection or compression molding, on the microstructure was investigated for PC/SAN blends by McLaughlin.[24] CM samples provided spherical dispersion of the minor component; coarse, labyrinth phase cocontinuity of CM samples was obtained for 50 and 60 wt % of PC, whereas for IM samples, concentration range of PC was extended up to 80 wt %.

Morphology gradients through the thickness of injection molded commercial PC/ABS blends were investigated by Hamada et al.[29] Distribution of PC domains through sample thickness had hyperbolic character with maximum in the center. PC exhibited lamellar structure, which grew larger and became more irregular towards core, and was more oriented in the skin. The same attempt was used to characterize blends at 90/10 wt % PC/ABS in.[30] In the center of the plaque, the morphology appeared as isotropic (in parallel and perpendicular directions) with the ABS phase dispersed in the PC matrix as large (1 μm) rubber particles and smaller spherical (0.3 μm) SAN particles. About half the distance from the center to the edge, morphology of free SAN changed from predominantly spherical to mostly string-like. Solitary string-like domains (free SAN) and string-like domains connected to the large spherical particles (bead-and-string morphology created by ABS), oriented in the injection direction, were observed closer to the edge of samples. The gradient in phase morphology (through the thickness of plaque) was created by the competition between the relaxation rate of the bead-and-string structure and the cooling rate after mold filling. Near the center, relaxation (break up of bead-and-string structure) was proposed to occur due to interfacial-tension-driven break-up and end-pinching mechanisms.

A very comprehensive study through thickness of injection molded PC/ABS blends was done by Lee et al.[31] Generally, regardless of composition, the blends morphology at the edge and close to that was different from that in the middle part. PC-rich compositions (60–90 wt %) showed rubber particles (1 μm) connected to SAN strings (bead-and-string structure) oriented in the injection direction at the edges of the samples. With the increase of distance from the edge, SAN strings gradually underwent relaxation—broke up into a series of spherical SAN particles. For that reason, in the center, large rubber particles at higher ABS content interconnected irregularly shaped ABS domains, and smaller free SAN particles were randomly dispersed. Intermediate compositions, that is, 40 and 50 wt % of PC were characterized by either interconnected bead-and-string structure or stratified sheet-like morphology of ABS at the edge. In the center, the ABS phase appeared to be continuous with irregular elongated holes as well as circular holes created when PC was etched away. The ABS-rich blends had PC domains dispersed in the continuous ABS phase. The PC domains were elongated in the injection direction near the edge, and were spherical in the center of the plaque.

An improvement of the mechanical properties of polymer blends (specially increase of stiffness and strength), in the process of cost-rise absence, might be reached by reinforcement with short fibers. General trend is to use fast, continuous production processes, which mostly involve flow patterns leading to fiber orientation. During the processing, flow fields lead to arrangement of immiscible polymer blends through deformation and orientation of dispersed domains. Although the equilibrium dispersed phase morphology is spherical, shear and elongational flow fields can impart nonequilibrium structure such as dispersed fibrillar domains oriented along flow direction.[7,9,32] Rheological properties of these materials are of a key importance during processing.

In this article, viscoelastic properties of injection as well as compression molded PC/ABS blends and their composites with glass fiber in molten state will be measured, and the influence of various factors such as morphology and fiber orientation varying with processing conditions will be discussed.

EXPERIMENTAL

Materials and sample preparation

PC Iupilon S3000NF (Mitsubishi Engineering Plastics, Japan) and ABS TFX 170NP (Techno-Polymer, Japan) were used for preparing the polymer blends and composites. The internal composition of ABS evaluated from ^{1}H NMR spectra measured in solution reveals 28, 13, and 59 wt % of acrylonitrile, butadiene, and styrene, respectively.

The ABS contents in the prepared PC/ABS blends were 0, 20, 40, 60, 80, and 100 wt %. Blends are indicated by a two digits number, where the first one indicates the PC content and the second one
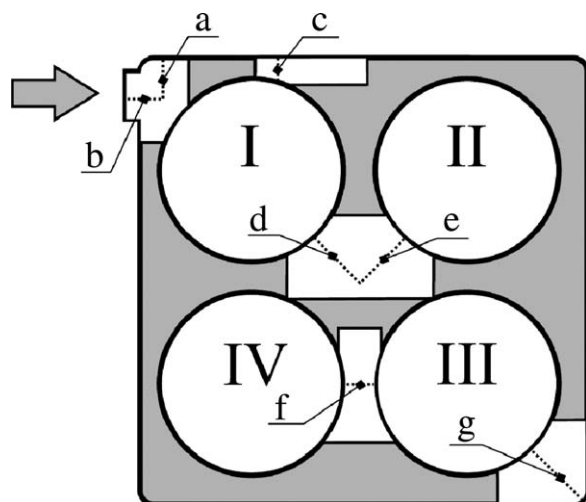
Figure 1 Schematic sketch of positions at IM samples. I–IV are specimens for rheological measurements. a–g denote places investigated with scanning electron microscope; dotted-lines show positions of the cutting surfaces. Arrow is pointing injection gate.

indicates the ABS content, for example, blend containing 20% PC and 80% ABS is denoted as blend 28. PC was dried at 130°C and ABS at 100°C for 5 h before dry-blending, which was followed by melt-mixing in a corotational twin screw extruder (TEX 30α, Japan Steel Works, diameter of screw was 32 mm) specially designed for fine compounding. The screw speed 90 rpm and temperatures in five zones of 250, 250, 240, 230, 220°C were set. Extrudates in the form of strings were cut into pellets, and dried at 100°C for 5 h before further processing by either compression molding (CM) or injection molding (IM). In the former case, temperature of 260°C and pressure of 9.8 MPa were used. In the latter, injection molding machine J55EL II, JSW with screw diameter of 25 mm was used for the preparation of testing samples for rheological measurements (shown in Fig. 1). The conditions were as followed: the cylinder temperatures were 260, 260, 250 and 240°C on the nozzle, front, middle, and rear zones, respectively. The temperature of mold cavity was kept at 80°C, injection rate of 50 mm/s and injection pressure of 138 MPa were used. In both cases, sheets with a thickness of 1 mm were produced, from which round specimens with a diameter of 25 mm for rheological measurements were cut.

As shown in our former works,[33,34] blend 64 followed log-additivity rule or exhibited positive deviations for storage and loss moduli irrespective from molecular weight of PC used. This blend was used as a matrix for series of composites prepared by incorporating glass fibers (GF) (diameter of 12 μm and initial length of 5 mm, 1150TEX, Nihon Sheet-Glass). Composites referred to as CMP1, CMP2,

and CMP3 contained 10, 22.2, and 31.6 wt % (corresponding to volume contents of 4.3, 11.3, 17.1%) fibers.

Measurements of rheological properties

Dynamic viscoelastic properties were determined with a rotational rheometer (Rheometric Dynamic Analyzer ARES) using a parallel-plate geometry (plate diameter 25 mm, gap between plates 1 mm) equipped with [RSI]Orchestrator[TM] software. Nitrogen atmosphere was used to eliminate degradation during measurements.

Strain sweep tests at the strain (γ_o) range of 0.01–100% for three angular frequencies (ω) 0.1, 1, and 10 rad/s were carried out to establish linear viscoelastic region. Test reveals independence of storage and loss moduli on the strains from 0.1 to 4%; strain 1% was selected as a representative value of linear viscoelastic region.

Measurements were carried out at 240°C and at angular frequencies in the range from 0.1 to 100 rad/s. In the case of compression-molded samples, temperatures 220 and 260°C were also considered to calculate the apparent activation energy of the materials.

Fiber content and fiber length distribution in the samples

The weight contents (Φ_f) of GF in the composites were determined gravimetrically after matrix incinerating. Glass fiber volume content (V_f) was calculated from the densities of the components. To examine the fiber length distribution, incineration residue was separated into filaments and spread on a glass plate from which photomicrographs were taken. Based on these photomicrographs, the length of approximately 800 filaments was measured, and the number (I_N) and weight (I_W) average fiber lengths in the specimens were computed.

Scanning electron microscopy observation

The influence of processing methods (compression and injection molding) on the structural arrangement was studied with scanning electron microscopy (SEM) on blends 64 (IM and CM) and 46 (IM).

Specimen surfaces were achieved by cutting the samples with an ultramicrotone (Ultratome ® III 8800, LKB—products AB, Sweden) followed by etching. The etching liquid used was prepared from 0.35 g of grinded potassium permanganate dissolved in a mixture of 10 mL of sulfuric acid and 10 mL of phosphoric acid. Samples were etched for 20 (or 40) s, and then the etching liquid was washed with water for 60 min.

TABLE I
Composition and Fibers Length Distribution in the Composites Prepared by Injection (IM)
and Compression (CM) Molding

Code		Weight fraction of fibers Φ_f (%)	Volume fraction of fibers V_f (%)	Number-average of fiber length I_N (μm)	Weight-average of fiber length I_W (μm)	Polydispersity index I_W/I_N	Aspect ratio
CMP1	IM	10.0	4.7	538	621	1.16	44.8
CMP2		22.2	11.3	595	689	1.16	49.6
CMP3		31.6	17.1	475	556	1.17	39.6
CMP1	CM	10.0	4.7	478	555	1.16	39.8
CMP2		22.2	11.3	447	514	1.15	37.2
CMP3		31.6	17.1	357	397	1.11	29.8

After the above treatment, samples were coated with a thin platinum (Sputter coater BAL-TEC SCD 050) film and examined in a scanning electron microscope Vega TS 5130 (Tescan, Czech Republic).

Cutting surfaces of IM samples from several positions of the sheets were denoted as A, B, C, D, E, F, and G. The schematic sketch (Fig. 1) shows the location of these cutting surfaces (A–G) in the sample, and their orientation to the injection gate indicated with a bold arrow. Compression molded sheets were examined at two positions, both placed in the middle of the sheet. The investigated cutting surfaces were perpendicular to each other.

RESULTS AND DISCUSSION

Fiber content and fiber length distribution

Although the average fiber lengths (I_N and I_W) of the CM samples are smaller than IM samples (Table I), crucial factor to compare the two preparation methods is the distribution of fiber lengths (Fig. 2). The distribution of fiber lengths for IM samples is wider than for CM ones. This trend becomes even more pronounced with the increased fiber content.
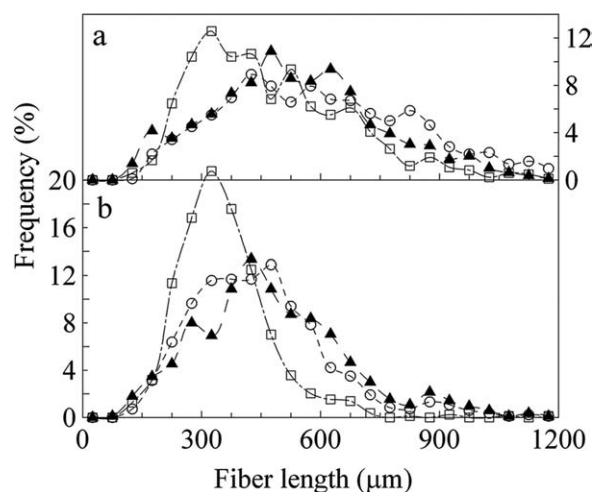
Figure 2 Fiber length distribution of glass fiber filled blend 64 (▲ CMP1, ○ CMP2, □ CMP3) prepared by (a) IM and (b) CM.

During injection molding, the fibers tend to orient in flow direction, and, therefore, the long fibers fraction are not as reduced as during compression molding. Distribution of fiber lengths for CM samples seems to be dependent on the fiber content; it becomes narrower with the increase of fiber content. This tendency is not observed for IM samples.

As reported by Kannan et al.,[35] the breakage of fibers occurs mainly during the compounding, followed by a minor consequent reduction during further processing. This is due to the resulting friction as the fibers are introduced to the solid polymer in the extruder, and it is, therefore, presumed that most of the fiber breakage occurs in the melting zone of the extruder. In the mentioned work,[35] the decrease in I_N with fiber content was explained by an increase in the frictional forces due to fiber–fiber contact resulting in greater fiber breakage. For PP/GF composites,[36] it was observed that polydispersity index increased from 1 to 1.7 for 20 wt % loading, and with rising of shear rate to nearly 10^4 s^{-1}, it raised to 2. Breakage of fibers was found to be independent of the die length, occurring mainly in the barrel.

Viscoelastic properties of PC/ABS blends and PC/ABS fiber filled composites

Viscoelastic properties (storage, G' and loss, G'' moduli) of injection molded PC/ABS blends and pure PC and ABS as a function of angular frequencies are shown in Figure 3 (storage modulus of CM blend 46 is incorporated as well).

Pure PC and blend 82 exhibited, over the whole measured frequency range, higher loss than storage modulus values. This difference in moduli at low angular frequencies is almost one decade, and becomes reduced with increasing ω. Blends 64 and 46 at low ω reveal higher storage than loss modulus, whereas at high ω they behave more viscous. The inflection point is in the first case 0.2 and in the second case 1 rad/s. For the remaining blends and pure ABS, two inflection points were observed.
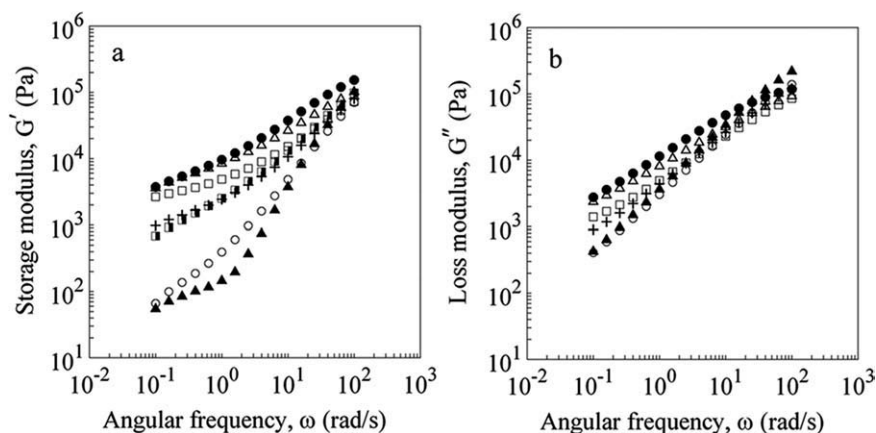
Figure 3 (a) Storage and (b) loss moduli as functions of angular frequency for pure materials (▲ PC, ● ABS) and PC/ABS blends (○ blend 82, + blend 64, □ blend 46, △ blend 28) prepared by IM and blend 46 (◧) by CM.

The effect of the processing route on G' and G'' is evident only at the low frequency region (Fig. 4), where the structure rising from the processing still remain unchanged upon shearing. Blend 46 seems to be affected the most; its G' of CM (included also in Fig. 3) was found to be 2/3 of decade smaller than G' of IM at low angular frequencies.

In most cases (Fig. 4), G' and G'' seemed to follow "log-additivity rule." The most pronounced positive deviations were observed at 0.1 and 1 rad/s for the storage modulus of the blends 46 and 64.

To emphasize the influence of glass fiber content on the viscoelastic properties of composites, the relative storage moduli $G'_r = G'_{composite}/G'_{matrix}$, and loss moduli, analogously, were calculated. Incorporation of GF influences the viscoelastic properties, specially at the lowest angular frequency 0.1 rad/s (Fig. 5), where all the composites (CMP1, CMP2, and CMP3) exhibit storage modulus higher than loss. At 1 rad/s, the loss modulus of CMP1 was higher than the storage modulus, whereas values of both moduli of CMP2 and CMP3 were almost equivalent. For angular frequencies of 10 and 100 rad/s, a predominant

viscous behavior for all composites was observed, that is, similarly to matrix. Thus, it seems that an increase in angular frequency alters the viscoelastic character of all the composites.

On the opposite to blends (see Fig. 4), composites alter with the way of their preparation significantly. Both moduli at all measured angular frequencies were for all IM composites higher than for CM composites. The most pronounced differences were detected at the lowest angular frequency (0.1 rad/s). The reinforcement build-up led to an increase in relative moduli, and further enlarged the differences between IM and CM samples. These results may be due to the difference of fiber orientation between IM and CM composites as will be shown in the following section.

In Figure 6, the influence of positions on viscoelastic properties in IM samples depicted in Figure 1 is shown. Almost no differences in moduli between positions II and IV were obtained for blend 64 and CMP1, whereas for CMP2, it shows deviations, even more pronounced in case CMP3. Thus, the sample position becomes more important as fiber content increases.
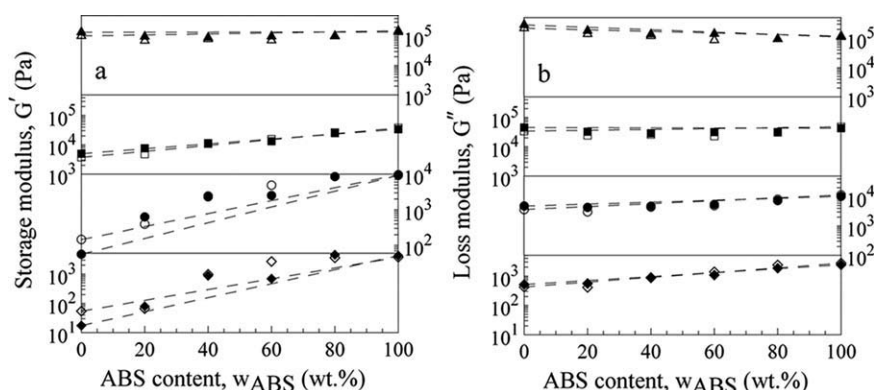
Figure 4 (a) Storage and (b) loss moduli as functions of ABS content for PC/ABS blends prepared by IM (open symbols) and CM (solid symbols) at various angular frequencies (rad/s): 0.1 (◇◆); 1 (●○); 10 (□■); 100 (△▲).
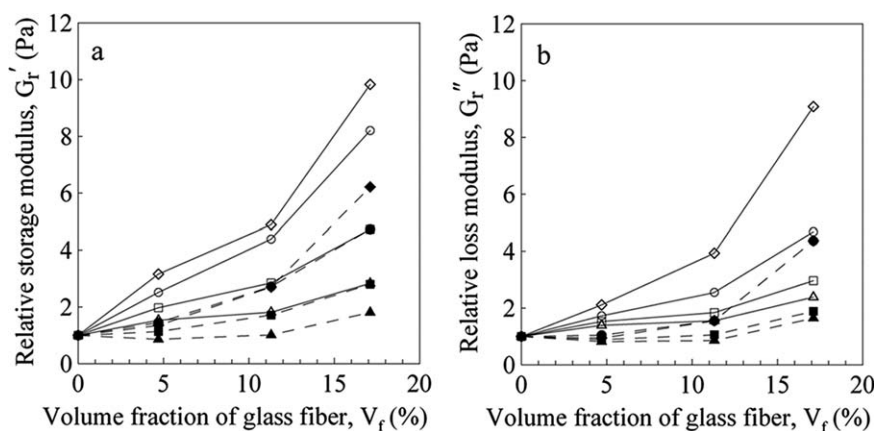
Figure 5 (a) Relative storage and (b) loss moduli as functions of glass fiber content for IM (open symbols) and CM (solid symbols) glass fiber filled blend 64 at various angular frequencies (rad/s): 0.1 ($\diamond\blacklozenge$); 1 ($\bullet\circ$); 10 ($\square\blacksquare$); 100 ($\triangle\blacktriangle$).

Temperature dependence of viscoelastic properties

Storage and loss moduli, measured for compression molded samples at three temperatures (220, 240, and 260°C), were plotted versus $1/T$, and from the slopes, the apparent activation energies (A_1 for storage and A_2 for loss modulus) were calculated (Table II).

Our measurements reveal that PC is higher temperature sensitive than ABS. In accordance, the temperature sensitivity of blends decreases with ABS content. Only blends 46 and 64, which are considered as compositions showing the most pronounced positive deviations from log-additivity rule, are exceptions, having almost the same A_1 and A_2 values. This is in agreement with work by Babbar et al.[17] suggesting that the cause of activation energy might be explained on the basis of miscibility of components in the blend. The ABS-rich blends had better interphase miscibility, and thus were less sensitive to temperature (210–230°C). On the opposite, Dobrescu et al.[37] reported from capillary measurements in the range of 240–260°C that pure PC is the lowest, pure ABS the intermediate, and the blend containing 60% of ABS is the highest sensitive to temperature.

From the determined activation energies, the thermal stability of the PC/ABS blends might be viewed. The blends where ABS phase forms the matrix can be assumed as having more stable morphology in comparison to the blends, where matrix is created by PC, which was found to have the most pronounced temperature sensitivity, and, therefore, their morphology is less stable.

In our work, incorporation of 10 wt % of glass fiber almost unaffected the sensitivity of the matrix, whereas for CMP2 (about 20 wt %), different behavior was observed. A sudden drop of apparent activation energy (more pronounced at lower angular frequency 0.398 rad/s) was detected. In general, loss modulus was found to be more sensitive to temperature changes than storage, contrary to work,[38] where polypropylene filled with 20% of glass fiber had the same temperature sensitivity for η' and G'.
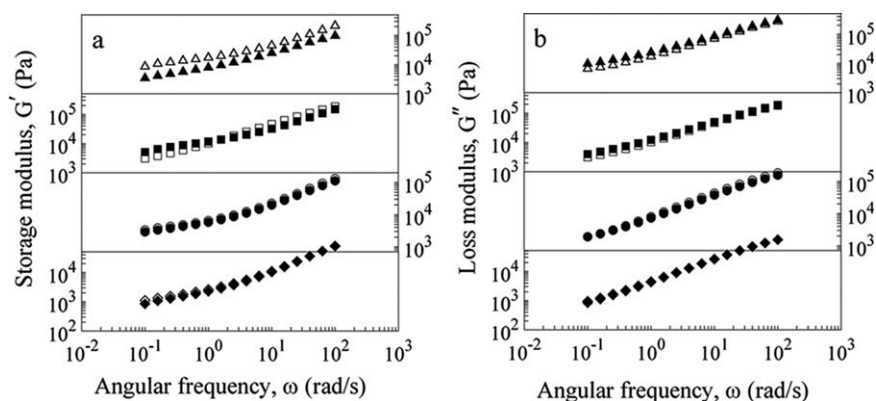
Figure 6 Comparison of (a) storage and (b) loss moduli at position II (open symbols) and IV (solid symbols) of IM samples for GF filled blend 64 as a function of angular frequency at various GF volume contents (%): 0 ($\diamond\blacklozenge$); 4.3 ($\bullet\circ$); 11.3 ($\square\blacksquare$); 17.1 ($\triangle\blacktriangle$).

TABLE II
Apparent Activation Energies of CM Samples Calculated from the Slopes of Storage (A_1)
and Loss (A_2) Moduli vs. $1/T$ plots

(1 kJ = 0.239 kcal)	Apparent activation energy A_1 (kJ/mol)			Apparent activation energy A_2 (kJ/mol)		
Angular frequency (rad/s)	0.398	3.98	39.8	0.398	3.98	39.8
PC	–	84.5	85.1	58.6	60.9	48.9
Blend 82	28.4	52.4	59.2	47.3	49.2	41.2
Blend 64	15.7	34.2	43.7	36.9	39.7	32.6
Blend 46	19.1	34.7	44.9	36.0	41.2	35.3
Blend 28	5.7	18.8	26.9	24.8	28.3	23.0
ABS	4.9	16.9	18.8	20.9	19.9	9.8
CMP1	12.8	32.9	44.0	36.1	40.2	33.7
CMP2	8.9	26.4	39.2	31.2	37.2	33.9
CMP3	14.8	29.3	43.3	34.9	40.4	38.5

Scanning electron microscopy observation

PC and butadiene were removed by etching leaving acrylonitrile and styrene appearing as brighter regions in the photomicrographs (small dark voids in bright acrylonitrile-styrene regions come from butadiene).

Figure 7 depicts SEM of IM blend 64 in the positions A and B close to the injection gate and D and E in the middle of the sample. In Figure 7(a), the narrow dimensions of dark particles are seen, whereas in Figure 7(b), their elongated dimensions are observed (cutting surfaces in these pictures are perpendicular to each other). This draw clears the evidence of oriented structure in the flow direction close to the injection gate. SEM demonstrated in the Fig. 7(c,d) with cutting surfaces perpendicular to each other show the particles with similar shape, giving evidence of structure just slightly oriented with flow.

The SEM pictures of two inverse compositions are showed in Figure 8, where in the left column cutting surfaces of blend 64, and in the right one of blend 46 are placed, demonstrating morphology in the positions C, F, G, and F (see Fig. 1). The phase mor-

phologies of the blends 64 and 46 have very similar cocontinuous character. In the places where—due to a minor influence of flow—the phase separation can occur, dissimilarity of the phase morphologies was detected to a small extent; see Figure 8(c) and (g), where the etched phase (PC) seems to form major and minor phase, respectively.

In case of the compression molded blend 64 (Fig. 9), large irregularly shaped ABS domains are present. In this case, the formation of the PC matrix is clearly evident in comparison to cocontinuous phase morphology of IM samples. Even though the determination of the exact domain size was not calculated, comparison of IM [Fig. 8(d,h)] and CM (Fig. 9) photomicrographs in the same scales gives the clear evidence that the dispersed domains at CM samples are several times larger than the domains in the IM samples at the investigated positions.

The size and the shape of the dispersed phase domains are varying with the processing method. Moreover, the position in the sample is important in the case of injection moulding samples.

Investigation of morphology through the samples is not included in our work. Nevertheless, skin-core
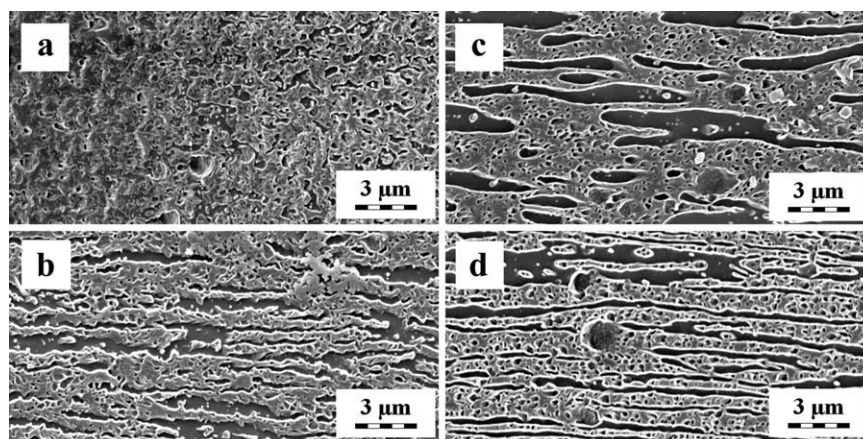
Figure 7 SEM of IM blend 64 taken close to the injection gate (a), (b), and from the middle of the sample (c), (d), corresponding to the positions A, B, D, and E depicted in Figure 1.
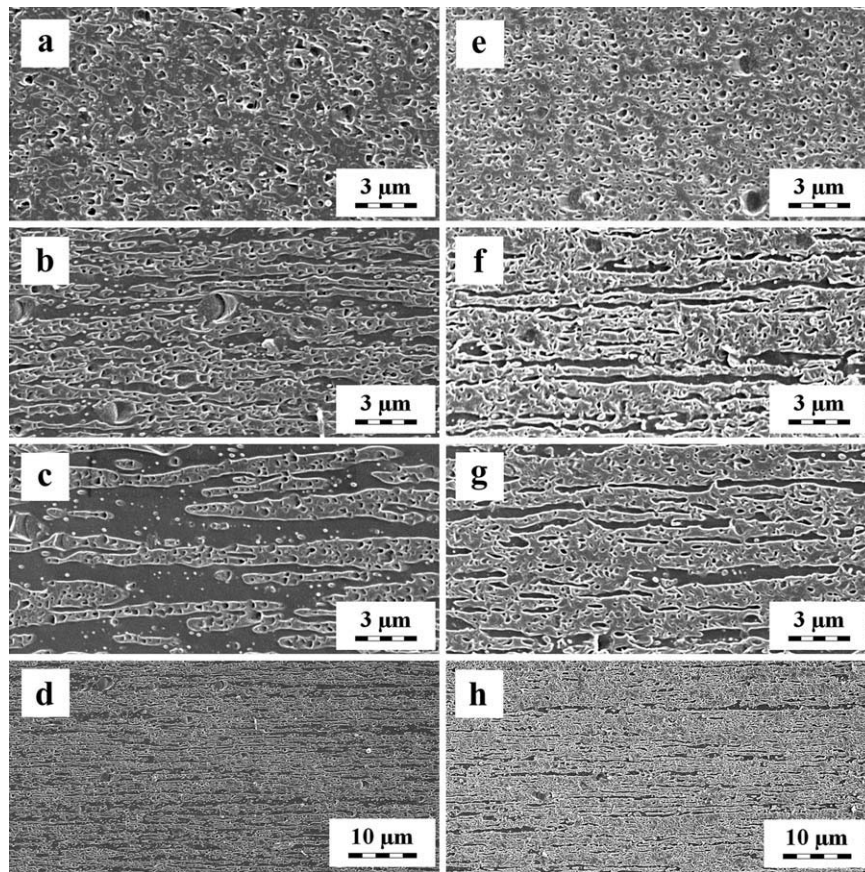
Figure 8 SEM taken from the positions C, F, G, and F from Figure 1 for blend 64 (a), (b), (c), and (d) and blend 46 (e), (f), (g), and (h).
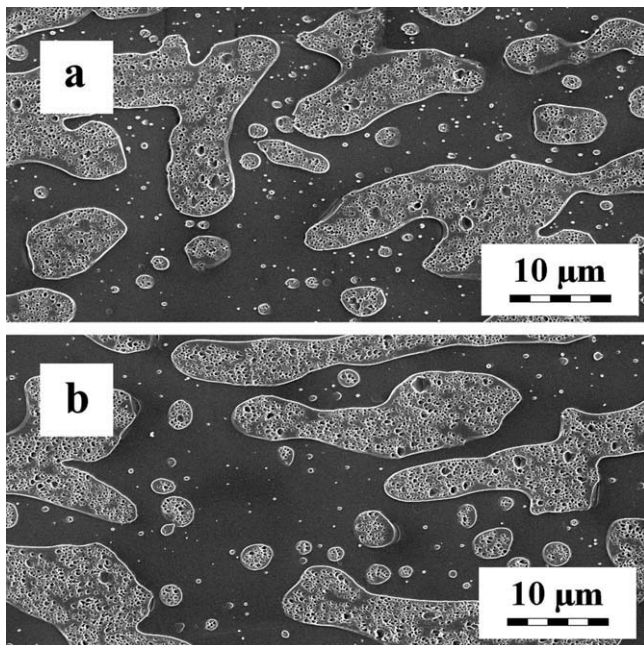
Figure 9 SEM of blend 64 taken from the middle of the CM sample (the cutting surfaces are perpendicular to each another).

structure with the highest distribution of PC on the core was reported for IM samples by Hamada and Tsunasawa.[39] SEM micrographs of the IM and CM samples of the blend 64 with 10% of glass fiber incorporation are depicted in the Figure 10. Fibers close to the injection gate (a) are rather oriented in the flow direction, whereas fibers located on the positions with minor influence of the flow (b,c) are oriented randomly. It should be stressed that fibers in the IM samples are three dimensionally randomly oriented. The zones close to the injection gate and the narrow layer close to the surface [top of Fig. 10(c)] are exceptions. In case of the CM sample (d), the fibers are more or less oriented in the plane direction.

CONCLUSIONS

Processing methods of the PC/ABS blends and PC/ABS/GF composites were compared via rheological and morphological observations. The obtained results can be summarized as follows.

Blends: processing route altered microscopical structure, and only slightly also linear viscoelastic

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