

Study of the Viscoelastic Properties of PC/ABS Blend Containing Triphenyl Phosphate and Nanoclay and Its Correlation with Morphology

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ABSTRACT: In this study, the effect of triphenyl phosphate (TPP), commonly used as flame retardant, also montmorillonite nanoclay and hybrid of them, on the morphology and rheological characteristic of PC/ABS (Polycarbonate/Acrylonitrile-butadiene-Styrene) blends are investigated. The blends were prepared via a direct melt blending process in a twin-screw extruder. Morphological properties were characterized by scanning electron microscopy, X-ray diffraction, and transmission electron microscopy. The results for the variations of complex viscosity (η^*) with angular frequency (ω) showed a good agreement with those obtained from Carreau model. A plateau mod-

ulus (G_N^*) was observed in the blends containing nanoclay, indicating the formation of a network structure that increases the modulus as the results of the intercalation of silicate layers of nanoclay. The complex viscosity is increased with the inclusion of nanoclay and TPP, but the effect is more evident with nanoclay. Also, the addition of nanoclay significantly enhances the non-Newtonian behavior of PC/ABS blends, particularly at low-frequencies. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1796–1804, 2010

Key words: nanocomposite; PC/ABS alloy; rheological properties; triphenyl phosphate; viscosity

INTRODUCTION

Polycarbonate (PC) is commonly used as a high-performance amorphous engineering thermoplastic, because of its distinct properties such as high-impact strength, transparency, heat resistance and dimensional stability, excellent electrical properties, colorability, high-gloss, flame retardancy, and high-heat distortion temperature (HDT). However, it is notch sensitive and also difficult to process, because of its high-melt viscosity hinders the fluidity and the residual stress resulting from the process could cause fractures. To improve these, efforts have been made to develop polymer blends and alloys.¹

Acrylonitrile-butadiene-styrene (ABS) copolymer is the most popular rubber-toughened thermoplastic with several advantages, such as low-cost, good processability, and low-notch sensitivity, however, it suffers from a relatively low-mechanical properties.¹ To overcome the problems with the mechanical properties and also HDT, it is common to blend ABS with other high-performance engineering plastics such as

PC. As ABS has a T_g about 95°C, addition of PC enhances the mechanical performance, whereas improving HDT.^{1–3} The desired mechanical properties and HDT can be achieved by changing PC/ABS ratio.

Thermoplastics including PC/ABS blends are easily combustible, and however have several applications in electronics, electrical, and car industries where the plastic parts used must have a low-flammability. Therefore, flame retardants (FRs) are added to reduce the probability of burning in the initial phase of the fire.¹ To achieve an optimum level of fire retardancy, a large amount of nonhalogenated types, needs to be used in the formulation. However, the addition of large amounts of FRs could decrease the mechanical properties of resin^{4,5} and also affects its rheological behavior.¹

In parallel, nanocomposites have attached considerable interest by the FR polymer community since 1997, because of their improved fire properties.⁶ It has been suggested that, the presence of clay in a polymer can enhance the char formation providing a transient protective barrier and hence slowing down the degradation of the matrix.⁷

However, when polymer-layered silicate nanocomposites were evaluated by other testing methods using limited oxygen index and the vertical burning test (UL-94), do not perform better than the polymer

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TABLE I
Compositions of Formulations

Compound	PC (wt %)	ABS (wt %)	TPP (wt %)	Nanoclay (wt %)
PC/ABS	65	35	–	–
PC/ABS/2% nano	63.7	34.3	–	2
PC/ABS/4% nano	62.4	33.6	–	4
PC/ABS/6% nano	61.1	32.9	–	6
PC/ABS/10%TPP	58.5	31.5	10	–
PC/ABS/13%TPP	56.55	30.45	13	–
PC/ABS/15%TPP	55.25	29.75	15	–
PC/ABS/2%nano/8%TPP	58.5	31.5	8	2
PC/ABS/2%nano/10%TPP	57.2	30.8	10	2
PC/ABS/2%nano/12%TPP	55.9	30.1	12	2
PC/ABS/4%nano/10%TPP	55.9	30.1	10	4
PC/ABS/6%nano/10%TPP	54.6	29.4	12	6

without nanoclay.⁸ Because of the aforementioned drawbacks in the application of conventional FRs and nanoclay individually, researches have been focused on their simultaneous use as FR systems.^{8,9}

The objective of this research is to investigate the effect of the presence of TPP and nanoclay on the morphology and rheological properties of PC/ABS alloys. For this purpose, the variations of storage modulus (G'), η^* , and $\tan \delta$ with ω for various blend systems are studied. The rheological behavior of the blends are then interpreted according to Carreau model.¹⁰ In addition to PC, ABS, and PC/ABS systems, the blends containing TPP, nanoclay, and also TPP/nanoclay hybrid are used for this investigation.

EXPERIMENTAL

Materials and methods

PC (Makrolon 2858 of Bayer Company, Germany) with density of 1.2 g/cm³ and MFI of 10 g/10 min (at 300°C, 1.2 kg), and ABS (SD0150, Acrylonitrile 27%, Tabriz Petrochemical Company, TPC, Iran) with density of 1.04 g/cm³ and MFI of 1.8 g/10 min (at 230°C, 3.8 kg) were supplied as pellets. Halogen-free FR used in this research was additive-type Triphenyl Phosphates (TPP), Merck (Germany), with 9.5% phosphorus content. Nanolin DK2, a modified organoclay (methyl tallow bis-(2-hydroxyethyl) alkyl quaternary ammonium salt as modifier) with a cation exchange capacity of 110–120 meq/100 g was obtained from Zheging Fenghong Clay Chemicals of China.

Compounding procedure

All ingredients (PC, ABS, TPP, and nanoclay) in a predetermined weight percentage were mixed in dry state in tumbler. The formulations were prepared via melt mixing in a modular co-rotating twin-screw extruder, manufactured by Brabander (Germany), with temperature profile of 200 to 250°C from the

hopper to die, L/D = 40 and rpm = 300. The PC/ABS ratio was kept constant at 65/35 wt % (weight percent) in all formulations. The composition of the formulations are given in Table I.

Characterization

Morphology

The dispersion state of the silicate layers of nanoclay in PC/ABS alloy was evaluated by X-ray diffractometry (XRD) and transmission electron microscopy (TEM). XRD experiments were performed at room temperature on a Siemens D5000, D/max – rA X-ray diffractometer (30 KV, 10 mA) with Cu-K α ($\lambda = 1.54178 \text{ \AA}$) irradiation scanning at a rate of 2°/min in the range of 1.5–10°. TEM specimens were prepared at room temperature using an ultra microtome with a diamond knife. TEM images were obtained by Philips EM208S model (with an acceleration voltage of 100 kV). The morphology of the PC/ABS blend was examined in a scanning electron microscope (SEM; VEGA\ \ TESCAN). The sample was cryo-fractured in liquid nitrogen. Then acid etching was done to remove ABS phase. The detailed etching procedure is reported elsewhere.¹¹ The fractured surface was coated with a thin layer of gold before SEM examination.

Rheology

The dynamic oscillation rheological behavior of samples were measured in linear viscoelastic range of deformation using a MCR-300, Anton Paar (Germany). Rheometer at 230°C. Experiments were carried out with a 25 mm diameter disk and the gap distance was 1.5 mm. The linear viscoelastic range of deformations were characterized by strain sweep test at the frequency of 10 rad/sec. The response of the melt to the applied oscillatory deformation was evaluated in the frequency range of 0.01–100 rad/sec, at strain amplitude of 1%.

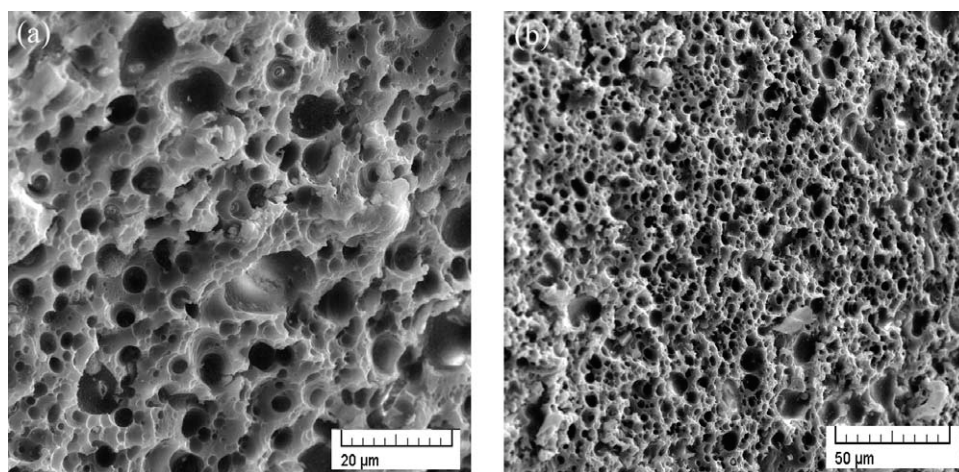


Figure 1 SEM fractographs of PC/ABS blend showing the dispersion of ABS spherical particles in the matrix of PC resin (a) 2000 (b) 800.

RESULTS AND DISCUSSION

Morphological characterization

The dispersion of ABS spherical particles in the matrix of PC resin reveals an emulsion type morphology for PC/ABS blend (Fig. 1), which is proved by the yield stress phenomenon observed in rheological study of the melts. The droplets of minor phase (ABS) dispersed in continuous major phase (PC) can visibly be seen in SEM images in Figure 1 as an emulsion type morphology.

Figure 2 shows the XRD patterns of nanoclay and nanoclay-contained formulations. Also, the results for 2θ and d -spacing values are summarized in Table II. The peaks correspond to the (001) plane reflections of the clays. The average basal spacing of nanoclay increases from 2.29 to 2.82 in mix with PC/ABS blend. The increased d -spacing suggests that the polymer chains intercalated into the gallery

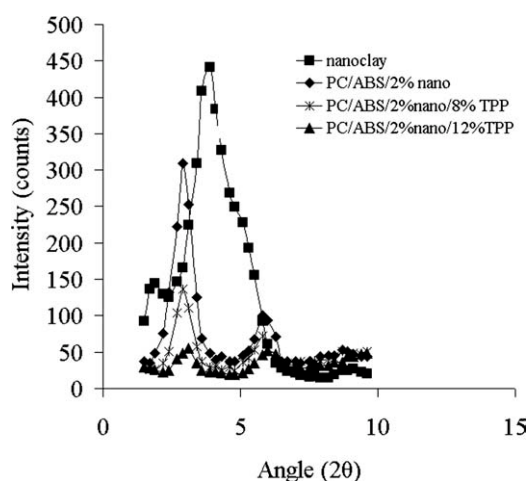


Figure 2 XRD patterns for nanoclay and nanoclay-contained formulations.

of nanoclay and increased the distance between the nanoclay layers.

From the analysis of XRD patterns, the peak corresponds to the reflections angle of d_{001} plane of the clay is appeared at $2\theta = 3.8$, for the nanoclay. This peak is shifted from 3.8 to 3.1 in PC/ABS/2% nano composites, which is the evidence for prevalent intercalation effects. Also, with the increase of TPP content the space between the layer of tactoids of nanoclay is increased, as the clay materials are intercalated with TPP.¹² The average basal spacing of the silicate layers (Table II) has increased from 2.29 in organoclay to 2.82 nm in the PC/ABS/2% nano composite. The increased basal spacing suggests that the polymer chains have intercalated the gallery of organoclay.

As it is evident, the first peak of nanocomposites (related to organoclay) are all shifted to the lower diffraction angles, indicating the prevalent intercalation effects.¹³ The secondary reflection at higher diffraction angles occurs in all the nanocomposites. This can be explained by the surfactant degradation caused by the high-temperature of processing.¹³

Figure 3 shows the TEM image of PC/ABS/2% nano. From the figure, the intercalation of silicate layers are evident, which confirms the XRD results and also interpret the plateau region found in G' - ω curves for nano-filled formulations [Figs. 6(b)7(b)].

TABLE II
XRD Parameters for Nanoclay-Contained Formulations

Compound	d -value (nm)	Angle (2θ)
Nanoclay	2.29	3.85
PC/ABS/2% nano	2.82	3.1
PC/ABS/8% TPP/2% nano	2.90	3.0
PC/ABS/12% TPP/2% nano	2.96	2.9

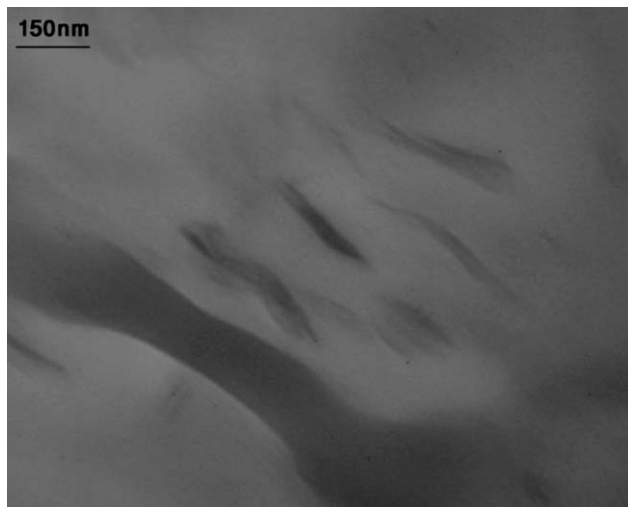


Figure 3 TEM image of PC/ABS/2% nano.

Rheological behaviors

The rheological measurements can be used as a mean to evaluate the flow behavior of polymers and for characterizing the polymer-polymer and polymer-filler interaction in polymer blends and composites. Linear viscoelastic properties of materials are sensitive to the structural changes.¹⁴ In polymer

melts the rheological behavior is affected by the molecular weight and architecture of the polymer.¹⁵ Also, the addition of additives that may be added for various purposes influences the rheological properties. In this section, the effect of TPP, nanoclay and their hybrids on the rheological behavior of PC/ABS blend are investigated.

The correlation of rheological behavior with morphology of PC, ABS, and PC/ABS Resins

In Figure 4, the variations of complex viscosity (η^*), storage modulus (G') and $\tan \delta$ vs frequency for PC, ABS, and PC/ABS blend are shown.

The viscosity curve of PC resin, shows a Newtonian plateau (η_0) at low-range of frequencies, which is about 6,850 Pa s. The general behavior of $\eta^*-\omega$ of ABS resin is different from that of PC, and no Newtonian plateau is observed at low-range of frequencies. Also, it shows a yield behavior that can be correlated to the dispersion of polybutadiene particles in SAN phase that affects the molecular mobility in ABS resin. The presence of yield stress, which must be exceeded for flow to occur, has been indicated as a common characteristic for suspensions, emulsions, and gels.¹⁶ The complex viscosity curve of PC/ABS

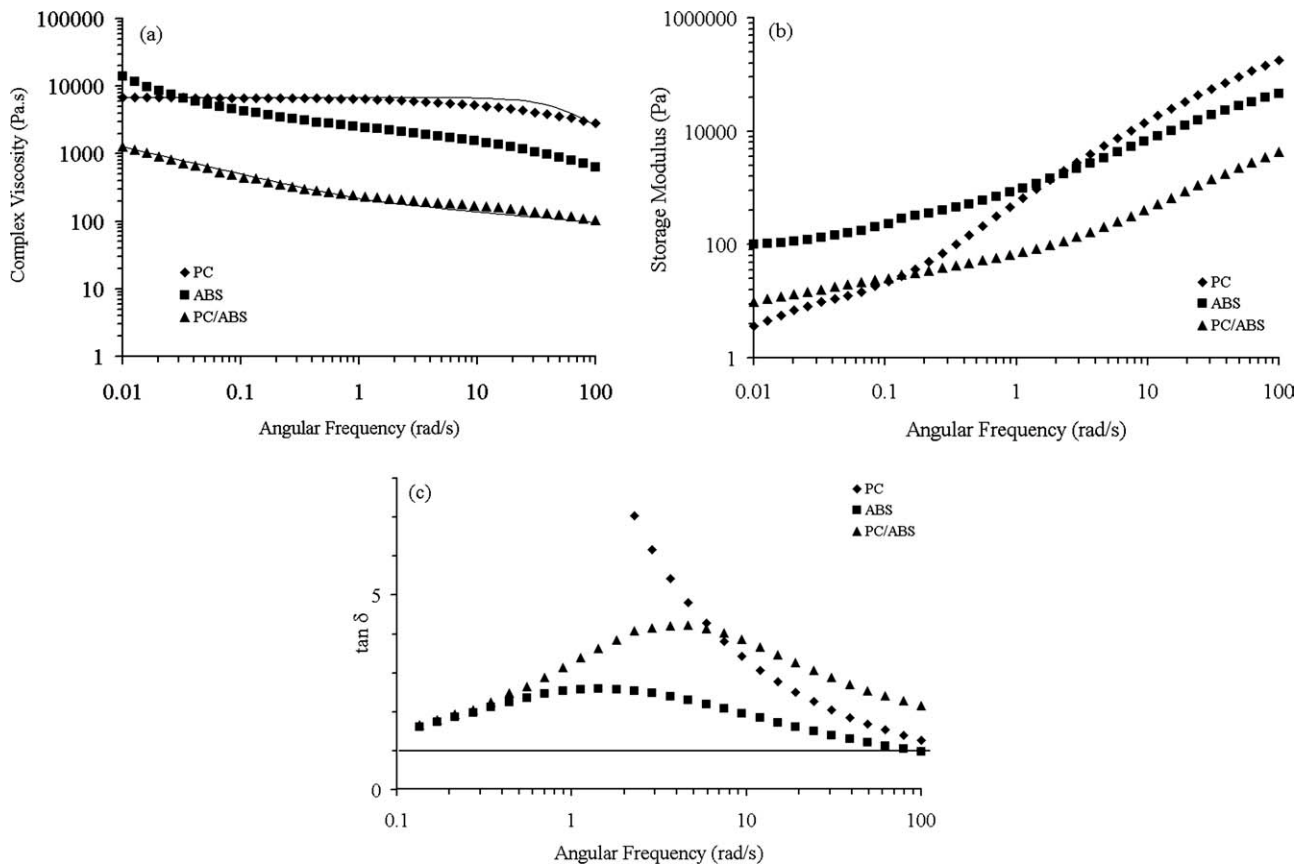


Figure 4 Variations of complex viscosity (a) storage modulus (b) and $\tan \delta$ (c) with frequency at 230°C for PC, ABS, and PC/ABS blend (In $\eta^*-\omega$ curves, those plotted based on Carreau model are distinguished with a solid line).

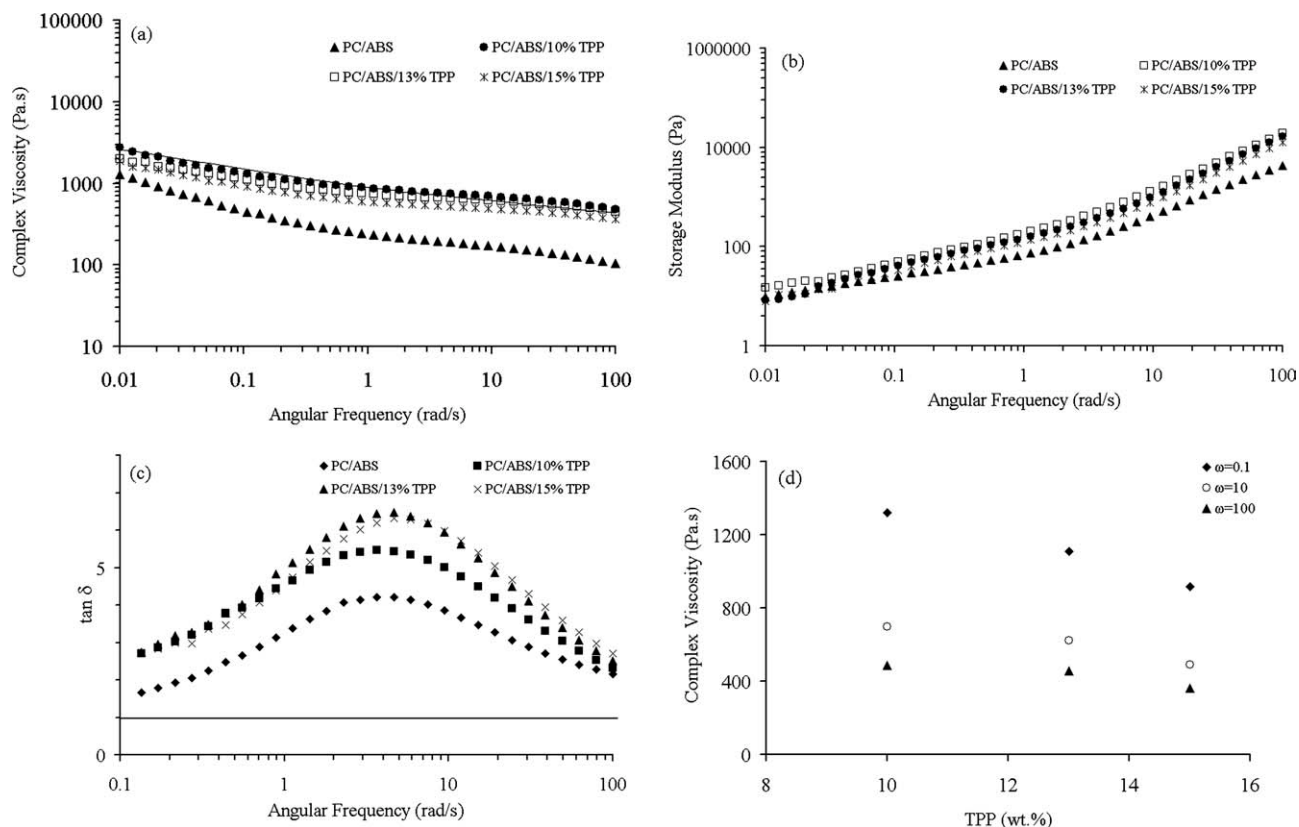


Figure 5 Variations of complex viscosity: (a) storage modulus, (b) $\tan \delta$, (c) with frequency for PC/ABS/TPP blends at various TPP contents, and (d) complex viscosity with TPP content at three different frequencies 0.1, 10, 100 s^{-1} , at 230°C (In $\eta^*-\omega$ curves, those plotted based on Carreau model are distinguished with a solid line).

blend shows yield behavior in low-range of frequencies, with values lower than PC and ABS resins [Fig. 4(a)]. This reveals the negative deviation behavior (NDB) in the viscosity of PC/ABS blend from log-additivity rule. The log-additivity rule, based on shear viscosity, can be used as a method for the evaluation of the miscibility of the blends.^{17,18} It is expected that, the miscible blends exhibit a linear relation if the blend components do not interact specifically.¹⁸ The NDB can be attributed to the flow, because of interlayer slip.¹⁹ A possible reason for the decrease of viscosity with the addition of ABS may be the solvation of the highly entangled structure of PC molecules by the ABS phase.¹⁵ The shear thinning viscosity behavior of ABS carries over to the blends, and the Newtonian plateau of PC resin is obliterated by blending with ABS resin and yield behavior appeared as is expected for emulsions.¹⁶ Figures 4(b,c) show the variations of storage modulus and $\tan \delta$ with frequency, for PC, ABS and PC/ABS blend, respectively. Neat PC appears to have different behavior to ABS and PC/ABS resin. The $\tan \delta$ of PC resin sharply decrease by increasing frequency. At low-rate of applied deformation most of the stress dissipate through molecular movement. By increasing the frequency the bigger molecules have not enough time to relax, and the elasticity of

melt increase and $\tan \delta$ of PC decrease at high-range of frequency. The $\tan \delta-\omega$ curve of ABS and PC/ABS blend is different from PC resin specially at low-frequencies. The elasticity of the melt of ABS and PC/ABS resin is higher than PC resin, which is due to the emulsion type morphology in both of these resins. The interaction between polybutadiene particles and SAN phase in ABS resin, and also the interaction between ABS droplets and PC in PC/ABS blend restrict the molecular mobility at low-frequencies and leads to increased melt elasticity. The $\tan \delta$ of PC/ABS blend is higher than PC and ABS resins in medium and high-range of frequencies. This is an evidence of lower melt elasticity and shows the NDB from log-additivity rule, as was mentioned earlier.

Effect of TPP on the rheological behavior of PC/ABS/TPP blends

The effect of TPP on the $\eta^*-\omega$ behavior, storage modulus (G'), and $\tan \delta$ of PC/ABS blend are shown in Figure 5. Moreover, the variations of η^* with TPP content at three different frequencies (i.e. 0.1, 10, 100 s^{-1}) is shown in this figure.

The $\eta^*-\omega$ curves of the blends containing TPP show a similar behavior and are almost parallel to each other and the viscosity decreases with

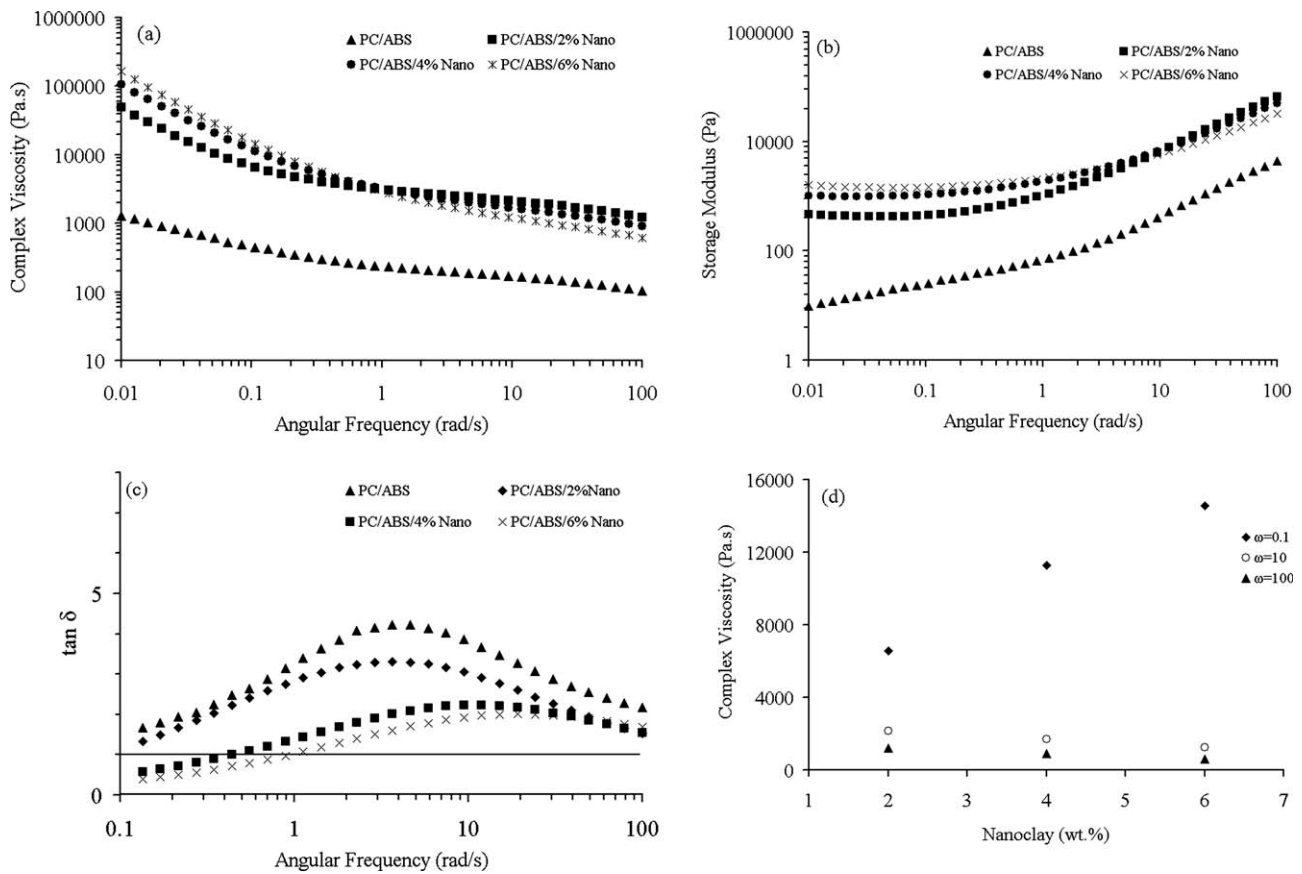


Figure 6 Variations of complex viscosity: (a) storage modulus, (b) $\tan \delta$, (c) with frequency for PC/ABS/nanoclay blends at various nanoclay contents, and (d) complex viscosity with nanoclay content at three different frequencies, 0.1, 10, 100 s^{-1} , at 230°C.

increasing TPP wt % [Fig. 5(a)]. At low-frequencies, the slope of the curves is significantly decreased, compared with PC/ABS blend. The storage modulus slightly decreases with increasing TPP content, however, it is still higher than that of PC/ABS blend [Fig. 5(b)]. With increasing TPP content the melt elasticity of PC/ABS blend is decreased, as shown in Figure 5(c). Also, at low-frequency, the yield stress is decreased [Fig. 5(d), $\omega = 0.1 s^{-1}$] and at medium and high-frequencies the shear thinning behavior is reduced [Fig. 5(d), $\omega = 10$ and $100 s^{-1}$]. TPP is a type of plasticizer²⁰ and decrease complex viscosity and storage modulus.

Effect of nanoclay on the rheological behavior of PC/ABS/nanoclay blends

The effect of nanoclay on the $\eta^*-\omega$ behavior, storage modulus (G'), and $\tan \delta$ of PC/ABS blend are shown in Figure 6. Also, changes of η^* with nanoclay content at three different frequencies (i.e. 0.1, 10, 100 s^{-1}) is illustrated in this figure.

Two different behaviors in the $\eta^*-\omega$ curves of the blends at low- and high-frequencies can be observed [Fig. 6(a)]. At low-frequencies, with increasing nanoclay content the viscosity is increased, whereas at high-

frequencies this is reversed. The addition of even small quantities of nanoclay leads to a non Newtonian behavior with a significant increase in viscosity especially at low-frequencies.²¹ This is better illustrated in Figure 6(d), where at low-frequencies ($\omega = 0.1 s^{-1}$), the viscosity of the blends is sharply increased with increasing nanoclay content. Also, a decreased shear thinning behavior at medium and high-frequency ranges ($\omega = 10$ and $100 s^{-1}$) is observed.

The storage modulus provides a measure of nanocomposite stiffness and its frequency dependence characterizes whether the material is in a liquid-like or solid-like state.²² In the other words, melt rheology can be used to characterize exfoliation of nanoclay and has been limited to qualitative assessment of a solid-like, because of the dispersing nanoclay particle forming and acting as a reinforcing network structure.²³ Plateau modulus (G_N°) in the nanocomposites, indicating that network structure has created and leads to higher modulus than blend without nanoclay.²³ According to Figure 4(b), for the blends containing nanoclay, the liquid-like state, which is observed for PC/ABS blend at low-frequency, is disappeared and the storage modulus becomes almost constant. This indicates a transition from a Newtonian liquid to an ideal hookean solid,

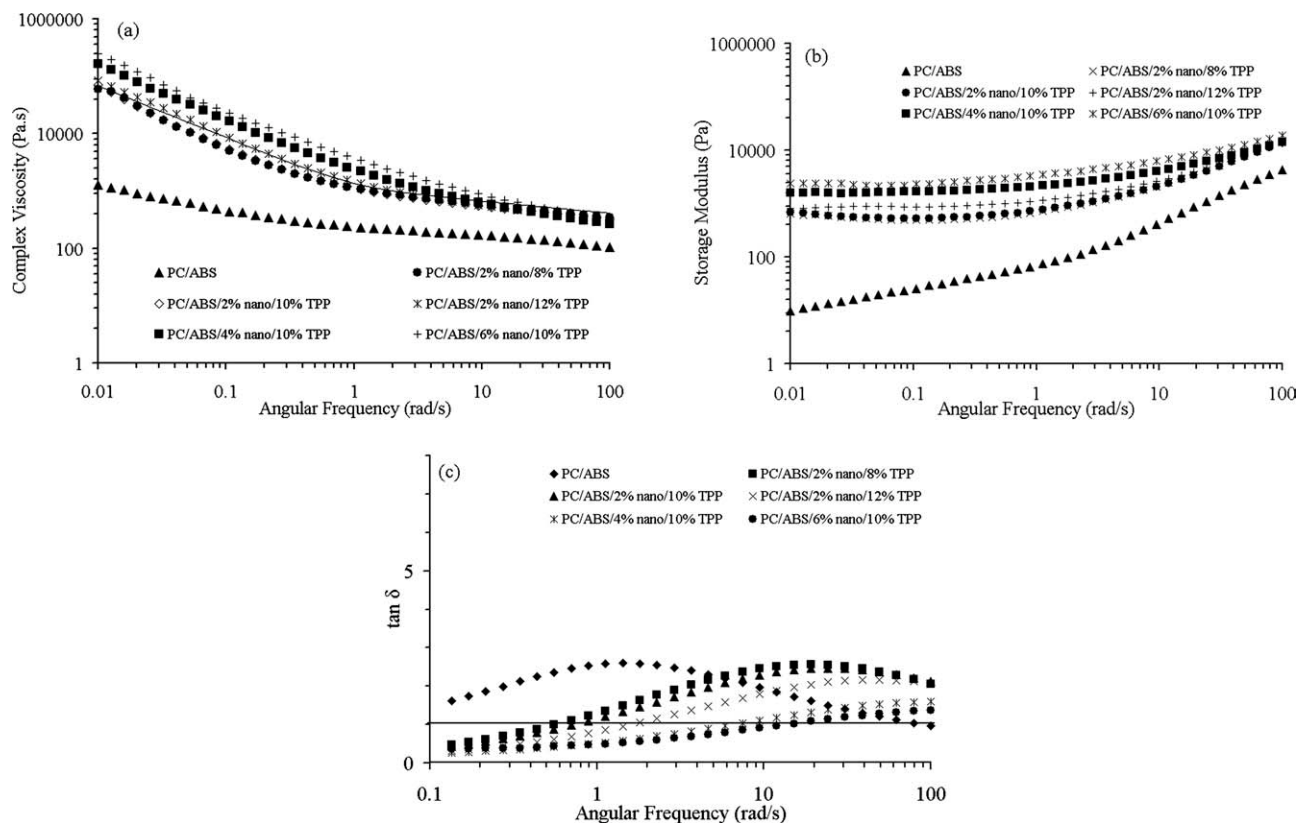


Figure 7 Variations of complex viscosity: (a) storage modulus, (b) $\tan \delta$, and (c) with frequency at 230°C for PC/ABS/TPP/nanoclay blends (In $\eta^*-\omega$ curves, those plotted based on Carreau model are distinguished with a solid line).

which accompanies the formation of a mechanically stable network structure in the test.²²

Figure 6(c) shows $\tan \delta$ of PC/ABS blend and its composites with various amounts of nanoclay. $\tan \delta$ is the ratio of G'' to G' and increase by enhancing damping behavior, which is directly related to viscose property of the melt. The $\tan \delta$ of PC/ABS and its composite with 2 wt % nanoclay is higher than one in all range of frequencies and located on the upper side of reference line of $\tan \delta = 1$. It means that the G'' is bigger than G' in all the range of tested frequencies. At the peak of $\tan \delta$ the viscose behavior of the melt is in its maximum comparing with melt elasticity. By increasing nanoclay content to 4 and 6 wt %, the melt elasticity of PC/ABS blend is increased and the peak of $\tan \delta$ shifted to higher frequency [Fig. 6(c)]. This is a typical behavior that is usually observed in filled thermoplastics.^{10,24}

Effect of TPP/nanoclay hybrid on the rheological behavior of PC/ABS/TPP/nanoclay blends

Figure 7 presents the response of complex viscosity, storage modulus, and $\tan \delta$ against frequency for PC/ABS/TPP/nanoclay blends at various TPP/nanoclay ratios.

As it can be seen, complex viscosity and storage modulus are only slightly affected by TPP content,

whereas they are remarkably affected by nanoclay content [Figs. 7(a,b)] because of the behavior of changes in PC/ABS/TPP/nanoclay blends is more similar to PC/ABS/nanoclay than PC/ABS/TPP. The complex viscosity of the blends containing both TPP and nanoclay [Fig. 7(a)] is higher than that of the blends containing either TPP or nanoclay [Figs 5(a),6(a)]. This observation is attributed to the simultaneous effect of TPP and nanoclay. Also, these blends show different viscosity values at low-frequencies, depending on TPP/nanoclay ratios. The storage modulus of the blends containing TPP/nanoclay [Fig. 7(b)] is improved in comparison with other blends [Figs. 5(b),6(b)]. The effect of TPP/nanoclay hybrid on $\tan \delta$ is shown in Figure 7(c). As it is evident, the hybrid system leads to a further increase of melt elasticity of PC/ABS blend as compared with nanoclay-contained blend.

In Figure 8, the variations of complex viscosity of hybrid blends with TPP [Fig. 8(a)] and nanoclay [Fig. 8(b)] at three different frequencies, 0.1, 10, 100 s^{-1} are shown. A similar trend is observed as for the blends, which only contained nanoclay [Fig. 6(d)]. From the results obtained from Figures 7 and 8, one can conclude that the rheological behavior of PC/ABS/TPP/nanoclay blend is mainly controlled by the presence of nanoclay rather than TPP.

Figure 9 shows the relationship between the storage modulus (G') and loss modulus (G'') with the

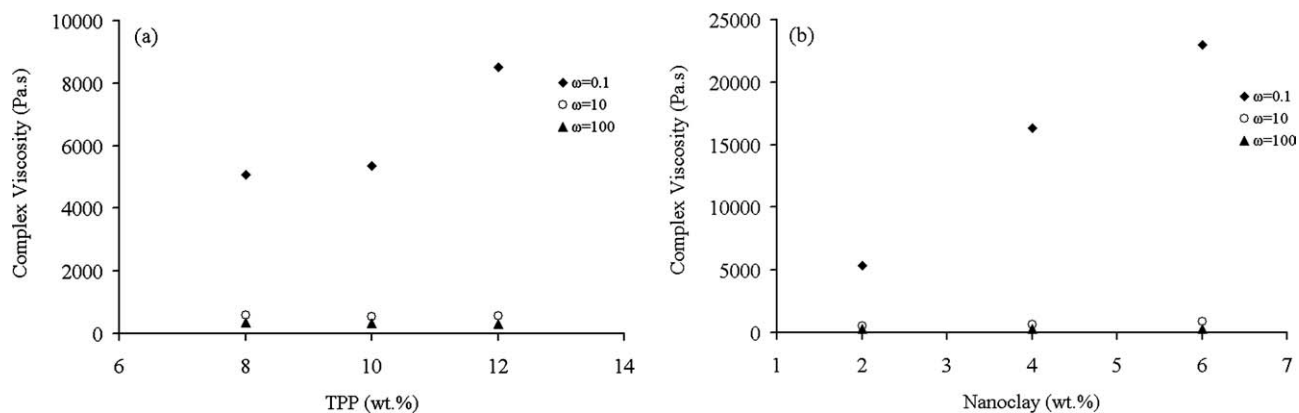


Figure 8 Variations of complex viscosity with (a) TPP content and (b) nanoclay content at three different frequencies, 0.1, 10, 100 rad/s, at 230°C for PC/ABS/TPP/ nanoclay blends.

frequency. For comparison purposes, only one formulation is used from each group, randomly. This kind of plot is used to describe the rheological behavior of the blends and was introduced by Han in 1983 and later on the plot G' vs G'' was named as modified Cole-Cole plot by Harrel and Nakayama.²⁵ This plotting technique reveal structure features of polymers. The curve that has more storage modulus, has higher melt elasticity.

As it is evident, at low-frequencies PC/ABS blends shows a behavior similar to PC, whereas at higher frequencies this is shifted to ABS. The dynamic of ABS and PC resin is different in shear field and because of hydrodynamic effect of ABS droplets in the movement of PC macromolecules as matrix resin in PC/ABS blend the elastic part of modulus (storage modulus) shows a significant increase at higher range of shear rates (frequency). The increased elasticity of the PC/ABS is because of emulsion type morphology observed in SEM images. At lower frequency, there is enough time for the relaxation of PC molecule against applied stress and induced deformation and the general behavior of PC/ABS blend is more similar to PC matrix resin.

All the blends except the hybrid one show an almost similar behavior from the elasticity point of view. The hybrid blend is set above the reference line (the line that G' is equal to G''). Above this line, the elasticity of melt is more than its viscous counterpart. This is in agreement with the results reported for the hybrid systems containing nanoclay and traditional FRs.²⁶

Modeling of the rheological behavior

Modeling of the rheological behavior of PC resin

The experimental data of complex viscosity against frequency of PC resin [Fig. 4(a)] showed a Newtonian plateau, which was then changed to a power-law-like behavior at high-frequencies. The following equation [eq. (1)] has been suggested to correlate the complex viscosity with frequency:¹⁰

$$|\eta^*| = |\eta_0^*|(1 + \lambda^2\omega^2)^{-N} \quad (1)$$

where η_0^* is the zero shear viscosity (6850 Pa s); η^* , complex viscosity; ω , frequency; λ , relaxation time (0.01848 s); and N is the power-law index (0.65). Using the eq. (1) and by substituting the relevant values, the complex viscosity is calculated theoretically and the plot of $\eta^*-\omega$ is shown in Figure 4(a) (solid line). The results show that the experimental and the calculated values are in good agreement with each other and that the eq. (1) can be used to predict the viscosity behavior of PC resin.

Modeling of the rheological behavior of the blends with yield stress

The blends PC/ABS, PC/ABS/TPP, and those having hybrid of TPP/nanoclay show yield behavior at melt state. Also, their $\eta^*-\omega$ curves show a linear power-law-like behavior, with two different slopes in low- and high-frequency ranges. For these blends the following equation [eq. (2)] is used to evaluate the experimental data.¹⁰

$$|\eta^*| = \frac{K\omega^{n'}}{(1 + \omega^2)^{(n' - n''/2)}} \quad (2)$$

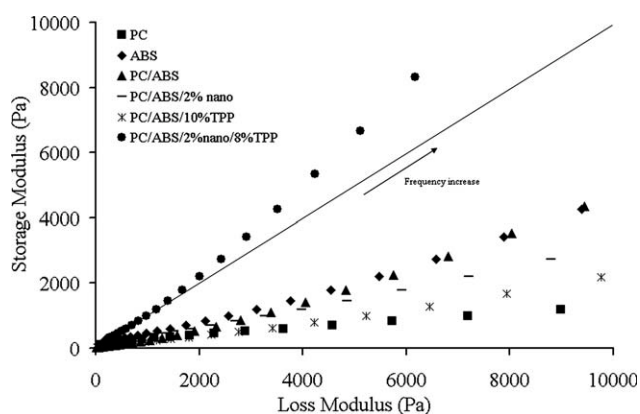


Figure 9 Cole-Cole diagram for various formulations.

TABLE III
Viscose Parameters of Various Blends

Compound	K	n'	n''
PC/ABS	200	-0.4	-0.16
PC/ABS/10% TPP	865	-0.24	-0.15
PC/ABS/2% nano/8%TPP	1079	-0.9	-0.21

where K , complex viscosity at frequency of 1 rad/s and at $n' = n''$; n' , slope of the $|\eta^*|-\omega$ curve in the region of $0.1 \leq \omega \leq 1$; n'' , slope of the $|\eta^*|-\omega$ curve in the region of $1 \leq \omega \leq 10^2$.

At very low- and high-frequency ranges, $\omega \ll 1$ and $\omega \gg 1$, the following power-law equations [eqs. (3) and (4)] can be obtained:

$$\eta^* = K\omega^{n_1-1} \quad \omega \ll 1 \quad (3)$$

$$\eta^* = K\omega^{n_2-1} \quad \omega \gg 1 \quad (4)$$

where n_1 and n_2 are power-law exponents equal to $(1-|n'|)$, and $(1-|n''|)$, respectively. The viscose parameters of K , n' , and n'' for the blends are shown in Table III.

The $\eta^*-\omega$ curves plotted according to model parameters given in Table III are shown in Figures 4(a), 5(a), 7(a) (solid line). It is seen that eq. (2) can predict properly the complex viscosity behavior of these blends in a wide range of frequencies by relevant viscose parameters.

However, in cases where the $\eta^*-\omega$ curves show an initial yield stress followed by a plateau and then a frequency-thinning region, like what is observed for ABS resin and formulations that have nanoclay, neither of the two equations suggested above can be used. In such circumstances, it might be necessary to break up the curves into two or three regions and fit separate equation for each region.²⁷

CONCLUSIONS

This systematic study was carried out to understand the effect of TPP, nanoclay, and hybrid of them as FRs, on the morphology and rheological characterizations of PC/ABS blends, and leads to the following conclusions:

PC/ABS blend showed a yield behavior in the complex viscosity curve in all range of frequencies, with values lower than PC and ABS. This proved a negative deviation in viscosity behavior of this blend from log-additivity rule.

In TPP-contained formulations, the melt viscosity was increased, and melt elasticity and yield stress were decreased by increasing TPP content.

XRD results proved an intercalated structure for nano-filled systems. This was supported by TEM image. Also, an improved intercalation was achieved in presence of TPP.

In nano-filled formulations, at low-frequencies, with increasing nanoclay content the viscosity was increased, whereas at high-frequencies this was reversed. Also, the addition of even small quantities of nanoclay led to a non Newtonian behavior with a significant increase in viscosity and melt elasticity of PC/ABS blend.

In composites containing hybrid of nanoclay and TPP, it was concluded that the rheological behavior of the blend is mainly controlled by the presence of nanoclay rather than TPP. From the Cole-Cole diagrams an improved elasticity and ease of processing was concluded for the hybrid system.

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References

- Sohn, J. I.; Lim, S. T.; Park, S. H.; Choi, H. J.; Jhon, M. S. *J Mater Sci* 2003, 38, 1485.
- Zhang, X.; Chen, Y.; Zhang, Y.; Peng, Z.; Zhang, Y.; Zhou, W. *J Appl Polym Sci* 2001, 81, 831.
- Wang, S. h.; Hu, Y.; Zh, W.; Yong, T.; Chen, Z.; Fan, W. *Polym Degrad Stabil* 2003, 80, 157.
- Tjong, S. C.; Meng, Y. Z. *Eur Polym J* 2000, 36, 123.
- Keitz, J. D.; Barow, J. W.; Paul, D. R. *J Appl Polym Sci* 1984, 29, 3131.
- Zhang, S. H.; Richard Hoorrocks, A.; Hull Richard; Baljinder, K. *J Polym Degrad Stabil* 2006, 91, 719.
- Bourbigot, S.; Gilman, J. W.; Wilkie, C. A. *J Polym Degrad Stabil* 2004, 84, 483.
- Wangs, S. H. Y.; Zong, R. *J Appl Clay Sci* 2004, 25, 49.
- Kristin, H.; Pawlowski, B. *J Polym Degrad Stabil* 2008, 93, 657.
- Jahani, Y.; Ehsani, M. *Polym Eng Sci* 2009, 49, 619.
- Greco, R.; Astaria, M. F.; Dong, L.; Sorrentino, A. *Adv Polym Technol* 1994, 13, 259.
- Fakult, V. *Mg-Al Layered Double Hydroxide: A Potential Nanofiller and Flame-Retardant for Polyethylene*, Ph.D thesis, Technischen Universität Dresden, 2007.
- Dong, Y.; Bhattacharyya, D.; Hunter, P. J. *Adv Compos Mater Struct* 2007, 334, 841.
- Munstedt, H.; Auhl, D. *J Non-Newtonian Fluid Mech* 2005, 128, 62.
- Khan, M. M. K.; Liang, R. F.; Gupta, R. K.; Agarwal, S. *J Korea-Aust Rheol* 2005, 17, 1.
- Foong, M. L.; Tam, K. C.; Loh, N. H. *J Mater Sci* 1995, 30, 3625.
- Utracki, L. A. *J Rheol* 1991, 35, 1615.
- Fang, Y.; Carreau, P. J.; Lafleur, P. G. *Polym Eng Sci* 2005, 23, 1254.
- Lin, C. C. *Polym J* 1979, 11, 185.
- Lauridsen, F. S.; Cohr, K. H.; Andersen, T. *Danish Ministry of the Environment* 2007, 1142, 1.
- Mokamoto, P. H.; Maiti, P.; Kotaka, T.; Hasegawa, N.; Usuki, A. *Nano Lett* 2001, 1, 295.
- Nguyen, Q.; Donald, G. *Barid Polym* 2007, 48, 6923.
- Nazare, S.; Hull, T. R.; Biswas, B. *J Vinyl Addit Technol* 2005, 11, 21.
- Jahani, Y. *Polym Eng Sci* 2007, 47, 2041.
- Harrell, E. R.; Nakayama, N. *Modified cole-cole plot as a tool for rheological analysis of polymers*; In *Current Topics in Polymer Science, Rheology and Polymer Processl Multiphase System*, Ottenbrite, R. M.; Utracki, L. A.; Inoue, S., Eds.; Karl Hanser: New York, 1987, p 149.
- Lan, T. *Polymer* 2007, 48, 2345.
- Aroon Shenoy, V. *Rheology of filled polymer system*; Kluwer Academic Publishers: Dordrecht/Boston/London, 1999; p 343.