

# Phase Separation, Physical Properties and Melt Rheology of a Range of Variously Transesterified Amorphous Poly(Ethylene Terephthalate)–Poly(Ethylene Naphthalate) Blends

O. BECKER,<sup>1,2</sup> G. P. SIMON,<sup>1</sup> T. RIECKMANN,<sup>2</sup> J. S. FORSYTHE,<sup>1</sup> R. F. ROSU,<sup>1</sup> S. VÖLKER<sup>3</sup>

<sup>1</sup> School of Physics and Materials Engineering, CRC for Polymers, Monash University, Clayton, Victoria 3800, Australia

<sup>2</sup> Department of Process Engineering and Plant Design, University of Applied Sciences Cologne, D-50676 Cologne, Germany

<sup>3</sup> Institute of Thermal Engineering, University of Kassel, D-34109 Kassel, Germany

Received 7 September 2000; accepted 26 January 2001

**ABSTRACT:** Amorphous, partially transesterified poly(ethylene terephthalate)/poly(ethylene naphthalate) (PET/PEN) blends of different levels of transesterification and blend composition were investigated in terms of resultant phase behavior, thermal transitions, and melt rheological properties. Intrinsic viscosities of the lowest transesterified material were found to be significantly below those of a physical blend of an identical composition, but at higher levels of transesterification, there was little difference. This was similarly found in melt rheometry measurements, where the zero-shear rate viscosity of the low and highly transesterified mixtures were similar. Both solution and melt rheometry indicated that the molecular weight decreased by thermal degradation from processing. This is believed to play an important role in determining the final molecular architecture and properties. For similar levels of ester interchange, there was a minimum observed in zero shear melt viscosity at around 40 wt % PEN. This is likely due to competition between the slightly transesterified copolymer chains having poorer packing in the melt and reduced entanglement. Differential scanning calorimetry and dynamic mechanical thermal analysis were used to investigate the phase behavior of partially and fully transesterified blends. Results for the glass transition of the highly transesterified blends were compared with the theoretical values calculated from the Fox equation and were found to be close, although slightly lower. A correlation between the melting temperature of the blend and the degree of transesterification was shown to exist. This correlation can be used to estimate the degree of ester exchange reaction from these melting transitions. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1556–1567, 2002

**Key words:** phase separation; polyester blends; PET; PEN; transesterification

## INTRODUCTION

Poly(ethylene terephthalate) (PET) is the most commonly used material in high-barrier packag-

ing applications.<sup>1</sup> Despite being attractive in the beverage-packaging industry, its thermal and barrier properties exclude a number of attractive applications such as packaging of oxygen- or UV-sensitive foods (beer, sparkling wine, fruits) and hot-fill applications.

Recently, the use of PET/PEN blends for improved packaging has gained increasing interest. Significantly improved properties such as thermal resistance, mechanical properties, dimensional properties, and gas barrier properties were

Correspondence to: G. P. Simon (george.simon@spme.monash.edu.au)

Contract grant sponsor: Deutscher Akademischer Austauschdienst (DAAD); contract grant sponsor: CRC for Polymers.

*Journal of Applied Polymer Science*, Vol. 83, 1556–1567 (2002)  
© 2002 John Wiley & Sons, Inc.  
DOI 10.1002/app.10126

reported for poly(ethylene naphthalate) (PEN) compared to the more commonly used PET.<sup>2</sup> Incorporation of dimethyl-2,6-naphthalenedicarboxylate (NDC) in PET through copolymerization has shown to substantially improve thermal, mechanical,<sup>3</sup> and barrier<sup>4,5</sup> properties. However, random incorporation of NDC can hinder the development of crystallinity induced during the stretch-blow molding. In fact, the copolymer will only crystallize at either very high ( $\geq 85$  mol %) or very low ( $\leq 15$  mol %) NDC compositions.<sup>6</sup> This composition severely restricts optimization of the material properties. Melt-blending PET with PEN overcomes this problem, and crystallization can be achieved over all compositions.<sup>6</sup> As shown in previous work,<sup>7</sup> these partially transesterified blends can decrease the oxygen transmission of the PET/PEN blend compared to the random copolymer analogs with the same composition. Apart from the attractive increase of barrier properties, phase separation can be observed in PET/PEN blends of low-ester exchange levels. Although miscibility and phase separation of PET/PEN blends were investigated in the past,<sup>8-13</sup> the factors affecting the transesterification mechanism between PET and PEN have only recently become clearer. Evidence exists of the relative importance of the three possible reaction mechanisms, alcoholysis, acidolysis, and direct mid-chain ester exchange in the literature. Kenwright et al.<sup>13</sup> recently showed that hydroxy end groups participate in the transesterification reaction. That is, an alcoholysis mechanism is supported. Effects from carboxyl end groups and direct ester-ester exchange are much less.<sup>14</sup> The transesterification reaction kinetics decreased markedly after end-capping the hydroxy end groups in the polyesters by an esterification reaction with trifluoroacetic acid. It was concluded that the transesterification reaction between PET and PEN followed second-order kinetics.<sup>14</sup>

It is generally accepted that transesterification is a necessary requirement for the miscibility of polyesters. For two immiscible polyesters such as PET and PEN to transesterify, there must be some degree of compatibility already present. The two polymer chains must have good, intimate contact for a transesterification reaction to take place. If there is macrophase separation, the transesterification is limited only to the interface between the phases. This assumption was challenged by Guo and Brittain,<sup>11</sup> who concluded, by using NMR, that single-phase formation in the melt is a necessary condition for transesterification to take place. It is most likely that significant

miscibility and transesterification are necessary for the formation of a single phase. It appears that fully random copolymers are not needed for the melt miscibility and that miscibility or homogenization occurs when the average sequence length of terephthalic acid unit is between 4 and 8.<sup>14</sup>

This article examines a series of materials blended for different residence times and looks at aspects such as thermal transitions, phase separation, and rheological properties of commercially useful PET/PEN blends, and, relating them to chemical variables such as the degree of transesterification and intrinsic viscosity. Most other studies have focused on a few concentration ranges, a single reaction condition, and mainly characterized the resultant materials with a particular technique in the solid or melt phase. In a number of cases, they were solution cast and melt processed which, although allowing good control of reaction conditions, is not consistent with the usual commercial situation involving shear flow in an extruder. In this work, we have attempted to combine all of these different aspects into materials that have been blended in an extruder to allow a comparison and correlation between the various characterization methods as a function of a range of compositions and degrees of transesterification.

## EXPERIMENTAL

Amorphous PET/PEN blend films were produced on a Brabender single-screw extruder. A PET resin from Bakrie Kasai (Japan) [BK-2180, intrinsic viscosities (IV)  $0.83 \pm 0.2$  dl/g], containing isophthalic acid as a comonomer, and a PEN copolymer of Mitsubishi (NC 900Z), containing 8 mol % terephthalic acid to facilitate transesterification, were used for blend production. A PEN-rich copolymer was used in this work, rather than neat PEN homopolymer to simulate commercial practice where such a copolymer is used because it is closer matched to PET with regards to the melting point and rheological properties. This copolymer will hence further be denoted PEN. Prior to processing, resins were dried at 170°C for 15 h under nitrogen atmosphere. Amorphous blends of 20, 40, 60, and 80 mol % PEN were processed on a Brabender single-screw extruder at different screw speeds (and thus residence times) to produce materials of different degrees of transesterification. For comparison, the PET and PEN constituent materials were processed at 50 rpm. The

extruder temperature ranged from 275 to 285°C at the die lip. To ensure amorphous samples, the extruded sheet was quenched by using stacked, chilled rolls at 5°C.

The degree of transesterification was determined from  $^1\text{H-NMR}$  results using a Bruker DRX 500 MHz NMR spectrometer. A method described by Steward et al.,<sup>4</sup> where a physical PET/PEN blend with no ester exchange reaction has 0% transesterification and the statistical random copolymer is defined to have 100% transesterification, was used to determine the degree of ester exchange reaction.

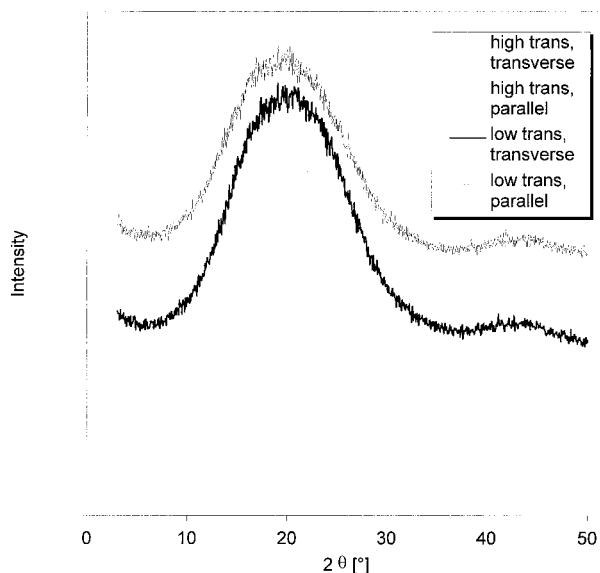
Wide-angle X-ray spectroscopy (WAXS) analysis was performed using a Rigaku Geigerflex generator with a wide-angle goniometer. An acceleration voltage of 30 kV and a current of 30 mA were applied using Ni-filtered Cu-K- $\alpha$  radiation.

IV were determined in a 3:2 weight mixture of phenol and 1,2-dichlorobenzene solution. The materials (125–135 mg) were dissolved in 35 ml solvent at 133°C. Measurements were carried out at 25°C in a Ubbelohde viscometer. Viscosity measurements were run in duplicate.

Steady shear rheological measurements were carried out on a Rheometrics SR 200 controlled stress rheometer at a temperature of 265°C under a nitrogen atmosphere to prevent PET degradation from moisture. Samples were dried at 150°C for 24 h prior to measurements. The steady shear viscosity was measured by using a 25-mm-diameter parallel plate geometry with a constant gap spacing.

Differential scanning calorimetry (DSC) analyses were carried out by using a Perkin–Elmer DSC-7. The DSC was calibrated with an indium and a zinc standard. Samples (8–12 mg) were sealed in an aluminum pan and heated to a temperature of 280°C at a scanning rate of 10 K/min under nitrogen atmosphere.

Dynamic mechanical analysis (DMA) was performed by using a Perkin–Elmer Dynamic Mechanical DMA7 Analyzer. A dynamic mechanical probe was used in the penetration probe configuration. Temperature calibration was carried out with an indium standard. Samples were loaded with a static stress of 1000 mN and a dynamic stress of 800 mN at a frequency of 1 Hz. The temperature range was 60–150°C and performed under a helium atmosphere. It should be noted that the mode used was not able to determine absolute values of loss or storage modulus.



**Figure 1** Transverse and parallel WAXS intensities of low and highly transesterified PET/PEN blends containing 40 mol % PEN.

## RESULTS AND DISCUSSION

WAXS was performed on the blend samples to confirm the amorphous state of the quenched polymer films. Samples were analyzed parallel and transverse to the machine direction to detect potential anisotropy. Figure 1 shows parallel and transverse scans of two different blends containing 40% PEN. As was expected from the processing method which involved rapid quenching, there was no indication of significant crystalline content. That is, no sharp reflections in the WAX scans were observed. The intensities of the amorphous peak recorded parallel with the machine direction are only slightly less broad than the transverse scans; thus, little anisotropy of the samples can be inferred.

NMR analyses were performed to determine the degree of transesterification of the samples. The percentage of transesterification was determined as

$$\% \text{Trans} = \frac{100 \times 100 \times \% \text{NET}}{2 \times \% \text{N} \times (100 - \% \text{N})} \quad (1)$$

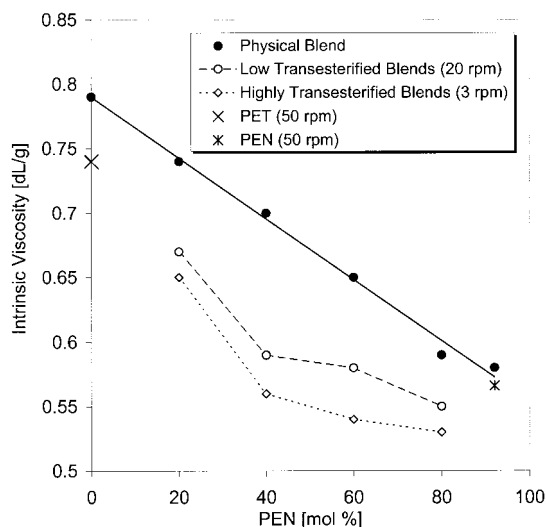
where %NET is the molar percentage of ethylene groups between two naphthalene dicarboxylate groups related to all ethylene groups between naphthalate and/or terephthalate. %N is the molar percentage of naphthalate related to all naphthalate and terephthalate groups.

**Table I** Transesterification, Relative Transesterification, and Thermal Transitions of PET/PEN Blends as Determined by NMR and DSC (some samples show double transitions)

Blend Composition (mol % PEN)	Extruder Screw Speed (rpm)	Degree of Transesterification (%)	Relative Transesterification $T_R$	Glass Transition Temperature $T_g$ (°C)	Cold Crystallization Temperature $T_c$ (°C)	Melting Temperature (°C)
0	50	0	—	74	144.8	250
20	4	29.1	2.77	83	189	236
20	7	20.3	1.95	81	179	242
20	12	18	1.68	80	167	245
20	18	15.9	1.48	81	161/195	247
20	30	14.6	1.33	81/112	153/191	246
40	3	26.8	1.95	92	—	233
40	8	19.6	1.35	82/103	194	242
40	12	17.3	1.29	80/105	170/194	245
40	16	15.1	1.27	78/106	161/189	247
40	20	14.5	1.10	79	154/186	249
60	3	30.4	1.52	100	—	243
60	8	23.1	1.15	80/104	208	249
60	12	22.4	1.14	80/108	208	249
60	16	21.3	1.09	77/110	206	250
60	20	23.1	1.04	78/111	207	250
80	3	48.3	1.28	110	214	246
80	8	39.6	1.03	111	210	251
80	12	35.9	1.01	112	210	251
80	16	28.6	1.04	114	208	251
92	50	87.2	—	118	219	251

The results of transesterification studies are summarized in Table I. Within a set of blends of the same composition, the level of transesterification and the %NET (i.e., the ethylene units between a terephthalate and a naphthalate group) increased with decreasing screw velocities because of the increased residence time. Because of the definition of % transesterification, a direct comparison of the transesterification of different sets of polymer blends is not representative. In addition, the parent PEN is a copolymer containing 8 mol % PET with a degree of 87.2% transesterification. A value of relative transesterification,  $T_R$ , that compares the level of transesterification before and after the reactive melt blending process in the extruder was thus used.<sup>15</sup> Results of the relative transesterification are shown in Table I. The majority of the following characterizations will be focused on the extreme low- and high-transesterified blends. The low transesterified blends refer to the samples produced at high-extruder screw speed (16–20 rpm) and therefore low residence time in the extruder. Correspondingly, the highly transesterified blends refer to the samples produced at low-extruder screw speed (3–4 rpm) or high-residence time.

IV were determined for low- and high-transesterified blends of each composition, as well as for the physical, nonreacted blends, to follow the changes in the molecular weight before and after melt blending. The physical blends were made by dissolution of the appropriate concentration of components in the solvent used to measure intrinsic viscosity. Although no films were cast in this work, previous results report that it is known that they would be immiscible.<sup>14</sup> In Figure 2, the relationship between intrinsic viscosity and blend composition is demonstrated for the physical blends, as well as low and highly transesterified materials. High intrinsic viscosity values relate to a high molecular weight ( $M_w$ ) of the polymer. The IV of PET was found to be 0.79 dL/g; the value for PEN copolymer was determined as 0.58 dL/g, although, because of the different chemistries, this cannot be related to a molecular weight difference. In all instances, the intrinsic viscosity decreased with increasing PEN content. It can be observed that the physical blends show the highest IVs and therefore the highest molecular weight. A trend line of best fit illustrates the linear relationship between IV and blend composition for the physical blends in Figure 2. In con-



**Figure 2** Intrinsic viscosities of physical blends and low and highly transesterified PET/PEN blends.

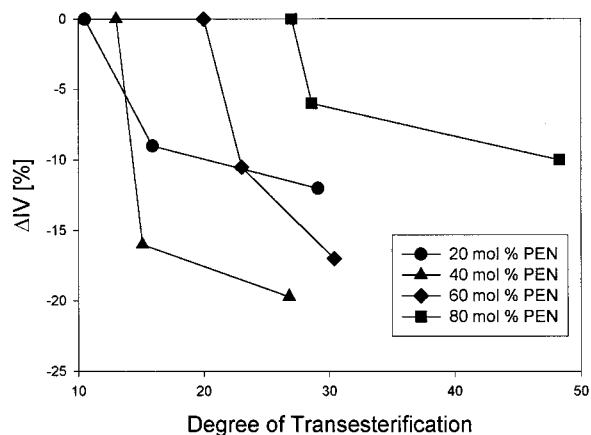
trast to the physical blends, the correlation between IV and mol % PEN for the melt-blended materials is not a linear relationship. At 40 wt % PEN, a marked drop in IV for the low transesterified sample (15% transesterification) can be seen. However, there is a lesser decrease in IV for a decrease to 27% transesterification (highly transesterified sample). The IV drop between each set of different samples of the same composition is illustrated in Figure 3.

There are two possible causes for the decrease in IV and molecular weight.<sup>16</sup> The first is the decrease that occurs because of transesterification where the number average molecular weight remains the same, while the molecular weight average changes until it is twice the number average molecular weight.<sup>16</sup> The other possibility is that thermal degradation and chain scission occurs (depending on environment) and that this dominates property change, PET being more susceptible than PEN to such a molecular weight change.<sup>16</sup> It was shown very recently that changes in molecular weight can be due to thermal degradation which occurs in addition to (and dominate) changes in molecular weight due to transesterification alone. That is, the transesterification is not sufficient to result in the experimental changes in melt viscosity. Although there is a significant change for low transesterification, there is little further change for almost twice this initial degree of transesterification.

Melt rheology of these materials is an important indicator of their structure in the amorphous, molten state. To minimize the potential for

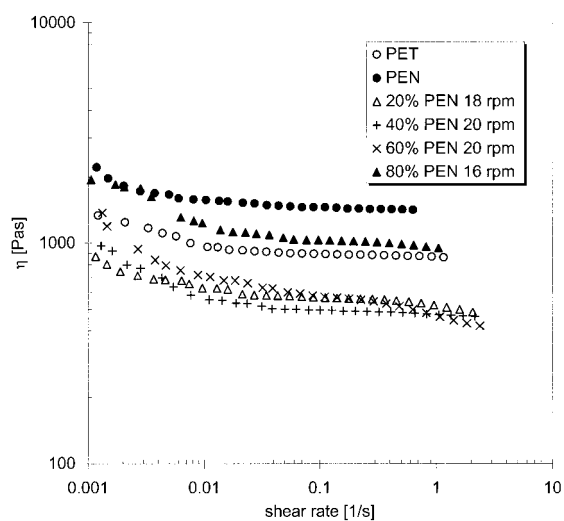
further transesterification, the rheological measurements were performed at 260°C, which is 20°C below the processing temperature and at shear rates lower than 3 s<sup>-1</sup>. The results for low and high transesterification are shown in Figure 4(a,b). It can be seen that in this range the materials were Newtonian (i.e., viscosity was relatively constant over the shear rates covered). As expected, the melt viscosity of PEN with its more rigid chains is greater than that of PET. Interestingly, in both cases, the blend viscosities are synergistically lower than that of either component, the transesterified materials remaining Newtonian in this region (Fig. 4a,b). To allow a meaningful comparison and to take advantage of the good data obtained at low shear rates, the data was extrapolated from the Newtonian region to the zero shear rate and the value of zero shear viscosity,  $\eta_0$ , was determined. This region is of special interest for polymer characterization and the rheological response depends on the size of the macromolecular random coil and specific interactions among macromolecules.

The zero-shear viscosity data as a function of PEN content, at high and low degrees of transesterification, is shown in Figure 5. As expected, all values of the blends lie below that of the homopolymers. A strong negative deviation is seen in both high- and low-transesterification blends. It can be seen that the viscosity has changed only marginally (slight decrease) for the highly transesterified blends, despite being significantly more transesterified. This result correlates with that of the intrinsic viscosity described earlier and indicates the blend viscosity is likely determined by the viscosity of the components and the effect of

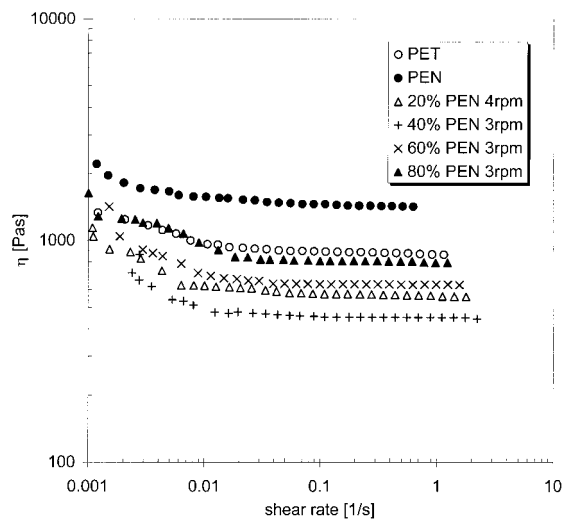


**Figure 3** Intrinsic viscosities as a function of transesterification for physical, high- and low-transesterified blends.

thermal degradation that occurred during the mixing process. The degree of transesterification clearly does not strongly influence the molecular weight (which would cause a change in viscosity) and is influenced more by the chemical concentration of the comonomer units, regardless of the degree that they are distributed to in the range of copolymer chains at differing degrees of transesterification. Reported rheological studies of blends of these materials are few. Kyotani et al.<sup>17</sup> did capillary rheometry at higher shear rates ( $\sim 10\text{--}5000\text{ s}^{-1}$ ) and high temperatures (280, 300, and 320°C) and found PEN to have a greater

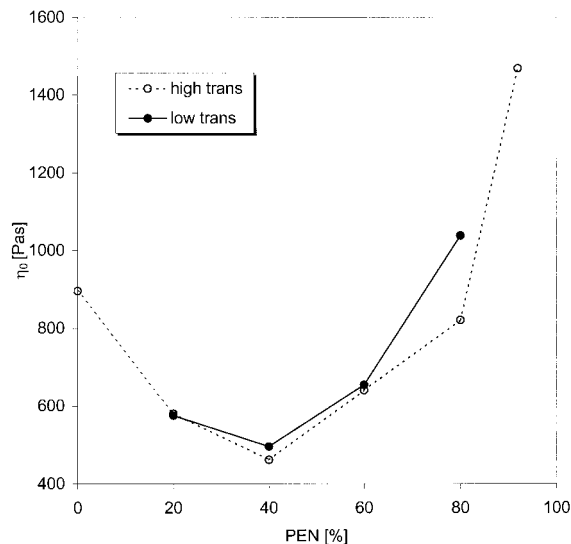


(a)



(b)

**Figure 4** (a) Melt viscosity as a function of shear rate for low transesterified PET/PEN blends. (b) Melt viscosity as a function of shear rate for highly transesterified PET/PEN blends.



**Figure 5** Zero-shear rate melt viscosities for low and highly transesterified PET/PEN blends.

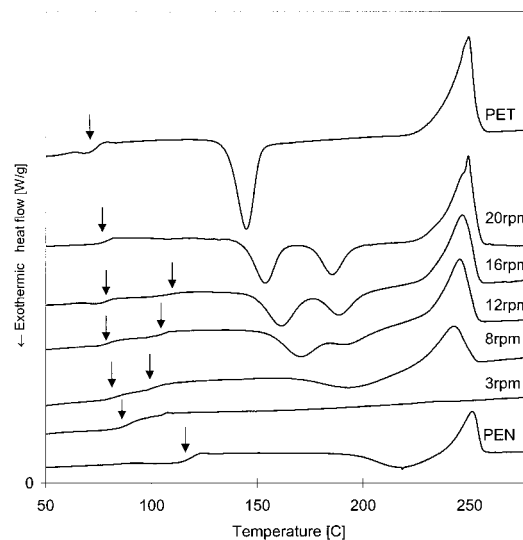
viscosity for all shear rates. In terms of a concentration dependence at a given shear rate, this was strongest at the lower shear rates. In general, a negative deviation was seen for viscosity as a function of PEN concentration but, perhaps due to the higher shear rates and reduced sensitivity to molecular structure, the curve maximum is less pronounced and certainly not a synergistic negative deviation. No explanation was given for this minimum.<sup>17</sup> A recent article by Lee et al.<sup>18</sup> undertook complex rheology measurements from about 3 to 700 rad/s, all at higher shear rates/frequencies than our measurements. At an angular frequency of 10 rad/s, they also found PEN was more viscous than PET, but (other than a deviant point at 50% PEN) observed a positive deviation from the rule of mixtures between the values of the two neat components. Limited preliminary oscillatory rheological data was reported by Tharmapuram and Jabarin<sup>16</sup> at 10 rad/s for up to 40% PEN. A minimum in the limited range studied was observed and assigned to the disruptive effect of the copolymers formed, the enhanced molecular mobility, and restricted packing in the melt, resulting in a lower viscosity. In our system, with PET and PEN (the latter being a PEN-rich copolymer) and at the low shear rates used, it appears that this disruptive packing may persist right across the composition range, regardless of whether the materials are one or two phase (as will be indicated later, when their miscibility in the solid state is reported, it appears that miscibility in the eventual solid state is not necessarily an indicator of true miscibility in the melt). Mis-

cibility in the molten state is a difficult phenomena to determine. One method used in blends involves dynamic rheology and if blends of the same constitution but different compositions are blended, if the storage modulus,  $G'$ , versus the loss modulus,  $G''$ , of all the blends overlap (form a master curve), the blends are miscible.<sup>19</sup> Because we did not perform oscillatory rheology, we could not make this judgment. However, Lee et al.<sup>18</sup> showed for their compositions, reaction conditions, and temperatures that the  $G'$  versus  $G''$  curves did overlap in the molten state, leading to the idea that there was good melt miscibility. Their blends did, however, also turn out to be miscible in the solid state on cooling, indicating their degree of homogeneity was fairly high in any case.

In summary, it appears that regardless of the degree of transesterification, the blend viscosity is lower than that of either component. It would probably be lower than the fully nontransesterified blends, but this is difficult to confirm because the rheological experiment would itself result in some ester exchange reaction. Blocky copolymers and more random copolymers alike seem to cause reduced packing in the melt and lower viscosities, even though incorporation of rigid naphthalate units into a terephthalate-rich chain could be expected simply to result in reduced chain mobility in the melt, and thus, greater viscosity.

DSC traces of the amorphous films were determined for each sample. The glass transition temperature ( $T_g$ ) was taken as the midpoint of the heat capacity step. The cold crystallization temperature ( $T_c$ ) and the melting temperature ( $T_m$ ) were determined from the maximum location of the enthalpy peak. Results of the characteristic thermodynamic values are shown in Table I. The DSC results confirm that the different extruder screw velocities dramatically influence the degree of transesterification and thus miscibility. An example of the DSC traces for a set of blends containing 40 mol % PEN is given in Figure 6. Double cold crystallization peaks and double glass transitions can be observed for the low transesterified samples (as an unexpected exception, the 20 rpm sample shows only a single  $T_g$ ).

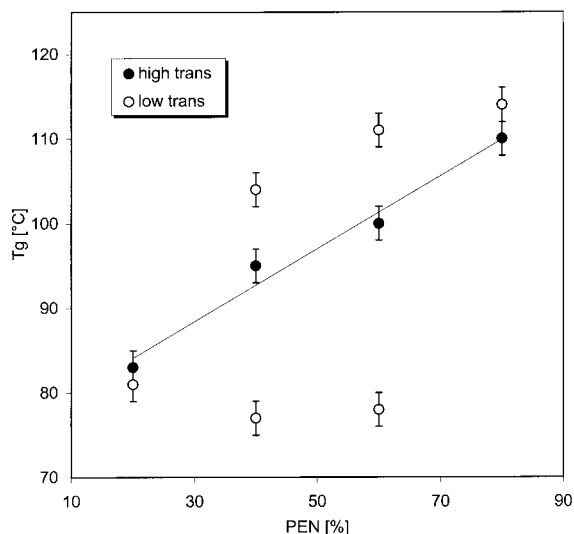
For each set of blends, samples produced at low-screw velocities (i.e., high relative transesterification) appear to be single-phase systems. The DSC traces show single glass transitions with either a single, small cold crystallization peak or no evidence of cold crystallization at all. According to the DSC traces, most of the following sets of less-transesterified samples (8 rpm) also



**Figure 6** DSC traces of PET/PEN blends containing 40 mol % PET. The blends were prepared at different extruder screw speeds.

indicated a single-phase system. However, these samples show an increasing ability to crystallize and higher melting peak temperatures because of the lower level of transesterification. Sufficiently long PET and PEN sequences clearly remain, which allow crystallization to occur. These samples appeared slightly hazy and because the samples were determined to be amorphous (from X-ray results), the haziness cannot be explained by crystallization. The haziness is thus indicative of a system containing more than one phase. Generally, samples show increasing indications of being immiscible with decreasing degree of (relative) transesterification.

Double  $T_g$ s can be observed largely in blends of high-extruder screw velocities containing 40 and 60% PEN. Most of the blends containing 20 or 80% PEN appear to have single  $T_g$ s, although their haziness indicates that it is a multiple phase system. However, it is likely that the lack of multiple  $T_g$ s may be related to a lack of sensitivity of the DSC at extreme blend concentrations.<sup>8</sup> The presence of single- or double-glass transitions as an indicator of miscibility is well illustrated for low- and high-extruder screw speeds in Figure 7. Although all blends produced at low-extruder screw velocities indicate a single-phase system, higher screw velocities favor a two-phase material. It can be seen that the samples blended for a longer time (lower screw speed) approach a roughly linear relationship between the mol % PEN and the glass transition temperature. Such a linear relationship between the PEN concentra-



**Figure 7** Single and double glass transition, determined for PET/PEN blends produced at low and high extruder screw speeds.

tion and the  $T_g$  was also reported for the synthesized, random copolymer.<sup>20</sup>

The Fox equation describes the relationship between the glass transition temperature and either copolymer or miscible blend composition<sup>21</sup>

$$\frac{1}{T_g} = \frac{w_{\text{PET}}}{T_{g\text{PET}}} + \frac{w_{\text{PEN}}}{T_{g\text{PEN}}} \quad (2)$$

where  $w_i$  is the weight fraction of the  $i$ th component in the copolymer (or blend) and  $T_g$  is the thermodynamic glass transition in absolute temperature units (K). Calculations were performed on the single-phase blends produced by the lowest extruder screw speeds (3–4 rpm), because these samples should be the closest to random copolymers. Predicted glass transitions and the determined values are shown in Table II. It should be noted that the blend containing 92% PEN represents the commercial PEN resin which was used for this study. The  $T_g$  of the pure PEN (100%) was calculated by using eq. 1 from the commercial PEN containing 8 mol % PET. All of the measured values are slightly (4–6°C) below the glass transitions predicted by the Fox equation and this difference is likely due to the copolymers produced by extended transesterification being slightly nonrandom and also subject to a decrease in molecular weight because of thermal degradation and transesterification.

An important factor affecting the ability of the polymer to form crystals is the sequence length of

the blocks in a chain. Because of the longer residence time in the extruder, the blends initially form block copolymers and eventually random, statistical copolymers, with a decreasing ability to form crystals, as has been reported elsewhere.<sup>22</sup> It can be seen from the DSC traces that the ability to crystallize decreases with longer residence time and higher levels of transesterification. Highly transesterified blends containing 40 and 60% PEN were not able to crystallize at the heating rate of 10°C/min used in this DSC experiment. According to the degree of transesterification determined from the NMR results, there may still exist some crystallizable blocks that could be made to crystallize by using lower DSC heating rates. However, the crystallization behavior was not the key topic of this work and has been reported in detail elsewhere.<sup>9,23</sup> All cold crystallization temperatures measured were intermediate to the  $T_c$ s of the pure polymers (i.e., 145°C for PET and 220°C for PEN). Double cold crystallization peaks were determined for the blends containing 20 and 40% PEN mixed at higher extruder screw speeds, whereas the blends containing 60 and 80% PEN show a single  $T_c$  that comes close to that of the pure PEN. At high PEN compositions, the PEN component dominates the crystallization process and the crystallization of PET is dramatically hindered. The cold crystallization temperature of the PET-rich phase increased with the degree of transesterification and there appeared to be a quite sensitive relationship between  $T_c$  and the degree of transesterification. By contrast, for high PEN contents, transesterification had minimal effect on the  $T_c$  of PEN. Only a slight increase in the  $T_c$  of PEN was observed at high PEN compositions. It could be expected that PET crystallization would be affected by the presence of PEN, because at the

**Table II** Comparison of the Measured Glass Transitions as Determined by DSC for High Transesterified Blends and Predictions Calculated by the Fox Equation

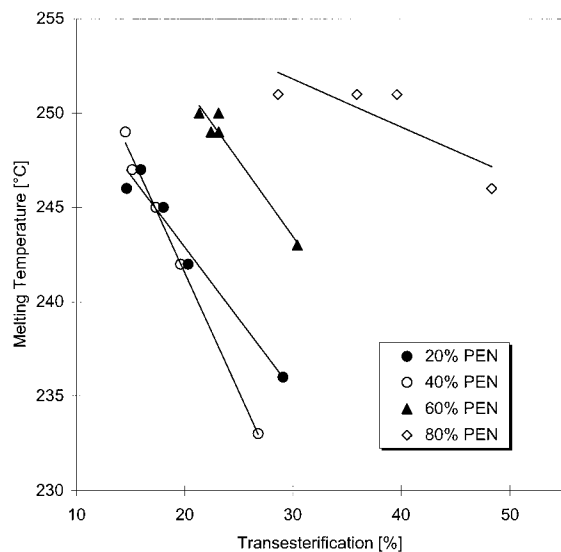
PEN Content (mol %)	Predicted $T_g$ (°C)	Measured $T_g$ (°C)
0	—	74
20	87	83
40	97	92
60	107	100
80	116	110
92	—	118
100	120	—



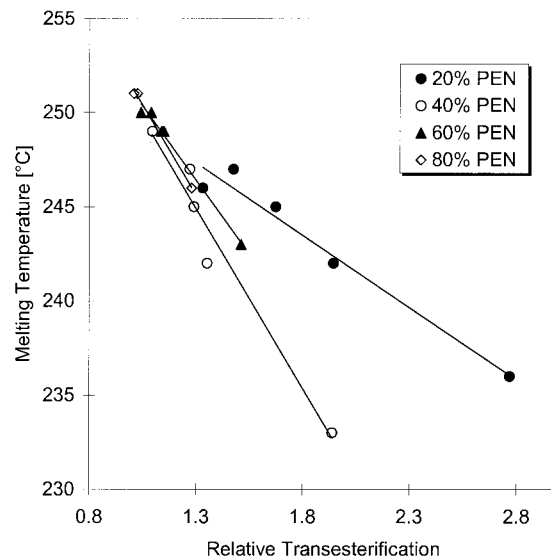
usual PET crystallization temperature any regions of PEN molecules that exist are immobile, discouraging further PET crystallization. Andersen and Zachmann<sup>9</sup> studied melt pressed blends of PET and PEN homopolymers. In their DSC investigations, double cold crystallization peaks and double melting peaks were also found in blends made by using short melt pressing times.

All blends show a single melting peak only. Because the peak temperatures of the single components are each close to 250°C, it is most likely that double melting peaks, if they occur, cannot be resolved because of their overlap.

Although the single component blends have almost the same melting peak temperature, an increase of the  $T_m$  with increasing PEN levels can still be observed over the differently reacted materials. It was previously reported<sup>24,25</sup> that non-regularity in the polyester structure decreases the melting temperature and is the reason for a decrease in melting temperature with increasing residence time and concomitant transesterification. Differences in crystallizability of heterogeneous polymers is related to the existence of distributions of crystallizable sequences of different lengths.<sup>24</sup> Crystal imperfections, which can be related to the molecular structure, will lower the heat of fusion and melting temperatures and be exploited to fractionate the material. For instance, PET containing small amounts of 1,4-cyclohexylene units as comonomer exhibits a direct correlation between the amplitude of the lower temperature melting peak with comonomer con-



**Figure 8** Melting temperature of PET/PEN blends as a function of transesterification.



**Figure 9** Melting temperature of PET/PEN blends as a function of normalized transesterification.

tent.<sup>25</sup> The fact that the PEN used for the blends is a copolymer containing 8 mol % PET units could explain why blends containing low PEN levels are more affected by changes in the transesterification than the blends of higher PEN concentrations (the PEN copolymer is initially highly transesterified). Figure 8 shows the melting behavior of the blends as a function of the degree of transesterification. The melting peak position decreases with a higher degree of transesterification. The melting point of blends containing 20–40% PEN appear to be more sensitive to the degree of transesterification (reducing significantly with increased transesterification) than blends with a higher PEN content. For blends containing 20% PEN, a change from 14.6 to 29.1% transesterification was related to a decrease of 10 K of the melting peak. In Figure 9, the same correlation is shown for the normalized transesterification. A trend line is shown for each set of data points. It can be observed that all trend lines show a similar slope and therefore a similar sensitivity to the value of normalized transesterification (the blend containing 20% PEN shows a slight difference in the slope). Hence, the melting temperature can be used to determine the degree of transesterification or relative transesterification, respectively.

Dynamic mechanical thermal analysis (DMTA) is another important way to characterize these materials. The location of the maxima of the loss modulus,  $E''$ , and the loss tangent,  $\tan \delta$ , as determined from the DMTA traces in our work, are

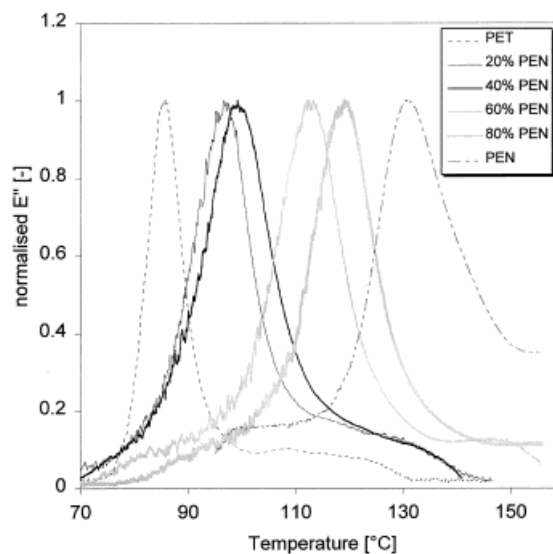
**Table III Values of  $\tan \delta$  and  $E''$  Peaks for PET/PEN Blends of Different Compositions, Produced at Different Extruder Screw Velocities, as Determined by DMTA**

Sample	$\tan \delta_{\max}$ [—]	$\tan \delta_{\max}$ [—]	$E''_{\max}$ [—]	$E''_{\max}$ [—]
Pure PEN	—	136.5	—	130.5
Pure PET	90.0	—	85.5	—
20% PEN 4 rpm	102.0	—	96.5	—
20% PEN 7 rpm	103.2	—	98.2	—
20% PEN 12 rpm	99.6	—	95.4	—
20% PEN 18 rpm	100.0	—	95.6	—
20% PEN 30 rpm	96.7	—	91.3	—
40% PEN 3 rpm	106.9	—	99.0	—
40% PEN 8 rpm	—	118.7	97.2	—
40% PEN 12 rpm	90.3	120.0	88.4	114.9
40% PEN 16 rpm	91.4	121.6	87.5	116.5
40% PEN 20 rpm	87.2	123.5	87.3	115.9
60% PEN 3 rpm	—	120.7	—	113.2
60% PEN 8 rpm	88.6	125.4	89.5	114.7
60% PEN 12 rpm	89.8	125.3	89.8	115.0
60% PEN 16 rpm	89.5	124.9	87.4	115.3
60% PEN 20 rpm	89.3	129.0	87.6	124.5
80% PEN 3 rpm	—	126.1	—	119.1
80% PEN 8 rpm	—	125.8	—	117.1
80% PEN 12 rpm	—	130.8	—	119.8
80% PEN 16 rpm	85.5	131.6	85.5	125.5

shown in Table III. Generally, the  $E''$  peak occurs at lower temperatures compared to the  $\tan \delta$  peak. Therefore, the loss modulus peak is better separated from the cold crystallization event and less influenced by such phase transformations. Additionally, it was found that the loss modulus was less noisy in this study and easier to analyze. To allow easier comparison of  $E''$  curves (absolute values are not valid in the penetration probe mode), the loss modulus was normalized by dividing all values of a given analysis by their maximum loss value (peak height).

Figure 10 illustrates the loss modulus of highly transesterified blends of different compositions and all blends show only a single peak. The loss modulus peak, which is a measure of the glass-rubber transition, is monotonically shifted to higher temperatures with increasing PEN content. This is in agreement with the  $T_g$  results determined in our work by using DSC as well as the linear correlation found by Aoki et al.<sup>26</sup> In their recent, detailed study of dynamic mechanical properties of random PET/PEN blends, it was found that the  $T_g$  is a linear function of the blend composition independent of the level of transesterification. Most of the less transesterified blends appeared broader than the more highly transesterified blends because of a greater num-

ber of underlying phases. In contrast to the work of Aoki et al.,<sup>26</sup> some of the lower transesterified blends of 40% PEN show a strong, well-separated second peak due to the minor component concentration, as illustrated in Figure 11. The sets of

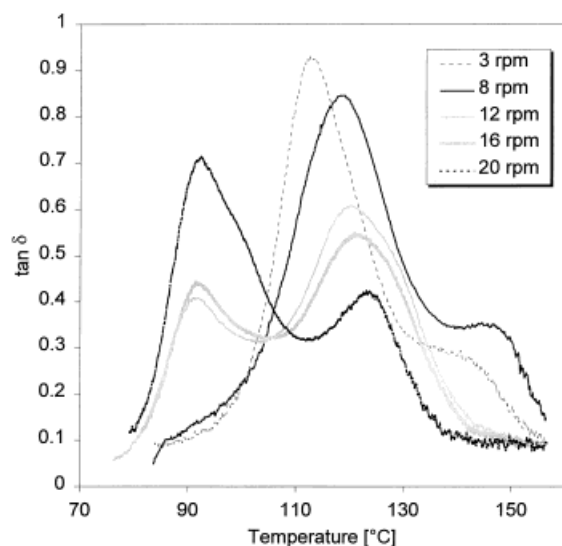


**Figure 10** Normalized loss modulus as a function of temperature for high transesterified PET/PEN blends at 1 Hz.

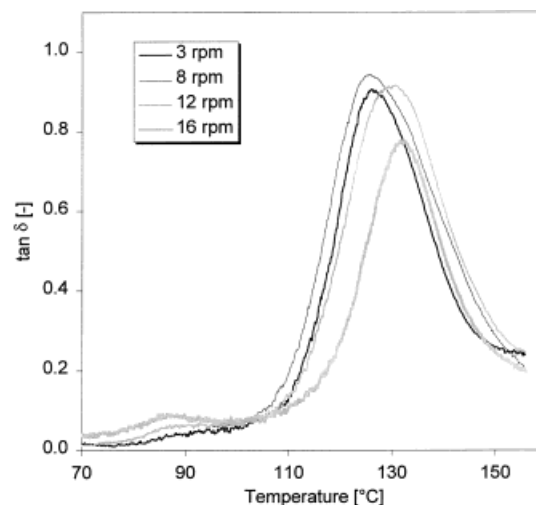
blends containing 20, 60, or 80% PEN showed only single peaks or a very small second peak of the component with the lower concentration. An example is given for the set of blends containing 80% PEN in Figure 12. The differing behavior of the blends containing 40% PEN compared with the sets of 60 and 80% PEN can be explained by the dominating influence of the PEN component, even though it was the minor phase. This was shown already in the context of the DSC analysis, where the thermal transitions of blends containing 40% PEN were strongly influenced by the PEN phase.

## CONCLUSIONS

PET/PEN blends of different levels of transesterification and blend composition were prepared from PET and a PEN copolymer containing 8 mol % terephthalic acid. A relative value of transesterification facilitated ease of comparison of properties between the different set of blend concentrations. Intrinsic viscosity measurements indicate that some substantial deviation from that determined by the rule of mixtures between the components and is ascribed to reduced molecular weight due predominantly to thermal degradation, as well as some reduction occurring because of transesterification itself. Melt viscosities of the blends were found to be synergistically lower than the viscosities of



**Figure 11**  $E'$  measured at 1 Hz as a function of temperature for PET/PEN blends containing 40 mol % PEN, produced at different extruder screw velocities.



**Figure 12**  $E''$  measured at 1 Hz as a function of temperature for PET/PEN blends containing 80 mol % PEN, produced at different extruder screw velocities.

the homopolymers and not merely an average between them, with very little difference in viscosity between high- and low-transesterified blends. It appears that any form of copolymer formed (be it the result of smaller or larger amounts of transesterification) leads to an ensemble of chains more poorly packed in the melt than expected, and hence, showed lower viscosity. The outcome of DMTA and DSC investigations were in good agreement. Although overlapping transitions were found in some cases, single- and double-thermal transitions could be used as an indication of single- and multiple-phase systems. It was found that all thermal transitions were strongly influenced by the degree of ester exchange reaction. An almost master-curve type of correlation between the melting temperature of the blend and the relative degree of transesterification was found, with the exception of the 20% PEN sample. This correlation allowed a simple, straightforward, and fast estimation of the degree of transesterification from a DSC scan for a given PET and PEN pair.

Ole Becker gratefully acknowledges the support of this work by the Deutschen Akademischen Austauschdienst (DAAD). Ian Willing from CSIRO Molecular Science is acknowledged for the NMR spectra and CSIRO for use of the Brabender extruder. The IV measurements were performed by Leading Synthetics (Australia). The CRC for Polymers is acknowledged for financial support for obtaining IV measurements.

## REFERENCES

1. Nentwig, J. *Neue Verpackungen* 1991, 12, 44.
2. Tacker, M. *Zeitschrift für Lebensmitteltechnik* 1997, 48(1-2), 48-51.
3. Teijn Ltd., U.S. Pat. 3,937,754 (1976).
4. Hoechst Celanese, WO 96/35571 (1996).
5. Continental PET Technologies, WO 95/16554 (1995).
6. Callander, D. High Performance PEN & Naphtalate Based Packaging Resins; Bev-Pak Americas'94: Tarpon Springs, FL, April 11-12, 1994.
7. Forsythe, J.; Rosu, R.; Simon, G.; Becker, O.; Harrington, J.; Damiris, J.; O'Shea, M. *Materials Research Forum* 1999; Proceedings, Australia, 25-26 November 1999.
8. Stewart, M. E.; Cox, A. J.; Naylor, D. M. *Polymer* 1993, 34(19), 4060.
9. Andresen, E.; Zachmann, H. G. *Colloid Polym Sci* 1994, 272, 1352.
10. Lee, S. C.; Yoon, K. H.; Park, I. H. *Polymer* 1997, 38, 19, 4831.
11. Guo, M.; Brittain, W. J. *Polym Prepr* 1998, 39, 385.
12. Okomoto, M.; Kotaka, T. *Polymer* 1997, 38, 6, 1357.
13. Kenwright, A. M.; Peace, S. K.; Richards, R. W.; Bunn, A.; MacDonald, W. A. *Polymer* 1999, 40, 5851.
14. Collins, S.; Kenwright, A. M.; Pawson, C.; Peace, S. K.; Richards, R. W.; MacDonald, W. A.; Mills, P. *Macromolecules* 2000, 33, 2974.
15. Becker, O.; Simon, G. P.; Rieckmann, T.; Forsythe, J.; Rosu, R.; Völker, S.; O'Shea, M. *Polymer* 2001, 42, 1921.
16. Tharmapuram, S. R.; Jabarin, S. A. ANTEC 2000—Proceedings of the 58th Annual Technical Conference and Exhibition, Vol XLVL; Orlando, FL, May 7-11, Society of Plastic Engineers, pp 2120.
17. Kyotani, M.; Pudjiastuti, W.; Saeed, A. J. *Macromol Sci—Phys* 1999, 3(B38), 197-215.
18. Lee, H. M.; Suh, D. J.; Kil, S. B.; Park, O. O.; Yoon, K. H. *Korea-Australia Rheol J* 1999, 11, 3, 219.
19. Chuang, H. K.; Hen, C. D. *J Appl Polym Sci* 1984, 29, 2205.
20. Tibbit, J. M. *Future Pac'94*, November 16-17, 1994.
21. Fox, P. J. *Bull Am Phys Soc* 1956, 2, 123.
22. Jun, H. J.; Chae, S. H.; Park, S. S.; Myung, H. E.; Im, S. S. *Polymer* 1999, 40, 1473.
23. Connor, M. T.; Garcia Gutierrez, M. C.; Rueda, D. R.; Balta Calleja, F. J. *J Mater Sci* 1997, 32, 5615.
24. Lodefien, P.; Jonas, A. M.; Legras, R. *Macromolecules* 1999, 32, 7135.
25. Medellin-Rodrigues, F. J.; Phillips, P. J.; Lin, J. S.; Avila-Orta, C. A. *J Polym Sci Polym Phys Ed* 1998, B36, 763.
26. Aoki, Y.; Li, L.; Amari, T.; Nishimura, K.; Arashiro, Y. *Macromolecules* 1999, 21, 1923.