

# Effect of the Mixing Conditions on the Phase Structure of PP/PS Blends

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## SYNOPSIS

The effect of the rate and time of mixing in a batch mixer on the phase structure of polypropylene/polystyrene (PP/PS) blends with various rheological properties of the components was studied. Regions with substantially different average sizes of the dispersed particles were found in the studied blends. Differences between the average size of the particles in individual regions of the samples persist in all blends and mixing conditions under study. No dependence of the average particle size on the rate of mixing has been obtained for the PP/PS (75/25) blends. On the other hand, decrease of the average particle size with increasing rate of mixing has been found for the PP/PS (95/5) blend. These results are discussed as a consequence of the competition between the breakup and coalescence of the dispersed particles. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

It is well known that the phase structure of immiscible polymer blends affects their properties in a decisive manner. The phase structure is determined by the composition and component properties of a blend but also by the conditions of mixing. Therefore, great attention has been given to the phase structure formation in blends during their mixing. Although much important knowledge has been obtained, present understanding of this process is still far from complete.<sup>1-3</sup> This is caused by the extraordinary complexity of the investigated problem. Recently, the phase structure formation during the first period of mixing in an extruder<sup>4-6</sup> and a batch mixer<sup>4,7</sup> was studied. In both cases, sheets of the minor phase are formed at the beginning of mixing, which, subsequently, gradually burst into fibers and droplets. Contradictions exist between the results of various studies of further development of the droplet sizes. A gradual decrease in the droplet size with increasing time of mixing,<sup>8,9</sup> independence of the droplet size on time already after a short time

of mixing,<sup>10</sup> and an inhomogeneous evolution of the phase structure<sup>11-13</sup> were found in various studies. Three different types of dependencies of the average droplet size on increasing intensity of mixing (stress and rate of deformation in the melt) were obtained: monotonic decrease,<sup>9,14-17</sup> independence,<sup>10,18</sup> and nonmonotonic dependence.<sup>19,20</sup>

Differences in results of the studies are apparently caused by the fact that formation of the phase structure is a complex process. Its course is determined by the competition between the breakup and coalescence of dispersed droplets.<sup>1,2</sup> Therefore, dependence of the size of dispersed droplets on mixing conditions is affected not only by the properties of the components but also by the composition of a blend.<sup>8,20-23</sup> Analysis of experimental results is further complicated by the possibility of chemical reactions which can change properties of the components during mixing.<sup>12</sup>

In a batch mixer, the breakup of large droplets of the dispersed phase prevails over their coalescence during the first period of mixing. After a certain time of steady mixing, the dynamic equilibrium between the breakup and coalescence is established. From experimental results of preceding studies, it follows that the phase structure is homogeneous, i.e., the area containing several hundreds of the dispersed

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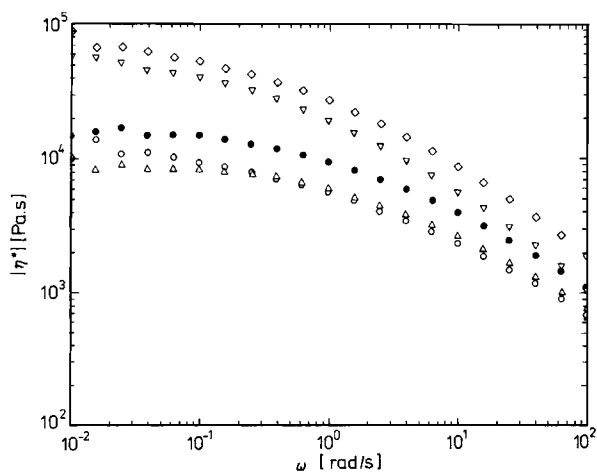
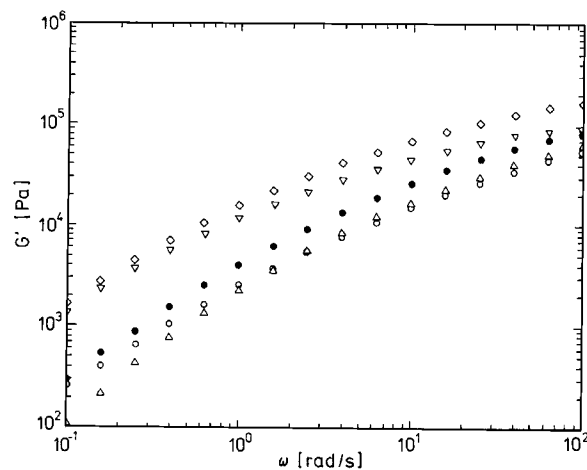
**Table I** Characteristic of the Components

Polymer	Code	$M_{10}^a$ (Nm)	$M_{20}^b$ (Nm)
Mosten 52 522	PP1	10.3	9.8
Mosten 52 422	PP2	14.0	13.4
Mosten 52 217	PP3	26.8	26.0
Krasten 127	PS1	9.0	8.3
Krasten 151	PS2	11.7	11.0

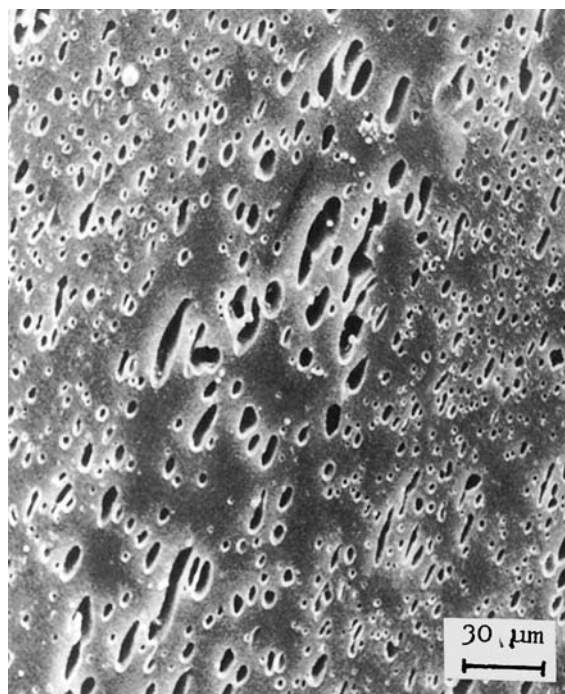
<sup>a</sup> Torque at 60 rpm and 10 min.<sup>b</sup> Torque at 60 rpm and 20 min.

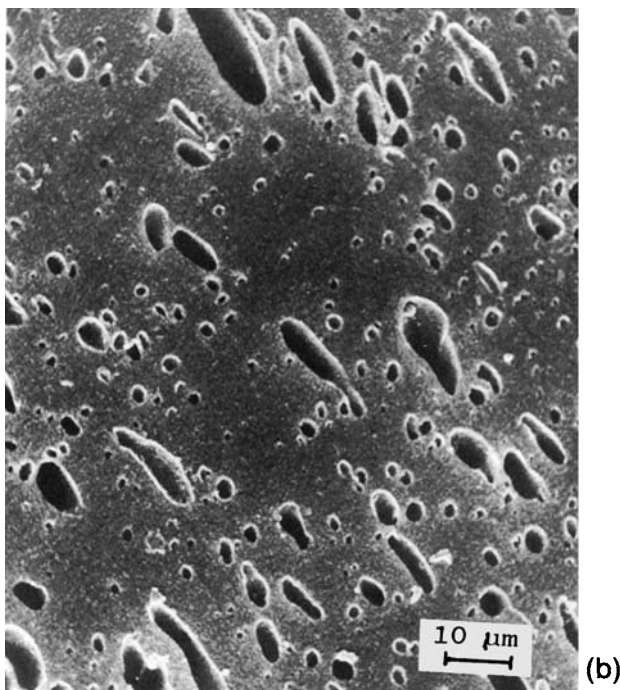
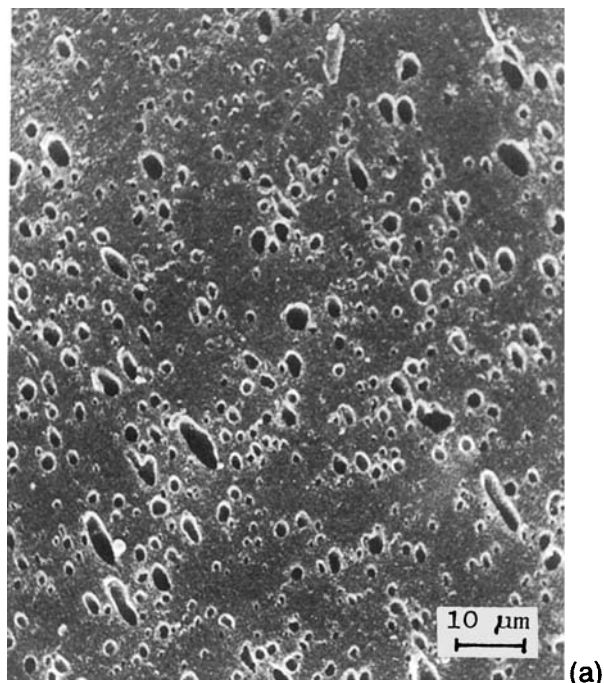
droplets can be considered as a representative one for the whole sample in this case.<sup>10,11</sup> It follows from the theoretical analysis of the phase structure formation in mixing that this conclusion is correct if characteristic times of the breakup and coalescence of droplets are longer than their residence time in places with substantially different parameters of a flow field. In the opposite case, only the local equilibrium between the breakup and coalescence is established. This leads to the droplet-size dependence on its position in a mixing chamber.

At present, there is no theory describing the time development of the size of dispersed droplets during mixing. Even the theoretical relations for the average droplet size in the steady state<sup>8,21-23</sup> are only approximate and they contain functions which are not fully determined for the mixing of viscoelastic polymers. It follows from an analysis of these theories that the droplet size should decrease with increasing intensity of mixing in the blends with a low content of the dispersed phase.<sup>20,23</sup> However, the

**Figure 1** The dependence of the absolute value of complex viscosity,  $|\eta^*|$ , on the angular frequency,  $\omega$ , for (○) PP1, (●) PP2, (◇) PP3, (△) PS1, and (▽) PS2.**Figure 2** The dependence of the storage modulus,  $G'$ , on  $\omega$  for (○) PP1, (●) PP2, (◇) PP3, (△) PS1, and (▽) PS2.

shape of the curve particle size vs. stress in mixing is dependent on the properties of components and on the blend composition for blends with higher contents of the dispersed phase.<sup>20,23</sup> For this reason, a systematic experimental study of systems with well-characterized components seems to be the best way to the elucidation of the dependence of the phase structure on mixing conditions.

**Figure 3** The phase structure of the PP1/PS1 (75/25) blend, mixed at 15 rpm for 10 min (quenched sample).



**Figure 4** The phase structure of the PP1/PS1 (75/25) blend, mixed at 60 rpm for 20 min (quenched sample): (a) area containing small particles; (b) area containing large particles.

In our preceding studies,<sup>11–13</sup> nonhomogeneous development of the phase structure was found in the polypropylene/ethylene-propylene elastomer blends. In blends mixed at a low rate for a short

time, regions with a fine phase structure and large elastomeric particles surrounded by the neat polypropylene matrix coexist. With an increasing rate and time of mixing, the number and size of the large particles gradually decrease. Eventually, the phase structure of the whole sample becomes homogeneous, i.e., an arbitrary region, containing several hundreds of dispersed particles, can be used for correct evaluation of the average size of dispersed droplets. All the studied polypropylene/ethylene-propylene elastomer blends had low interfacial tension and viscosity of the dispersed phase higher than the viscosity of the matrix. Similar studies of the effect of mixing conditions on the phase structure for the polypropylene/polystyrene (PP/PS) blends, with higher interfacial tension and viscosity of the dispersed phase lower (or comparable) than the viscosity of the matrix, are the objects of this article. Components with various rheological properties have been used. Study of the phase structure development in the PP/PS blends is also important for recycling of a mixture of common polymer wastes.

## EXPERIMENTAL

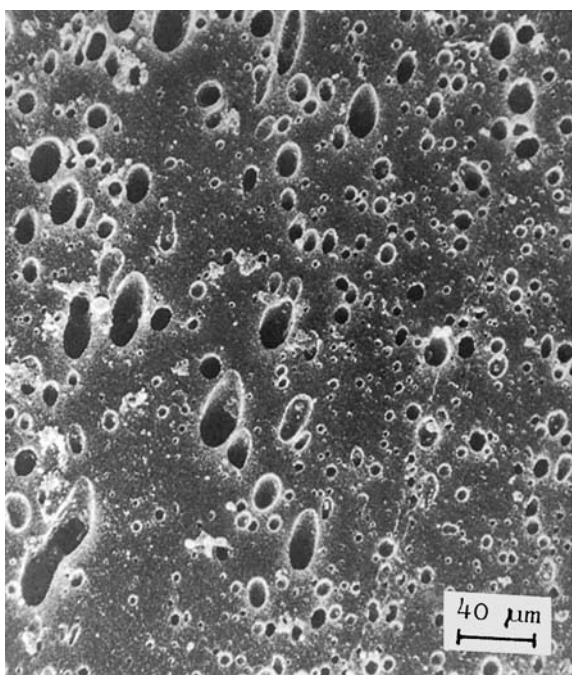
### Material

Three commercial grades of the isotactic polypropylene Mosten, manufactured by Chemopetrol, Litvínov, Czech Republic, were used in the investigation. Mosten 52 522 (PP1) and Mosten 52 422 (PP2) are injection-molding grades and Mosten 55 217 (PP3) is the blow-molding grade of PP. Two commercial grades of the PS homopolymer, Krasten 127 (PS1) and Krasten 151 (PS2), manufactured by Kaučuk Co., Kralupy, Czech Republic, were used. Krasten 127 is extended by 4.5% of naphthenic-paraffin oil. Krasten 151 does not contain any oil. Rheological properties of the polymers follow from Table I and Figures 1 and 2.

### Sample Preparation

The blends were prepared by mixing of the components in the electrically heated W50EH chamber of a Brabender Plasti-Corder at a constant temperature of 190°C in the melt. The method is described in Ref. 11. PP/PS blends containing 25 wt % of PS were mixed at 15–120 rpm for 5, 10, and 20 min. PP/PS blends containing 5 wt % of PS were mixed at 15–120 rpm for 20 min.

Samples of blends used to the investigation of the phase structure and tensile impact strength were



**Figure 5** The phase structure of the PP2/PS2 (75/25) blend, mixed at 30 rpm for 20 min (molded sample). Boundary between areas with large and small particles.

prepared by compression molding. The material from the chamber was placed in a preheated Fontijne table press. Blends were press-molded into the shape of plates at 190°C. After 6 min, the plate was transferred into the second press cooled by water.

### Tensile Impact Strength

The tensile impact strength,  $a_c$ , was determined at 23°C with the Zwick tester, which was equipped with a special fixture for test specimens according to DIN 53448. The maximum energy of pendulum was 4 J. Test specimens were cut from the press-molded plates. Values of  $a_c$  were determined as arithmetic means of measurements on 12 specimens. The relative probable error of measurement,  $\rho$ , was determined as

$$\rho = E/a_c \quad (1)$$

where the probable error,  $E$ , is defined by<sup>24</sup>

$$E = 0.8453 \sum \Delta / [n(n-1)^{1/2}] \quad (2)$$

$\sum \Delta$  is the sum of the absolute values of deviations of measured values from average ones and  $n$  is the number of measurements.

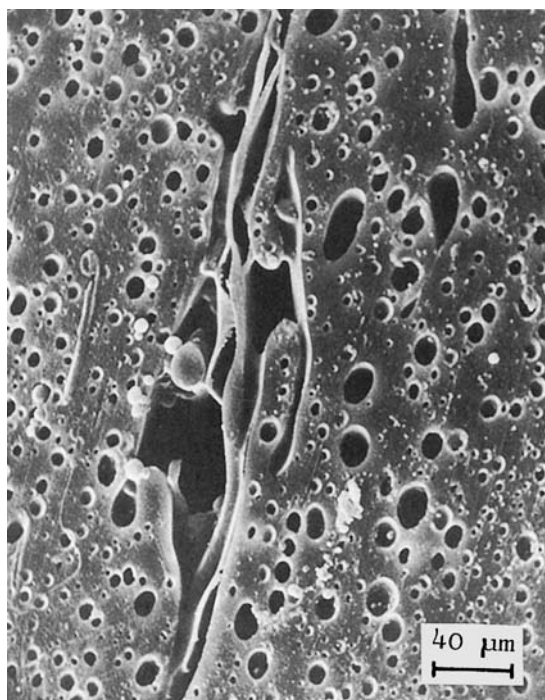
### Phase Structure

The phase structure of the compression-molded samples and samples quenched in cold water immediately after cessation of mixing was studied by the method described in Refs. 11 and 20. The scanning electron microscope JSM 35 in the secondary electron mode at the accelerating voltage 25 kV was used. The samples were cut with a glass knife in a vessel filled with liquid nitrogen. PS was etched off the sample surface with toluene.

The size of the particles was determined from one or several microphotographs containing several hundreds particles. The perimeters and planar areas of the particle image were determined by a mini MOP image analyzer (Kontron Co., Germany). The phase structure of the samples was characterized by the mean radius  $\bar{r}$  of the circles having the same perimeter and by the mean square radius  $\overline{r^2}$  of circles having the same area as the investigated particle image. Both  $\bar{r}$  and  $\overline{r^2}$  were calculated using the relations

$$\bar{r} = p / (2\pi n) \quad (3)$$

$$\overline{r^2} = A / (\pi n) \quad (4)$$



**Figure 6** The phase structure of the PP1/PS1 (75/25) blend, mixed at 15 rpm for 10 min. Breakup of long fiber.

**Table II** Dependence of the Phase Structure and Tensile Impact Strength on Mixing Conditions for the PP1/PS1 (75/25) Blend

$\Omega^a$ (rpm)	$t^b$ (min)	$(\bar{r}^2)^{1/2}^c$ ( $\mu\text{m}$ )	$P^d$	$a_c^e$ ( $\text{kJ/m}^2$ )	$\rho^f$ (%)
15	5	8.36	1.28	9.08	21.1
15	10	2.78	1.20	8.10	3.8
15	20	2.54	1.18	8.50	1.8
30	5	2.39	0.64	11.13	15.9
30	10	3.14	1.19	8.60	1.4
30	20	3.80	1.14	7.74	2.5
45	20	2.45	1.22	7.59	2.8
60	5	—	—	6.64	13.5
60	10	2.93	1.04	7.82	1.1
60	20	2.98	1.18	8.71	1.6
90	5	2.80	1.18	7.38	2.8
90	10	2.80	1.12	9.11	1.8
90	20	3.05	1.12	8.23	2.9
120	5	3.16	1.01	9.80	2.6
120	10	2.55	1.07	8.47	4.3
120	20	—	—	8.05	2.7

<sup>a</sup>  $\Omega$  = rate of mixing.

<sup>b</sup>  $t$  = time of mixing.

<sup>c</sup>  $(\bar{r}^2)^{1/2}$  = the mean square radius of particle image determined from eq. (4).

<sup>d</sup>  $P$  = polydispersity parameter determined from eq. (5).

<sup>e</sup>  $a_c$  = tensile impact strength.

<sup>f</sup>  $\rho$  = relative error of measurement of  $a_c$  determined from eq. (1).

where  $p$  is the total perimeter;  $A$ , the total area; and  $n$ , the number of particle images in the investigated domain of the sample. The parameter  $P$ , defined as

$$P = (\bar{r}^2)^{1/2} / \bar{r} \quad (5)$$

was also used in this study.  $P$  is larger than 1 for the system of circles with different diameters and smaller than 1 for an assembly of monodisperse images having a shape other than circular.<sup>11,20</sup>

### Rheological Characterization of the Components

The dynamic mechanical characteristics of all the components were measured at 190°C using a Rheometrics System Four rheometer. The measurements were carried out in the cone and plate geometry in the frequency range  $10^{-2}$ – $10^2$  rad/s. The dependencies of the absolute value of complex viscosity,  $|\eta^*|$ , and storage modulus,  $G'$ , of the polymers on frequency are plotted in Figures 1 and 2. The torque,  $M_{10}$  and  $M_{20}$ , after 10 and 20 min of mixing at 60 rpm and 190°C, can be used as an additional rheological characteristic of the components (see Table I).

## RESULTS AND DISCUSSION

It can be seen from Figures 3–6 that the phase structure of the PP/PS blends is inhomogeneous. Areas, usually bands (see Fig. 3), with strictly different average size of PS particles coexist in studied blends. This is different from the polypropylene/ethylene-propylene elastomer [PP/EP(D)M] blends, where isolated large particles and thoroughly mixed places were found. Surprisingly, a homogeneous phase structure, i.e., the structure where any area containing several hundreds of particles is representative for the whole sample, has not been achieved for any blend in any conditions of mixing. A highly inhomogeneous distribution of the PS phase was found in the samples mixed at a low rate for a short time. Existence of these inhomogeneities is manifested by the higher values of the relative error of the measured values of tensile impact strength (cf. Tables II–V). In these samples, large individual particles, typical of PP/EP(D)M blends, were also sporadically found. In some cases, these particles are elongated into long fibers. Besides the range of very short times and low rates of mixing, unambiguous dependence on the rate and time of mixing was found neither for the phase structure nor for the impact strength. With samples quenched immediately after the cessation of mixing, differences appear not only in sizes but also in anisometry of the particles in different areas of the sample.

It can be seen from Tables II–V that the average particle radius has a large scatter in the PP/PS (75/25) blends. The scatter is caused by the fact that the available method of particle-size evaluation does not make it possible to evaluate more than several hundreds particles per sample. Although we have used a representative area of the sample, i.e., an area with average size of the particles or an average value from areas with large and small particles for the evaluation, we did not avoid a considerable scatter of the results. Evaluation of large areas of the sample, containing several tens of thousands of the particles, is apparently the necessary condition for obtaining of a reliable average particle radius. It follows from Tables II–V that the investigated PP/PS (75/25) blends have no apparent dependence of the particle size on the time or on the rate of mixing. These conclusions are valid for the average particle size in the samples quenched after cessation of the mixing as well (see Table VI).

It follows from comparison of the average particle sizes in Tables II–IV that their size decreases with increasing viscosity of the PP matrix. However, this

**Table III Dependence of the Phase Structure and Tensile Impact Strength on Mixing Conditions for the PP2/PS1 (75/25) Blend**

$\Omega$ (rpm)	$t$ (min)	$(\bar{r}^2)^{1/2}$ ( $\mu\text{m}$ )	$P$	$a_c$ ( $\text{kJ/m}^2$ )	$\rho$ (%)
15	5	—	—	6.4	6.9
15	10	2.37	1.10	5.9	8.9
15	20	2.28	0.92	7.1	4.7
30	5	2.98	0.95	6.9	4.9
30	10	2.95	0.99	6.7	3.0
30	20	1.98	1.01	7.2	1.9
60	5	2.28	0.87	6.3	6.4
60	10	2.46	1.05	8.0	4.5
60	20	1.88	0.96	5.8	3.5
90	5	2.26	1.11	7.6	3.7
90	10	1.67	0.96	7.1	3.6
90	20	1.73	0.98	7.4	3.7
120	5	2.25	0.92	7.0	2.7
120	10	3.07	1.04	8.3	4.6
120	20	3.27	1.06	7.8	3.9

The symbols used in Table III represents the same physical quantities as in Table II.

decrease is substantially smaller than in the PP/EPM blends.<sup>11</sup>

A comparison of  $(\bar{r}^2)^{1/2}$  values for the compression-molded and quenched samples shows that the radius of the dispersed particles is higher in the compression-molded samples than in the quenched ones for all the blends under study. The ratio of the particle radii of the compression-molded and quenched samples is about 1.5. Coarsening of the

phase structure in the compression-molded, i.e., slower-cooled, samples is caused by the coalescence<sup>25</sup> in their melt and/or fusion of the PS particles due to their removal from the spherulite area at slow crystallization of the PP matrix.

In Table VII, morphological characteristics of the compression-molded samples of the PP/PS (95/5) blends are given. Also, these samples contained areas with different sizes of the dispersed particles. For

**Table IV Dependence of the Phase Structure and Tensile Impact Strength on Mixing Conditions for the PP3/PS1 (75/25) Blends**

$\Omega$ (rpm)	$t$ (min)	$(\bar{r}^2)^{1/2}$ ( $\mu\text{m}$ )	$P$	$a_c$ ( $\text{kJ/m}^2$ )	$\rho$ (%)
15	5	2.27	0.99	12.29	4.8
15	10	1.82	1.03	12.86	3.4
15	20	1.37	0.96	12.74	2.6
30	5	2.51	1.01	13.08	8.3
30	10	1.17	1.00	12.86	3.5
30	20	1.86	1.00	11.79	3.2
60	5	2.70	1.07	14.61	2.5
60	10	2.37	1.01	9.02	5.7
60	20	—	—	10.71	2.6
90	5	2.24	1.02	14.61	3.7
90	10	1.74	0.97	11.33	3.7
90	20	2.97	1.07	13.93	3.2
120	5	3.08	0.96	—	—
120	10	3.30	1.06	8.46	9.3
120	20	0.95	0.95	8.91	9.1

The symbols used in Table IV represents the same physical quantities as in Table II.

**Table V Dependence of the Phase Structure and Tensile Impact Strength on Mixing Conditions for the PP2/PS2 (75/25) Blends**

$\Omega$ (rpm)	$t$ (min)	$(\bar{r}^2)^{1/2}$ ( $\mu\text{m}$ )	$P$	$a_c$ ( $\text{kJ/m}^2$ )	$\rho$ (%)
15	5	3.78	1.10	3.97	12.6
15	10	4.65	0.98	7.24	3.5
15	20	3.14	0.94	8.52	2.5
30	5	5.52	0.99	7.67	7.0
30	10	4.54	0.81	7.56	1.4
30	20	3.17	1.01	8.31	1.1
60	5	4.55	1.00	6.27	6.6
60	10	4.21	0.99	8.20	4.1
60	20	4.17	0.97	6.97	2.2
90	5	2.70	0.94	7.18	4.3
90	10	4.52	1.04	7.29	3.0
90	20	2.47	0.93	8.47	1.3
120	5	3.60	0.99	7.29	2.2
120	10	3.36	0.93	7.77	3.0
120	20	3.15	0.96	7.93	2.6

The symbols used in Table V represents the same physical quantities as in Table II.

this reason, for plausibility of the average particle radii, determined for the PP/PS (95/5) blends, the same conclusions as for the PP/PS (75/25) are valid. Nevertheless, it can be seen from Table VII that the size of the dispersed particles decreases with an increasing rate of mixing. This is in agreement with the conclusion that the particle size decreases with an increasing rate of mixing for the blends with a low content of the dispersed phase. This conclusion follows from the analysis of theoretical expressions for the particle size in a steady flow.<sup>20,23</sup> Decrease of the particle size with increasing viscosity of the matrix also follows from Table VII for PP/PS (95/5) blends. (Samples mixed at the same conditions should be compared.)

Knowledge of the relation between the rate of mixing and the average stress in a mixed blend is the necessary condition for a correct interpretation of the dependence of the phase structure on the rate of mixing. It is well known that the flow field in the chamber of a Plasti-Corder is complex.<sup>26,27</sup> It is position-dependent and it also has a substantial elongational component besides the shear. Nevertheless, considering the phase structure formation in polymer blends, the flow field in the chamber is frequently described as a shear field with an average shear rate related to the kneader revolutions and average stress related to the measured torque. Dependencies of the torque,  $M$ , on kneader revolutions,

$\Omega$ , and shear stress,  $\tau$ , measured by a capillary or rotational viscometer, on shear rate,  $\dot{\gamma}$ , were compared for several polymers and kneading chambers.<sup>28,29</sup>

Miles and Zurek<sup>29</sup> found the linear relations

$$\dot{\gamma} = k_1 \Omega \quad (6)$$

$$\tau = k_2 M \quad (7)$$

with  $k_1 = 4.5$  and  $k_2 = 0.05$  for PS. Lee and Purdon<sup>28</sup> also found linear relations between  $\dot{\gamma}$  and  $\Omega$  and  $\tau$  and  $M$ . However, from their analysis, it follows that values of  $k$  parameters are dependent on the slope of  $\log \tau$  vs.  $\log \dot{\gamma}$  dependence. Moreover, different  $k$  parameters for PS and high-impact PS were found. Using the Lee and Purdon coefficients leads to lower values of  $k_1$  than 4.5 (type of chamber is not specified in Refs. 28 and 29).

It follows from the preceding discussion that the values of viscosities measured at about 100 rad/s can be used for qualitative comparison with torques at  $\Omega = 60$  rpm. It can be seen from Table I that  $M_{PP3} > M_{PP2} > M_{PS2} > M_{PP1} > M_{PS1}$  and from Figure 1 that  $\eta_{PP3} > \eta_{PP2} \sim \eta_{PS2} > \eta_{PS1} \sim \eta_{PP1}$ . The torques of both PS samples seem to be shifted to lower values in comparison with the values predicted from related viscosities under the assumption that the same relation between  $\eta$  and  $M$  is valid for PS and PP. Two possible reasons for this fact exist: (i) dependence of  $k_1$  on polymers under study,<sup>28</sup> and (ii) difference in the extent of degradation between various samples during mixing. Certainly, degradation during mixing (it is manifested by the difference between  $M_{10}$  and  $M_{20}$  for individual samples—see Table I) is more pronounced than in the viscosity measurement in a dynamic mode where mechanical loading is much weaker.

**Table VI Dependence of the Particle Size on the Mixing Rate for Quenched Samples of the PP/PS (75/25) Blends Mixed for 20 Min**

$\Omega$ (rpm)	$(\bar{r}^2)^{1/2}$ ( $\mu\text{m}$ )			
	PP1/PS1	PP2/PS1	PP3/PS1	PP2/PS2
15	1.10	1.52	0.87	2.04
30	2.35	1.83	1.61	—
60	1.03	1.03	1.92	1.12
90	1.37	1.14	1.41	1.98

The symbols used in Table VI represent the same physical quantities as in Table II.

**Table VII** Dependence of the Particle Size on the Rate of Mixing for Compression-molded Samples of the PP/PS1 (95/5) Blends Mixed for 20 Min

$\Omega$ (rpm)	$(\bar{r}^2)^{1/2}$ ( $\mu\text{m}$ )		
	PP1/PS1	PP2/PS1	PP3/PS1
15	—	0.54	0.46
30	0.70	0.44	0.44
60	0.56	0.39	0.30
90	0.41	0.39	—

The symbols used in Table VII represent the same physical quantities as in Table II.

It can be seen from Table VIII, containing the torques of the PP/PS blends after 20 min of mixing, that for all blends the torque increases with an increasing rate of mixing at low mixing rates. Maximum of the torque is achieved at a mixing rate between 60 and 90 rpm. At higher rates of mixing, the torque decreases. Decrease in the torque at high rates of mixing is apparently caused by the degradation of the PP matrix in long intensive loading. In this case, the viscosity gradually decreases with an increasing rate and time of mixing. This effect, which substantially complicates interpretation of the phase structure development, was studied in more detail<sup>12</sup> for the PP/EPDM blends.

It follows from the comparison of the torque values for the neat PPs and PP/PS (75/25) blends that PS1 drastically decreases the torque of the PP/PS1 (75/25) blends (cf. Tables I and VIII). The effect is especially strong for the PP3/PS1 (75/25) blend. The dependence of the torque of PP3/PS1 blends on their composition at a constant rate of mixing shows a high negative difference from the additivity rule in the whole composition range.<sup>30</sup> This type of dependence of the torque or viscosity of immiscible polymer blends on their composition is quite frequent.<sup>31,32</sup> Usually, it is explained as a consequence of the slippage on the components interface.<sup>32</sup> The formation of the PS layer on the surface, which can be deduced from small differences between the  $M_{20}$  of neat PS and related PP/PS blends, is not probable. Migration of PS into the surface layer in the Plasti-Corder chamber is prevented by intensive distributive mixing. Moreover, at some compositions of PP/PS blends, lower torques than in neat PS were found.<sup>30</sup>

Among torques of various PP/PS1 (75/25) blends, substantially smaller differences were found than between the torques of related neat PPs. This fact

can be explained by the surprisingly small effect of viscosity of the PP matrix on the size of the dispersed droplets in the PP/PS (75/25) blends. Droplet size is determined by the competition between their breakup and coalescence.<sup>1,2,6,21-23</sup> Breakup of the dispersed droplets is controlled by the viscosity ratio of the components and by the capillary number,  $Ca$ , defined as<sup>1,2,6</sup>

$$Ca = \tau r / \sigma \quad (8)$$

where  $\sigma$  is the interfacial tension. For blends with the matrix viscosity higher (or comparable) than the viscosity of the dispersed phase, droplet breakup is not too sensitive to the viscosity ratio<sup>1,2,31</sup> and breakup frequency increases with increasing  $Ca$ . The increase in  $Ca$  leads also to a decrease in probability of the droplet fusion after their collision.<sup>16</sup> Therefore, at a constant rate of mixing and constant interfacial tension, decrease in the size of the dispersed droplets is controlled by the increase in the stress. For blends with higher contents of the dispersed phase, stress in the blend<sup>6</sup> (not in the neat matrix) should be substituted into eq. (8). According to eq. (7),  $\tau$  in a blend is related to the blend torque. Differences between  $Ca$  (at constant  $r$ ) in PP/PS (75/25) blends are therefore substantially smaller than in dilute blends where  $Ca$  is controlled by the torques (or viscosities) of the related neat PP.

The persistence of the areas (containing more than several hundreds of particles) with a considerably different average size of the dispersed particles, even after a long intensive mixing, is surprising. So far, a similar effect has not been described in the literature. Two reasons, both associated with the residence time distribution of the volume element of blends in the chamber of a Plasti-Corder, can cause this effect. It is well known<sup>26,27</sup> that the characteristics of the flow field are dependent on the position in the chamber. Elements of the blend go through the areas, where different stresses are operating. The deformation history of a volume element can be characterized by the residence time distribution in the places with different stress. After a certain time of mixing, the times spent by all elements in places with a certain stress are approximately equal and the system will reach the steady-phase structure. If the residence time of a droplet in a place with a certain stress is shorter than the characteristic time of the breakup and/or coalescence of the droplets, distribution of the droplet sizes will be the same in the whole sample. In the opposite case, only the local dynamic equilibrium between breakup and coalescence of the droplets is estab-



**Table VIII** Torques of the PP/PS (75/25) Blends After 20 Min of Mixing

$\Omega$ (rpm)	$M$ (Nm)			
	PP1/PS1	PP2/PS1	PP3/PS1	PP2/PS2
15	4.5	4.9	8.0	10.0
30	5.8	6.9	12.0	12.7
60	8.9	8.4	12.2	14.0
90	8.5	13.5	12.8	12.1
120	8.8	8.2	11.0	12.4

The symbols used in Table VIII represent the same physical quantities as in Tables I and II.

lished and the droplet-size distribution in the mixing chamber is position-dependent. In the latter case, material containing areas with different average sizes of the particles is formed. In the former case, inhomogeneity of the sample can be caused by a too short residence time of the volume elements containing large particles in the places where high stress is operative. This effect is probably responsible for inhomogeneity which was found in the PP/EP(D)M blends mixed at a low rate for a short time.<sup>11-13</sup> In this case, the homogeneity of the phase structure should increase with increasing time of mixing, as was observed for the PP/EP(D)M blends.<sup>11-13</sup> Of course, an increase in the phase structure homogeneity can be retarded by a gradual decrease in the stress, i.e., torque, in a blend. The decrease was rather strong at higher rates of mixing for the blends under study.

At present, there exists only limited knowledge about trajectories of the individual volume elements in the Plasti-Corder chamber, about dynamics of the droplet breakup in complex flow fields, and about coalescence in blends with a higher content of the dispersed phase. Therefore, it is difficult to decide whether the residence times of the volume elements in a region with different characteristics of the flow field are longer than are the characteristic times of the breakup and coalescence in the studied systems. Experimentally, if the residence times are shorter than breakup and coalescence times, the inhomogeneities should gradually disappear with increasing time of mixing. In the opposite case, inhomogeneities are time-independent but they should gradually disappear with the increasing rate of mixing. Unfortunately, degradation of the PP matrix prohibits, for the system under study, the decision about the reason for the inhomogeneities with the help of long time mixing. We believe that further possible explanations of the inhomogeneous phase structure,

such as the method of chamber filling, are not plausible, because they cannot explain negligible differences between the phase structure of the samples after 5 (when blends are fully molten) and 20 min of mixing.

## CONCLUSIONS

Regions, containing several hundreds of the dispersed particles, with substantially different particle sizes were found in the PP/PS blends with the PP matrix, mixed in the chamber of a Brabender Plasti-Corder. These regions also persist in the blends mixed intensively for a rather long time. There are two tentative explanations of the effect: (a) characteristic times of the particle breakup and coalescence are shorter than its residence time in the regions with different stress, and (b) volume elements with large particles did not spend enough time in the places where high stress is operative. Fine homogeneous dispersion is not achieved in the samples intensively mixed for a long time due to the degradation of the PP matrix.

The decrease in the average particle size with increasing rate of mixing was obtained for the PP/PS (95/5) blends. No systematic dependence of the particle size on the rate of mixing was found for the PP/PS (75/25) blends. These results confirm conclusions following from the theory based on the competition between particle breakup and coalescence.

The size of the dispersed particles is higher for the compression-molded than for the quenched samples. This is caused by the coalescence and/or by the transfer of the dispersed particles during slower crystallization of the PP matrix.

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