# Improved Dispersive Mixing through Reduction in Flow Field Vorticity 

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## Synopsis


#### Abstract

Dispersive mixing is most efficiently accomplished with pure straining flow. Vorticity in the flow field inhibits this extending action; accordingly, the presence of shearing flow will decrease the overall effectiveness of dispersive mixing processes. A method to reduce the vorticity by inducing lubricated flow through development of a nonuniform distribution of the components of a polymer blend is described.


## INTRODUCTION

Very generally, mixing requires incorporation, distribution, and dispersion of the ingredients. Although in practice mixing operations are often empirically based on accumulated experience, considerable research attention has focused on this subject. With the exception of the mechanism by which filler is incorporated into a polymer melt, ${ }^{1,2}$ the incorporation step has been largely ignored, notwithstanding indications of its significance. ${ }^{3}$ Distributional ("extensive") mixing, on the other hand, has been evaluated for the case of laminar flow of polymeric fluids in the absence of dispersion. ${ }^{4}$ The extent of such mixing can be related to the development with time of the interfacial area between the components. For shear flow, this interfacial area, $A$, increases with mix time, $t$, according to

$$
\begin{equation*}
A=A_{0} \varepsilon t / 2 \tag{1}
\end{equation*}
$$

while for elongational flow

$$
\begin{equation*}
A=4 / 5 A_{0} \exp [\dot{\epsilon} t / 2] \tag{2}
\end{equation*}
$$

where $A_{0}$ is the initial interfacial area and $\dot{\epsilon}$ the deformation rate. The energy dissipated under these conditions is then

$$
\begin{equation*}
E=(4 \eta / t)\left(A / A_{0}\right)^{2} \tag{3}
\end{equation*}
$$

for simple shearing and for elongational flow it is given by

$$
\begin{equation*}
E=(12 \eta / t)\left(\ln \left[5 A / 4 A_{0}\right]\right)^{2} \tag{4}
\end{equation*}
$$

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where $\eta$ is the melt viscosity. This model predicts a much greater degree of extensive mixing for elongational flow than for shear flow with equivalent mix energies.

This report is concerned with the dispersive mixing of polymeric materials, whereby filler particles or blend components are reduced in size to the micron level or less. This dispersion is accomplished by subjecting the material to the high stresses accompanying its flow in, for example, an internal mixer, extruder, or calender. The details of how the induced flow brings about this dispersion, and the relative effectiveness of various types of flow fields, have been the subject of numerous investigations. ${ }^{5-16}$ In these studies typically individual particles are introduced into a well defined flow field, and the deformation rate is slowly accelerated until bursting. This particle breakup is then correlated with the level of stress generated by the flow field. The most versatile of these type experiments have been carried out in a four-roll apparatus, ${ }^{17}$ wherein the particle is centered between rollers whose relative rate and direction of rotation determine the nature of the two dimensional flow field. Specifically, the velocity gradient for a particle at the origin of a Cartesian coordinate system, each quadrant of which is occupied by a roller, is given by

$$
\dot{\epsilon}=G / 2\left\{\begin{array}{ccc}
1+\alpha & 1-\alpha & 0  \tag{5}\\
-1+\alpha & -1-\alpha & 0 \\
0 & 0 & 0
\end{array}\right\}
$$

where the ratio of the straining to the vorticity is given by

$$
(1+\alpha) /(1-\alpha)
$$

and $G$ is the roll speed. The abundant experimental and theoretical results accumulated on the dispersion of Newtonian fluid particles suspended in flowing Newtonian liquids demonstrate that a rotational component present in the flow inhibits breakup, particularly when the viscosity of the suspended droplet exceeds that of the fluid medium. The parameter $\alpha$ can thus be seen to reflect the strength of the flow field. Extensional flows $(\alpha=1)$ are capable of effecting dispersion at the lowest stresses (these stresses are commonly normalized by the surface tension since it is the restoring force which the flow field must overcome to fragment a particle), while pure rotation ( $\alpha=-1$ ) represents the other extreme, wherein flowing particles merely change their orientation but are not deformed (in the absence of inertial effects). Although the rheological characterization of fluids is usually carried out in shearing deformation, this flow type, being the superposition of extension and rotation (i.e., $\alpha=0$ ), is relatively weak. For example, a single droplet of a Newtonian liquid suspended in a continuous medium cannot be broken up by steady-state simple shear flow when the viscosity of this medium becomes significantly less than that of the dispersed particle, regardless of the magnitude of the shear stress exerted on it. ${ }^{6}$

These previous studies have been principally concerned with dispersion of isolated droplets at a stagnation point in steady flow fields. Under these idealized conditions insight into the basic mechanisms operative during mixing can be gained; however, distinct differences exist in realistic mixing
environments. For example, transients in the applied flow will destabilize the particle. ${ }^{6}$ Nonnegligible dispersed phase concentrations will also alter the observed dispersion behavior. Neighboring particles shield to some degree a given particle from the imposed flow with consequent reduction in local stresses, while at the same time the shear strains which develop in the continuous phase may be amplified by the presence of a high concentration of dispersed droplets, particularly if the latter are relatively viscous. The critical stress necessary for particle breakup will thus exhibit a complicated dependency on the dispersed phase concentration.

There is another, somewhat subtle, problem with model studies of dispersion. The particle of interest is invariably located at a stagnation point (in order to facilitate its observation); consequently, the fragments produced upon bursting are swept away. This eliminates any potential reformation of the original droplet. In actual mixing situations, however, the occurrence of coalescence of dispersed domains has been demonstrated to often be very extensive, even for polymeric fluids. ${ }^{18}$ Similarly reagglomeration of dispersed carbon black is a well established phenomenon, with observable influence on material properties. The implication of this potential coalescence is that not only must a critical stress be exerted to effect breakup, but obtaining of high dispersion also requires development of sufficient strain in the flow field. Particle reformation is thereby avoided by flow-induced separation and distribution of the fragmentation products.
It can be seen that a critical strain requirement for dispersion will lead to an energy criterion for mix quality if the local applied stresses are always sufficient to cause particle breakup and moreover are comparable for various mixers. This latter is conceivable if the stresses are limited by the adhesion that develops at the polymer/mixer interface. This adhesion is governed primarily by the temperature dependence of the frictional coefficient for the mixer surface. If the critical stress for particle breakup is low, good dispersion then only requires that the mixing continue long enough to expose all of the dispersed phase to the regions of high stress. In support of an energy criterion for mix quality, for example, it has been reported that the carbon black dispersion obtained after mixing rubber stocks in a variety of commercial mixers was found to be a single function of the energy of mixing. ${ }^{19}$ In all cases the stresses generated were evidently sufficiently high. The process of mixing is accomplished by the flow bringing all particles to the high stress regions of the mixer and subsequently ensuring separation of the fragments produced after the particle bursts.
A purpose of the investigation reported herein was to explore the effectiveness of different flow field types on the efficiency of mixing polymer melts with a high concentration of a dispersed phase of carbon black. In this case the viscosity ratio of the phases is infinite, and consequently, differences in the relative strength of shearing and extensional flow fields are expected to be magnified. An energy criterion is used to evaluate the results since, however tentative its fundamental validity, it is most useful from a practical point of view. An approach to improved mixing efficiency by the reduction of the degree of vorticity (i.e., higher $\alpha$ ) of the dispersion process is described. This is accomplished by reducing the frictional forces developed between the polymer and the mixer walls under the specific conditions prevailing during processing.

TABLE I
Conical Die Geometry

| Entrance radius (mm) | Exit radius (mm) | Convergence angle (deg) |
| :---: | :---: | :---: |
| 4.76 | 1.27 | 10 |
| 4.76 | 1.27 | 30 |
| 4.76 | 1.27 | 45 |
| 4.76 | 1.27 | 60 |
| 4.76 | 1.27 | 180 |

## EXPERIMENTAL

An SBR (styrene-butadiene copolymer) carbon black masterbatch (Firestone Tire and Rubber Company's Mastermix MX1847 with 82.5 phr N339 carbon black and 62.5 phr oil) was used for the conical die mixing experiments. This compound is ideally suited for dispersive mixing studies since the carbon black is already incorporated and uniformly distributed throughout the rubber matrix, but the particles are existent as large aggregates. Blends samples were prepared, both without filler and with 50 phr N326 carbon black, by mixing on an unheated two roll mill an SBR (Firestone S1502) with low levels of polydimethylsiloxane (PDMS) obtained from the Dow Chemical Company (Silastic 430).

Mixing in different flow fields was studied by using conical dies of different converging angles (Table I) attached to a constant pressure reometer (Monsanto Automated Capillary Rheometer). Flow in a converging die combines shearing near the die walls with elongational flow in the central region. The total deformation, defined as the ratio of the final to initial cross-sectional area of the die, was for all dies equal to $1400 \%$. By lubricating the die walls with silicone grease, the shear stress can be reduced to zero, generating essentially extensional flow with a deformation rate that increases as the melt proceeds through the die. ${ }^{20}$ Flow rates were measured at $100^{\circ} \mathrm{C}$ for various applied pressures. The die swell resulting from this tube flow was determined by monitoring the extrudate shrinkage. For blend samples, the steady-state apparent shear viscosities were extracted from the measured pressure drop in a constant flow rate rheometer (Instron 3211). Dynamic viscosities were characterized with an automated Rheovibron using a sandwich shear geometry. The specimen dimensions (circa 1.2 mm thick with typically a $6 \mathrm{~mm}^{2}$ area) were chosen to minimize the load and thus the effect of load cell compliance. Samples were bonded to the shear fixture for dynamic testing with a cyanoacrylate adhesive.

The degree of "macrodispersion" of the carbon black stocks was assessed from roughness analysis of cut surfaces of the materials after curing. Using a Federal Products Model 2000 Surf-Analyzer System, a carbon black dispersion index can be calculated from the frequency of peaks (which correspond to deflection of the stylus as it traverses an undispersed filler particle at the surface) and the peak amplitudes. This dispersion index is a measure of the percentage of carbon black existing as particles smaller than $10 \mu \mathrm{~m}$ in size. The mix quality of a carbon black-filled elastomer can also be judged from the magnitude of the dynamic elastic modulus measured at low strains. This
modulus will reflect the state of agglomeration of the carbon black. This degree of connectivity of the dispersed filler is referred to as the microdispersion, since it relates to the structural arrangement of particles on a submicron scale, whereas the macrodispersion described by the dispersion index measures breakup of filler aggregates down to the submicron level. The electrical conductivity of carbon black-reinforced polymers is also strongly influenced by the extent of microdispersion. Conductance measurements were made on samples by painting the ends of test specimens with colloidal silver and affixing wires for connection to a resistance meter.
Adhesion measurements in the 180 degree peel geometry were carried out on peroxide crosslinked samples ( 0.5 phr Vulcup R) prepared by molding two sheets of the material together for 30 minutes at $150^{\circ} \mathrm{C}$. Since the adhesion testing was found to result in destruction of the test pieces (the bonding exceeded the mechanical strength of the peel specimens), samples were also prepared in which a Teflon-coated nylon mesh was inserted between the two sheets. This reduces the contact area by roughly half and therefore induces failure at the interface, enabling a relative measure of adhesion to be obtained.

## RESULTS

Flow into and through a conical die consists of both shear flow near the walls of the die as well as extensional flow within the center regions. When the die surface is lubricated, the induced slippage at the wall largely suppresses the shear flow. The resulting deformation is essentially extensional flow with a strain rate that varies with die radius, $R$, according to ${ }^{20}$

$$
\dot{\epsilon}=\left[\begin{array}{rrr}
2 & 0 & 0  \tag{6}\\
0 & -1 & 0 \\
0 & 0 & -1
\end{array}\right] \frac{Q}{\pi R^{3}(1-\cos (\theta / 2))}
$$

where $Q$ is the (constant) mass flow rate and $\theta$ the convergence angle of the conical die. Displayed in Figure 1 is the measured pressure drop through a conical die as a function of volume flow rate for both elongational and the mixed flow field types. It is seen that, at an equivalent stress level, markedly higher flow is obtained when the shearing is eliminated by lubrication of the die walls (with the effect gradually diminishing as the lubricating grease is worn away). This result is anticipated. More significant is the comparison of the dispersive effectiveness of these two flow field types (Fig. 2). It is intriguing to find that the absence of shear flow not only does not decrease the carbon black dispersion, but in fact actually effects an improvement in the process. Shearing is a relatively weak flow type, as discussed above, but moreover its inherent vorticity works against any straining action, so that extensional deformation present in the flow is less effectively utilized.

Analogous phenomena have been observed in studies of flow-induced breakup of Newtonian droplets. ${ }^{8}$ Shearing of a suspended particle causes a rotation that can lead to alternate elongation and compression of the particle. If the drawing out of the droplet does not reach the level necessary for bursting, the extended particle rotates into adjacent quadrants where it


Fig. 1. The measured pressure drop accompanying flow of the carbon black-reinforced SBR through conical dies with $30(\square), 60(\Delta)$, and $180(\nabla)$ convergence angles, respectively. The data obtained with the lubricated flow is indicated by the solid symbols, while the open symbols refer to mixed (shear and extension) flow field results.
experiences compressive forces that tend to restore it to the original spherical shape.
Not only does the presence of vorticity in the flow field inhibit dispersion of the carbon black, but it also has a significant influence on the swell of the extrudate upon emergence from the die. The extrudate swell found for


Fig. 2. The carbon black dispersion index obtained after the indicated number of passes of the material through a die with $(X)$ and without $(O)$ lubricated walls.

TABLE II
Effect of Flow Field Type on Extrudate Swell

| Convergence <br> angle of die | Extrudate swell (\%) |  |  |
| :---: | :---: | :---: | :---: |
|  | Mixed flow | Elongational flow |  |
|  | 90 | 194 |  |
| 45 | 99 | 130 |  |
| 60 | 127 | 142 |  |

lubricated flow is contrasted to that resulting from the mixed flow field in Table II. The greater effectiveness of pure straining flow in extension of the molecules leads to larger die swell as the chains relax upon exit from the capillary. The rotational component present in shear flow inhibits development of this orientation with consequently less swell of the extrudate. Optimal use, whether for particle dispersion or molecular orientation, of any extensional capacity of the flow field clearly requires reduction of the vorticity.

It can be seen from Figure 1 that the convergence angle of the die exerted only a small influence on the pressure drop accompanying flow. The carbon black dispersion was not found to significantly depend on either this angle or on the flow rate employed. This indicates that the critical stress for rupture of the carbon black agglomerates is less than that which develops at the slowest flow rates in the die with the most gradual convergence.
The energy of mixing for the capillary extrusion can be expressed as the product of the pressure drop, $\Delta P$, and the number of passes, $N$, through the die

$$
\begin{equation*}
E=\Delta P N / \rho \tag{7}
\end{equation*}
$$

where $\rho$ is the material density. In Figure 3 the carbon black dispersion for elongational flow and the mixed flow field is plotted versus this specific energy of mixing, illustrating the obvious superiority of pure straining flow fields. In view of the fact that commercial mixing equipment, including both extruders and internal mixers, have been found to impose primarily shearing flow, ${ }^{19}$ it is obvious that improvements in their dispersion efficiency are obtainable. The expenditure of energy on weak (less straining) shear flow should be avoided, which simultaneously allows full advantage to be taken of whatever extensional flow is available to bring about dispersion. Although the design of mixing equipment that introduces less vorticity into the flow pattern would be desirable, the alternative approach, suppression of shearing by changing the material's flow characteristics, can also improve mixing efficiencies.

Application of lubricant to the mixer is not generally feasible, but another means to alter the flow characteristics of a polymer during mixing is through blending. The rheology of simple fluid blends is complex, and when the fluids are viscoelastic the situation is edven more complicated. Although there are various models which attempt to predict, for example, the viscosity of polymer blends, these describe poorly the available experimental results. ${ }^{19,21}$ The qualitative expectation is that the processing behavior of a blend will be


Fig. 3. The measured dependence of carbon black dispersion on the energy of mixing in extensional (filled symbols) and mixed (open) flow field types.
intermediate between that of the components. In fact, however, polymer blends often display anomalous rheological properties. A primary origin of this behavior is the interaction between the morphology of a blend and its rheology. The blend morphology can rearrange in order to better accommodate the applied stresses. ${ }^{22}$ This principal of minimum energy dissipation ${ }^{23}$ often gives rise to a sheath/core configuration in which one component accumulates toward the surface of the material. In the vicinity of the walls of the mixing vessel, the velocity gradients tend to be highest since a no slip condition usually prevails. The presence here of the blend constituent of lower viscosity can therefore minimize shearing stresses. It should be noted that the mechanism by which the blend components take up a low energy arrangement in the high velocity gradient regions is a largely unexplored area. If steady flow is carried out long enough this stable configuration evidently can be achieved, but the kinetics and detailed mechanism of the process are unknown.
The complex dynamic shear viscosity was measured for a series of SBR samples containing from 0 to $2 \%$ by weight of the PDMS. As expected, such low levels of PDMS effected a negligible change in this bulk property, as is seen in Figure 4. This is in accord with various mixing rules derived for the viscosity of multiphase polymer blends, which all weight the contribution of a component by its concentration in the blend. ${ }^{19,21}$ Steady-state shear viscosities were also measured for the SBR/PDMS blends. In marked contrast to the dynamic viscosity, the steady-state viscosity is seen to be a decreasing function of the level of PDMS incorporated in the SBR (Fig. 4). The PDMS (which was 3 to 5 times lower in viscosity than the SBR copolymer as seen in Fig. 5) is evidently in relatively high proportion at the surface of the material during flow through the capillary die. The lower apparent viscosity of the blends likely has then two origins. The lower viscosity of the PDMS will


Fig. 4. The viscosity at $80^{\circ} \mathrm{C}$ of the SBR copolymer blended with the indicated quantities of polydimethylsiloxane. The steady-state viscosity, both at $4.5 \mathrm{~Hz}(\ominus)$ and at $15 \mathrm{~Hz}(\mathrm{O})$, is reduced by incorporation of small quantities of PDMS, which, however, has no measurable effect on the dynamic viscosity (*).


Fig. 5. The shear rate dependence of the dynamic viscosity at $80^{\circ} \mathrm{C}$ for the SBR (filled symbols) and the PDMS (open). The obtained respective power law indices are indicated.


Fig. 6. The viscous energy dissipation (in arbitrary units) for two power law fluids as a function of relative proximity to the capillary wall.
reduce the shearing stresses at the wall where the velocity gradients are largest. Specifically for power law fluids such as these (Fig. 5), the shear rate at a radial distance $r$ from the center of a tube of radius $R$, is given by ${ }^{11}$

$$
\begin{equation*}
\dot{\epsilon}=-\left(\frac{v_{0}}{R}\right)\left(\frac{\Delta+1}{n}\right)\left(\frac{r}{R}\right)^{1 / n} \tag{8}
\end{equation*}
$$

where $v_{0}$ is the centerline fluid velocity and $n$ the power law index. The energy dissipated per unit time per unit volume decreases with distance from the wall as displayed in Figure 6. It is clear that the PDMS will significantly reduce the energy expended in shearing by virtue of its lower viscosity when it occupies the region near the tube wall. A second effect that gives rise to a lower apparent shear viscosity for the blend is the slippage promoted at the interface due to the lubricity of the PDMS. The flow field vorticity is hence decreased. Analogous to the experiments with the die coated with silicone grease, the reduction of shearing is accompanied by a decreased energy dissipation during flow. The disparity between the behavior in dynamic versus steady flow of the SBR/PDMS blends is thus accounted for by the effect of processing on the blend morphology.

It is of interest to assess the mix quality obtainable with this induced lubricated flow. Accordingly, carbon black was incorporated into the SBR on a two-roll mill, in one case after $2 \%$ PDMS had been blended into the SBR and in a second case without the PDMS. Although no torque or energy consumption measurements were available, a difference in flow behavior on the mill was evident. The presence of the PDMS resulted in significantly less adhesion to the rolls. The flow field on a roll mill is complex, consisting of both extensional flow as the slab of material enters the nip region between the

TABLE III
Properties of Carbon Black-Filled SBR Mixed on a Two-Roll Mill

|  | SBR | SBR w/2\% PDMS |
| :--- | :---: | :---: |
| Dispersion index (\%) | $98 \pm 2$ | $98 \pm 1$ |
| Bound rubber (\%) | $46.1 \pm 0.7$ | $46.0 \pm 0.7$ |
| $\mathrm{E}^{\prime}$ (MPa) $^{\mathrm{b}}$ | $0.62 \pm 0.02$ | $0.61 \pm 0.02$ |
| Loss tangent $^{\mathrm{b}}$ | $0.15 \pm 0.01$ | $0.14 \pm 0.01$ |

${ }^{\text {a }}$ Average of three samples.
${ }^{\mathrm{b}}$ Measured at 1.1 Hz with a dynamic strain amplitude of $10^{-4}$.
rollers, along with shearing induced by the roll surfaces. It is this latter that is suppressed by slippage at the interface of the polymer and the rolls. The velocity of the roll surface exceeds that of the blend material located adjacent to this surface, with a consequent reduction of the velocity gradient. In fact when the distance between the rolls was made very small, the adhesion of the blend to the rolls was insufficient to draw the material through the rolls. The extensional flow is largely unaffected by these surface conditions, and the net effect of blending is generation of a more purely straining deformation, analogous to flow in a lubricated die.

The dispersion obtained after this mixing on the roll mill was found to be essentially equivalent for the SBR and the SBR/PDMS blend (Table III). It is seen that the bound rubber measured for the two compounds wat equivalent and quite high, indicating that an extensive interaction of ... inller particles with the polymer was promoted during milling. These resuits demonstrate at the very least that shearing during mill mixing of the SBR is not necessary; the extensional component of the flow is sufficient to achieve high dispersion. The microdispersion of the carbon black in these mill mixed stocks was assessed after crosslinking by measurement of the dynamic modulus and the electrical resistivity of the materials. The state of agglomeration of the filler particles is very sensitive to strain. At low dynamic strain amplitudes the modulus reflects the connectivity of the carbon particles and it can be seen (Table III) that an equivalent filler structure is obtained in the SBR with or without the PDMS. Larger deformations break up this network of particles and, in addition to giving rise to a strain dependence in the modulus, cause the electrical resistivity to be very sensitive to deformation. Consequently, in preparing the test specimens for conductance measurements the agglomerated carbon black network is fractured leading to an initially high resistivity. The process is reversible, with an equilibrium conductivity attained which is determined by the arrangement of the filler within the polymer network and is thus a reflection of the mix quality. ${ }^{24}$ The electrical conductivity of the SBR compounds and the time dependence of the carbon black reagglomeration were found to be identical (Fig. 7). It can be concluded from these results that the PDMS does not measurably alter the physical and chemical interactions of the polymer at the carbon black surface. The obtained filler network and its reinforcement of the SBR are unaffected by the presence of PDMS.

An obvious practical concern in the use of a lubricating polymeric additive is the potential for adhesion problems in the final product. The PDMS, however, is brought to the surface during processing by the particular nature


Fig. 7. The reformation of carbon black network structure in the SBR (*) and the SBR blended with $2 \%$ PDMS ( O ) as reflected by the decrease with time of the electrical resistivity. The results for the two materials are equivalent within the experimental error of about $10 \%$.
of the flow field during milling, in combination with the tendency for a blend morphology to arrange in a fashion whereby the energy associated with deformation is minimized. This does not imply that the surface ultimately obtained will necessarily be enriched in PDMS, particularly when the material is subsequently subjected to forming operations that impose different deformation conditions. This concept is illustrated by compression molding and curing the mill-mixed blends at high temperature. The flow of the material during this molding does not effect any segregation, but rather serves to promote homogenization. The only driving force for segregation during molding arises, not from minimization of dissipative energy associated with flow, but rather from a tendency to minimize surface energies. The viscosity of the SBR, however, is too high for any significant rearrangement of the blend morphology by diffusion. Energy-dispersive X-ray measurements were obtained from the surface of a molded SBR sample containing $2 \%$ PDMS, and, by cutting the piece, also obtained from the interior of the specimen. As evidenced by equivalence of the relative intensity of the Si emission from the surface and the bulk (Table IV), the PDMS is seen to be uniformly distributed throughout the SBR after molding. Obtaining a nonuniform distribution of the dispersed phase requires sufficient exposure to a flow field with a spatially varying velocity gradient.

Adhesion measurements were performed on these blends after molding. The specimens exhibited a cohesive failure mode during the testing; moreover, when the interfacial area of the test pieces was reduced to force the failure to be localized there, the level of adhesion was found to be independent of the presence of PDMS. These results, which emphasize the point that the small quantity of PDMS in the blend does not accumulate at the surface during

TABLE IV
Energy-Dispersive X-Ray Results on Homogeneity of Composition of SBR-PDMS Blend after Molding

|  | Si intensity ${ }^{a}$ | Au intensity $^{b}$ | Ratio |
| :--- | :---: | :---: | :---: |
| Surface | 81.2 | 89.8 | $0.90 \pm 0.02$ |
| Bulk | 80.2 | 86.4 | $0.93 \pm 0.03$ |

${ }^{a}$ Counts per second from silicon of the PDMS.
${ }^{\text {b }}$ Signal from gold coating used as reference for calibration of Si intensities from surface and from interior of the SBR.

TABLE V
Properties of SBR after Crosslinking

| \% PDMS | Adhesion $\left(\mathrm{J} / \mathrm{m}^{2}\right)^{\mathrm{a}}$ | Modulus (MPa) $^{\text {b }}$ | Tensile strength (MPa) |
| :--- | :---: | :---: | :---: |
| 0 | 2100 | 0.93 | 1.3 |
| 0.5 | 2500 | 0.90 | 1.3 |
| 1.0 | 3200 | 0.99 | 1.2 |
| 2.0 | 2600 | 0.95 | 1.3 |

${ }^{\mathrm{a}}$ To self (i.e., autoadhesion).
${ }^{\mathrm{b}}$ Secant modulus at $100 \%$ tensile strain.
molding, are displayed in Table V, along with the tensile data ohtained for the series of crosslinked blends. As expected, these latter bulk imoperties a a immeasurably affected by $2 \%$ or less of added PDMS.

The use of polymer blending to achieve viscosity reduction is in this manner distinctly different from the more conventional practice of incorporating plasticizers and other processing aids to a formulation. These monomeric or oligomeric materials possess sufficient mobility to migrate to the surface, so that interfacial effects and compatibility become important in governing their distribution in the material. When low molecular weight additives accumulate at the surface, adhesion and processing problems can ensue; on the other hand, if they are uniformly distributed throughout the bulk of the material, they significantly reduce the viscosity only when present in concentrations high enough to affect other physical properties. Contrarily, polymer blends develop a nonuniform distribution of components only through deformation in flow fields with velocity gradients having the necessary spatial variance.

## SUMMARY

The extending action of a flow field will be hindered by the rotational nature of any shearing flow present within it. An effective means to inhibit this vorticity, thereby facilitating breakup of dispersed domains, is by inducing wall slippage in the flowing melt. Although optimal utilization of lubricated flow clearly requires recourse to mixers of different design than those currently in wide usage, there likely exist situations in which advantage can be taken of the principle of minimum energy dissipation in two-phase flow to more efficiently obtain improved mix quality. Attention herein has focused only on dispersive mixing; however, it must be pointed out that elimination of
wall slippage could inhibit the distributional capability of a mixing device. Applications of this concept, on the other hand, may extend beyond obtaining better dispersive mixing to include technologies in which molecular orientation is a critical aspect of material properties. The development of high performance fibers is one obvious example.

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