

Effects of Coupling Agent on the Rheological Behavior and Processability of Polypropylene

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Synopsis

An investigation was made into the effect of coupling agents on the rheological behavior and processability of polypropylene. For the study, each of the following three commercially available coupling agents, a titanate coupling agent (Kenrich Petrochemicals, KR-TTS) and two silane coupling agents (Union Carbide, A1100 and Y9187), was melt-blended with polypropylene (PP). Melt blending was performed using a twin-screw compounding machine. It was found that the zero-shear viscosity of polypropylene was decreased by 1 order of magnitude after it had been extruded through the twin-screw compounding machine and that, when coupling agents were added to it, its viscosity was higher than that of the PP *without* the coupling agents, undergoing the same deformation history through the twin-screw compounding machine. Independent measurements of the molecular weight of the materials show that the weight-average molecular weight (\bar{M}_w) of the extruded PP is 3.77×10^5 , whereas the \bar{M}_w of the virgin PP (before extrusion) is 4.80×10^5 , indicating that considerable molecular degradation occurred during extrusion and the \bar{M}_w of the PP extruded *with* coupling agent is greater than that of the PP extruded *without* coupling agent. In other words, the molecular weight measurement supports the viscosity measurements of the PP investigated *with* and *without* coupling agent. Also measured were the elongational viscosity of the PP *with* and *without* coupling agent, which was then correlated to the melt drawability of the materials investigated.

INTRODUCTION

In recent years, the use of coupling agents in the development of particulate-filled thermoplastic composites has attracted the attention of polymer researchers. However, our understanding of the role of coupling agent in enhancing certain mechanical properties of particulate-filled thermoplastic composites is far from complete. Because of the multiphase nature of particulate-filled thermoplastic composites, the use of coupling agent requires an understanding of the chemical and physical phenomena occurring at all interfaces.

Ishida and Koenig¹⁻³ and Chiang and Koenig^{4,5} have investigated the problems associated with the interface between a silane coupling agent and glass fiber and between a silane coupling agent and a thermosetting resin (e.g., unsaturated polyester; epoxy resin), using Fourier transform infrared spectroscopy. The review articles by Plueddemann⁶ and Ranney et al.⁷ about a decade ago, and by Ishida⁸ more recently, and the recent monograph by Plueddemann⁹ discuss various subjects dealing with the chemical and physical phenomena associated with the use of coupling agents in polymeric composite materials.

It seems rather apparent that some coupling agents are effective in improving certain mechanical properties of particulate-filled or reinforced thermoset composite materials, because a *thermosetting resin* (e.g., unsaturated polyester resin; epoxy resin) used as a matrix may react chemically with the coupling agent. However, it has also been reported in the literature¹⁰⁻¹³ that when *thermoplastic resins* having no functional group (e.g., polypropylene, polyethylene) were used as matrix, particulate-filled (e.g., CaCO₃, talc) thermoplastic composite materials, also, exhibit some improvement in their mechanical properties in the presence of coupling agents. In his recent monograph,⁹ Plueddemann has suggested several possible mechanisms that might explain how some thermoplastic composite materials in the *presence* of coupling agent undergo an improvement in their mechanical properties. Such proposed mechanisms include: (1) interdiffusion of coupling agent segments with nonreactive matrix molecules, forming crosslinkages (or chemical bonds) at fabrication temperature; (2) formation of interpenetrating networks in the interphase region consisting of coupling agent and matrix.

Very recently, we investigated the rheological behavior and melt drawability of polypropylene in the *presence* of a small amount of additives, commonly referred to as coupling agents when used in particulate-filled polymer composites. The investigation was motivated by our previous study,¹⁰ revealing that the same additives (i.e., silane and titanate coupling agents) appear to have changed the morphology of the polypropylene phase, when used together with calcium carbonate (CaCO₃) as filler. In this paper, we shall report the highlights of our findings.

EXPERIMENTAL

Materials. The polymer employed is a commercial grade of polypropylene (Resin E115) manufactured by the Exxon Chemical Co. As coupling agent, we used: (a) isopropyltriisosteroyl titanate (Kenrich Petrochemicals, KR-TTS); (b) γ -aminopropyltriethoxy silane (Union Carbide, A1100); (c) *N*-octyltriethoxy silane (Union Carbide, Y9187). For comparison purposes, we also used stearic acid.

The procedure employed for adding the individual coupling agent to the polypropylene resin was as follows: (1) The coupling agent was dissolved in a solvent (i.e., KR-TTS in toluene; A1100 and Y9187 in acetone) to prepare about 400 mL of the mixture; (2) polypropylene resin (in pellet form) was mixed thoroughly with the coupling/solvent mixture, using a plastic bag; (3a) the PP/KR-TTS mixture was first put into an oven at 60°C and then dried, by evaporating the toluene in an open hood for 1 week; (3b) the PP/A1100 and PP/Y9187 mixtures were dried by evaporating the acetone in an open hood for one week. In this way, we were able to attach a small amount of coupling agent (0.3 wt %, 1.0 wt %, 5.0 wt %) to the surface of the PP pellets (ca. 3-4 mm diameter).

The dried materials were then extruded at 200°C and pelletized, using a twin-screw compounding machine (Werner and Pfleiderer ZKS-28). The purpose was to achieve the homogeneous distribution of a coupling agent in the polypropylene, by melt-blending the resin and coupling agent. The homogenizing of the material was achieved by conveying and kneading with

TABLE I
Materials Investigated

	Polymer	PP	PP	PP	PP
Batch 1	Coupling agent	KR-TTS	Y9187	A1100	—
	Amount (wt %)	1.0	1.0	1.0	—
Batch 2	Coupling agent	KR-TTS	Y9187	A1100	Stearic acid
	Amount (wt %)	0.3 and 5.0	0.3 and 5.0	0.3 and 5.0	0.3 and 1.0

screw bushings and kneading elements assembled in the twin-screw compounding machine. The material was discharged through a die plate and into a water bath. The strands quenched in the water bath were then cut into pellets. Table I describes the materials investigated.

Rheological Measurements. For the measurement of the steady shearing flow properties, we compression-molded the pellets at 180°C to obtain disks (2 cm diameter and 3 mm thick), using a hydraulic press. Rheological measurements were conducted at 200°C, using a Model R-16 Weissenberg Rheogoniometer (Sangamo-Weston Controls, Bognor Regis, Sussex, England).

For elongational viscosity measurements, we extruded the pellets at 180°C through a cylindrical die, using a single-screw extruder, to obtain strands of about 4 mm diameter, which were cut into lengths of about 30 cm. Elongational viscosity was measured at 180°C, using an apparatus very similar to that designed by Ida and White.¹⁴

Melt Drawability Test. In order to obtain information on melt drawability, we melt-spun the pellets into ambient air, using an apparatus as schematically shown in Figure 1. During the melt spinning experiment, we increased the takeup speed gradually until the thread broke, and determined the maximum draw-down ratio, $(V_L/V_0)_{\max}$, in which $(V_L)_{\max}$ is the maximum takeup speed at which the thread breaks and V_0 is the average linear velocity of the melt inside the spinnerette hole.

RESULTS AND DISCUSSION

The Effect of the Type of Coupling Agent. Figure 2 gives plots of viscosity (η) and first normal stress difference ($\tau_{11} - \tau_{22}$) versus shear rate ($\dot{\gamma}$) for the virgin polypropylene (PP) as received by the resin manufacturer,

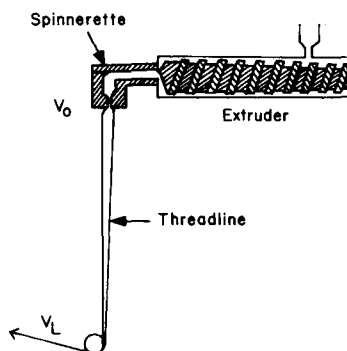


Fig. 1. Schematic describing the melt spinning apparatus employed for melt drawability test.

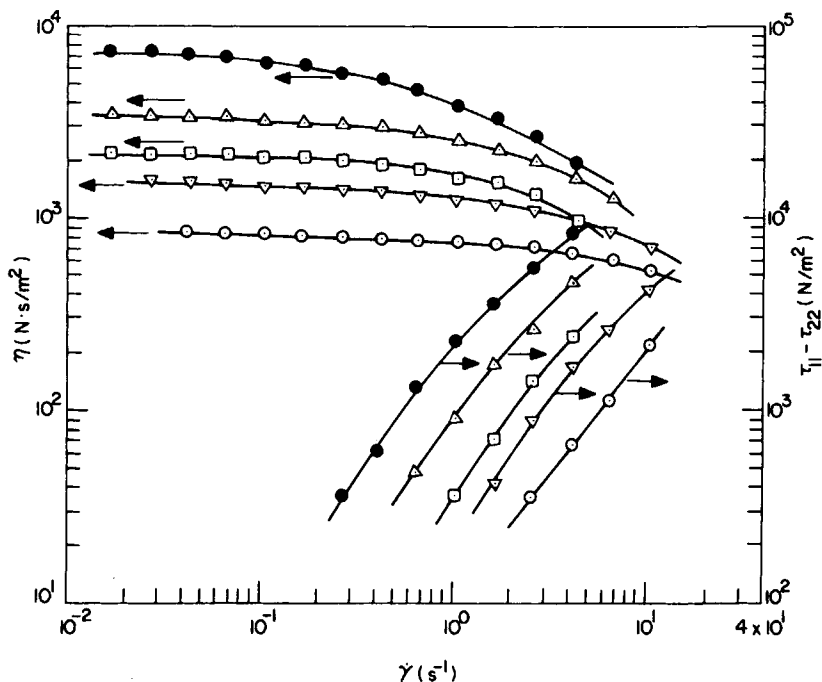


Fig. 2. η and $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ at 200°C: (●) virgin PP; (○) PP after extrusion; (Δ) PP/KR-TTS (1.0 wt %); (\square) PP/A1100 (1.0 wt %); (∇) PP/Y9187 (1.0 wt %).

the PP that had been extruded in a twin-screw extruder, the PP/KR-TTS mixture, the PP/A1100 mixture, and the PP/Y9187 mixture. Note that the mixtures of PP and silane or titanate coupling agent were prepared by extruding in a twin-screw compounding machine. It is seen that, at low shear rates, the viscosity of the PP extruded in a twin-screw extruder is about 1 order of magnitude lower than that of the virgin PP, and that shear-thinning behavior begins at $\dot{\gamma} = 0.1 \text{ s}^{-1}$ for the virgin PP, whereas it begins at about $\dot{\gamma} = 2.0 \text{ s}^{-1}$ for the extruded PP. At the time when the viscosity measurements were first taken, we speculated that such a large decrease in η of the extruded PP might have been due to the thermal and/or shear degradation of the virgin PP when it was extruded in the twin-screw extruder. As will be discussed below, our speculation later was supported by independent measurements of molecular weights of the materials.

It is of interest to note in Figure 2 that, over the range of shear rates tested, the viscosities of all the PP/coupling agent mixtures are higher than the viscosity of the *extruded* PP, and yet lower than the viscosity of the *virgin* PP. It should be remembered that the PP *with* coupling agent had been subjected to the same deformation and thermal histories as the PP *without* coupling agent. It is seen further in Figure 2 that, of the three coupling agents investigated, the titanate coupling agent (KR-TTS) causes the smallest decrease in the viscosity of the *virgin* PP, compared to the two silane coupling agents (A1100 and Y9187).

Figure 2 reveals further that, over the range of shear rates investigated, the melt elasticity (i.e., $\tau_{11} - \tau_{22}$) of the materials follows the same trend as their melt viscosity. However, when η and $\tau_{11} - \tau_{22}$ are plotted against

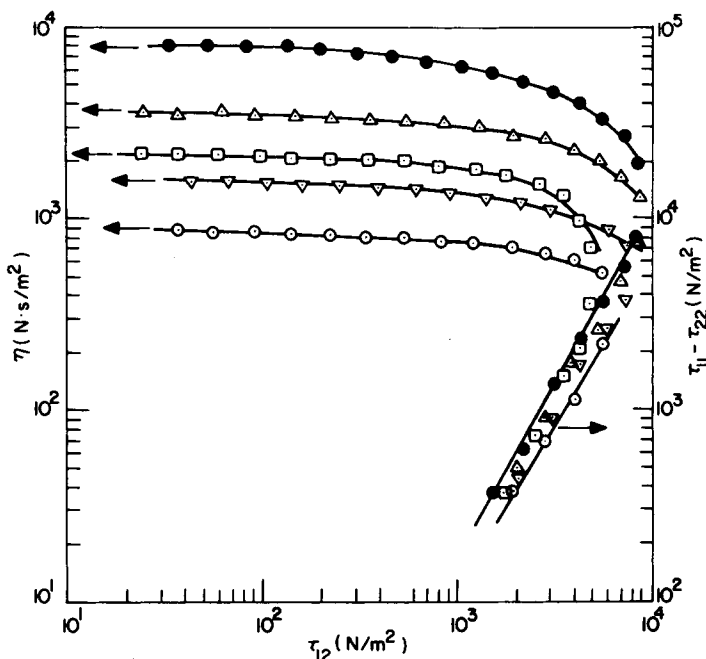


Fig. 3. η and $\tau_{11}-\tau_{22}$ vs. τ_{12} at 200°C. Symbols are the same as in Fig. 1.

shear stress (τ_{12}), instead of against shear rate ($\dot{\gamma}$), as shown in Figure 3, the trend of η with regard to the effect of the coupling agents remains the same, whereas the effect of the coupling agents on $\tau_{11} - \tau_{22}$ becomes quite suppressed, almost indistinguishable among the three different coupling agents.

To determine the molecular weights of the five samples employed for the rheological measurements, independent experiments were carried out using gel permeation chromatograph. All samples were first dissolved and filtered hot in 1,2,4-trichlorobenzene (TCB). They were then run at 140°C in TCB at 1.5 mL/min using a series of two 25-cm Shodex A-80 M/S columns from Perkin-Elmer. Figure 4 shows the molecular weight distribution curves of the five samples, and Table II gives a summary of their number-average (\bar{M}_n), weight-average (\bar{M}_w), and z -average (\bar{M}_z) molecular weights. It is very revealing to see that considerable decrease in molecular weight (MW) occurred when the *virgin* PP was extruded in a twin-screw extruder, and that very little change in the MW occurred for the PP/KR-TTS mixture. Note in Table II that the use of the silane coupling agent A1100 decreased both the \bar{M}_n and \bar{M}_w of the PP more than the silane coupling agent Y9187, but the \bar{M}_z of the PP/A1100 mixture was slightly higher than that of the PP/Y9187 mixture. A close examination of Figure 2 indicates that shear-thinning behavior of the PP/A1100 mixture begins at a shear rate lower than that for the PP/Y9187 mixture. This may now be explainable in terms of molecular weights listed in Table II.

It is a well-known fact that polypropylene is very susceptible to degradation in the presence of oxygen. When the oxidative degradation occurs, the molecular weight distribution (MWD) is expected to become broader,

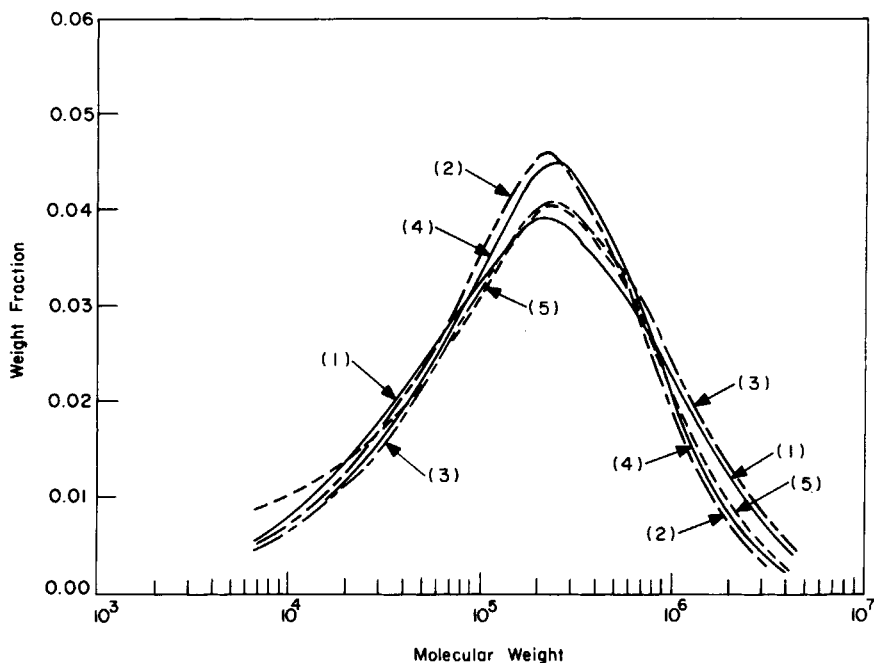


Fig. 4. Molecular weight distribution curves: (1) virgin PP; (2) PP after extrusion; (3) PP/KR-TTS (1.0 wt %); (4) PP/Y9187 (1.0 wt %); (5) PP/A1100 (1.0 wt %).

due to fragmentary breakdown. Table II shows that the PP *extruded without* coupling agent has a much narrower MWD than the *virgin* PP, and a much smaller \bar{M}_z than that of *virgin* PP. This seems to suggest that, when processed in a twin-screw extruder, the PP *without* coupling agent underwent shear degradation, as well as oxidative degradation.

It is noted above that, under identical shearing deformation and thermal histories in a twin-screw extruder, the PP/KR-TTS mixture exhibits a much smaller viscosity reduction than the PP extruded *without* coupling agent (see Fig. 2). Table II reveals that, in the *presence* of the titanate coupling agent KR-TTS, the \bar{M}_n of the PP is indeed greater than that of *virgin* PP, and the \bar{M}_w remains essentially constant. This seems to suggest that the titanate coupling agent was effective in minimizing the shear degradation of the PP while it was extruded in the twin-screw extruder. One possible explanation, though speculative at present, is that the KR-TTS containing a long aliphatic chain and fatty acid may decompose in the twin extruder and, consequently, the decomposed aliphatic hydrocarbons might have acted

TABLE II
Summary of the Molecular Weight Measurements for the Materials Prepared in Batch 1

Material	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_z \times 10^{-5}$	\bar{M}_w/\bar{M}_n
Virgin PP	7.39	4.80	15.39	6.50
Extruded PP	8.19	3.77	9.65	4.60
PP/KR-TTS	8.56	4.84	13.97	5.65
PP/Y9187	8.48	4.13	10.83	4.87
PP/A1100	5.23	3.96	11.24	7.57

as lubricant. Note that the titanate coupling agent KR-TTS decomposes at about 150°C and the barrel temperature of the twin extruder was about 200°C. A close examination of Table II reveals further that the \bar{M}_n of the PP in the *presence* of KR-TTS is larger than that of the *virgin* PP. This seems to suggest that, in the presence of the KR-TTS, the smaller PP molecules might have undergone some kind of polymerization reaction. Indeed, Figure 4 shows that the MWD curve of the PP, in the presence of KR-TTS, is shifted to the right, compared to that of the *virgin* PP.

In the presence of the silane coupling agent Y9187, the \bar{M}_n of the PP is increased, whereas its \bar{M}_w is decreased, resulting in a narrower MWD (see Table II and Fig. 4). Note that the silane coupling agent Y9187 may not decompose at the extrusion temperature employed (up to 220°C). We may speculate that, in the *presence* of the silane coupling agent Y9187, some shear degradation of the larger molecules might have occurred, resulting in lower values of \bar{M}_w , and the smaller molecules might have undergone some kind of polymerization resulting in higher values of \bar{M}_n , compared to the *virgin* PP.

In the presence of the silane coupling agent A1100, both the \bar{M}_n and \bar{M}_w are decreased and the MWD has become broader than the *virgin* PP. We speculate that both shear and oxidative degradations might have occurred.

The Effect of the Concentration of Coupling Agent. Having observed the somewhat unexpected results presented above, we decided to repeat the rheological experiment by preparing a new batch of compounds containing different amounts of coupling agent, i.e., the effect of the concentration of coupling agent was investigated. For this, we prepared compounds containing 0.3 and 5.0 wt % of the same coupling agents as those used in the previous batch of compounds containing 1.0 wt % (see Table I).

Based on our previous experience, at the time when we prepared the second batch of compounds using a twin-screw extruder, we doubted that we could duplicate the deformation history that we had observed in the previous batch of compounds, and therefore, we also extruded the *virgin* PP *without* coupling agent in the twin-screw extruder. We prepared six different compounds, containing 0.3 and 5.0 wt % of coupling agent (see Table I).

Figure 5 gives plots of η vs. $\dot{\gamma}$ for the *virgin* PP and the *extruded* PPs at two different times, about 16 months apart. It is seen that the newly extruded PP (batch 2) has a much smaller viscosity reduction than the previously extruded PP (batch 1). This result confirms our earlier speculation that the observed reduction in melt viscosity is due in part to shear degradation, as well as oxidative degradation. Note that oxidative degradation alone is expected to be independent of the screw arrangement in a twin-screw extruder.

Figures 6–8 show the effect of the concentration of the coupling agents on η and τ_{11} - τ_{22} for the materials prepared in batch #2 (see Table I). For comparison purposes, the viscosities of the *virgin* PP and the *extruded* PP without coupling agent are also given in these figures. It is seen in Figure 6 that the viscosity of the PP containing 5.0 wt % A1100 is higher than that of the PP containing 0.3 wt % A1100, which in turn is higher than that of the PP extruded without coupling agent. It is seen in Figure 7, however, that the viscosity of the PP containing 0.3 wt % KR-TTS is higher

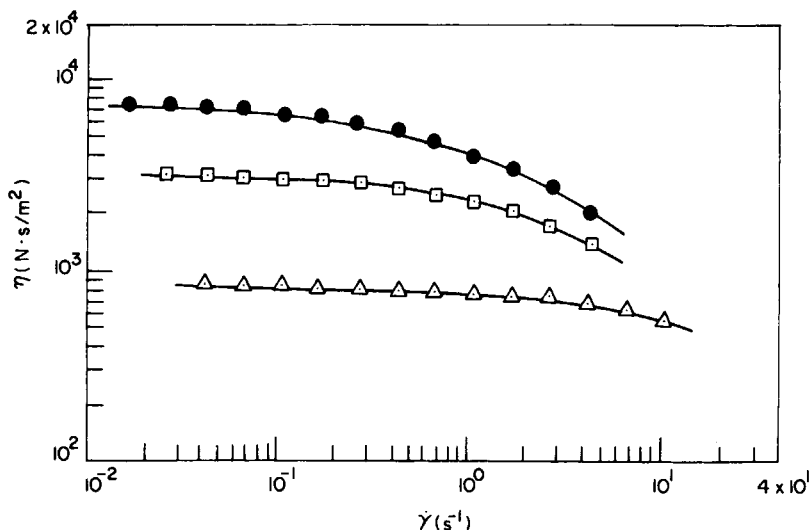


Fig. 5. η vs. $\dot{\gamma}$ at 200°C: (●) virgin PP; (△) PP after extrusion with one type of screw configuration (batch #1); (□) PP after extrusion with another type of screw configuration (batch #2).

than that of the *extruded* PP without coupling agent, which in turn is higher than that of the PP containing 5.0 wt % of KR-TTS. It is seen further in Figure 8 that the viscosity of the PP containing the coupling agent Y1987 is lower than that of the *extruded* PP without coupling agent, and that an increase in the Y9187 concentration decreases the viscosity further. It can be concluded, therefore, that the concentration of coupling agent greatly

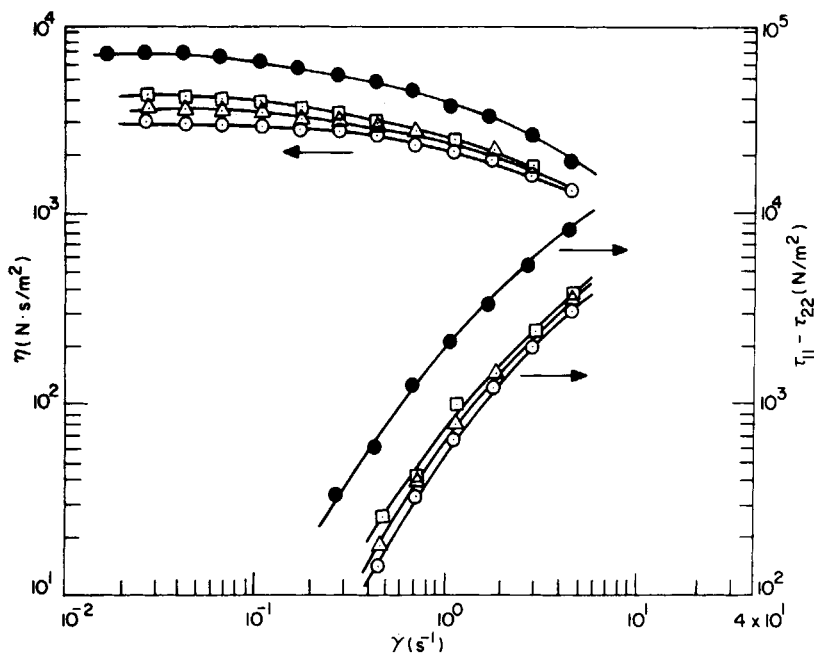


Fig. 6. η and $\tau_{11} - \tau_{22}$ vs. $\dot{\gamma}$ at 200°C: (●) virgin PP; (○) PP after extrusion; (△) PP/A1100 (0.3 wt %); (□) PP/A1100 (5.0 wt %).

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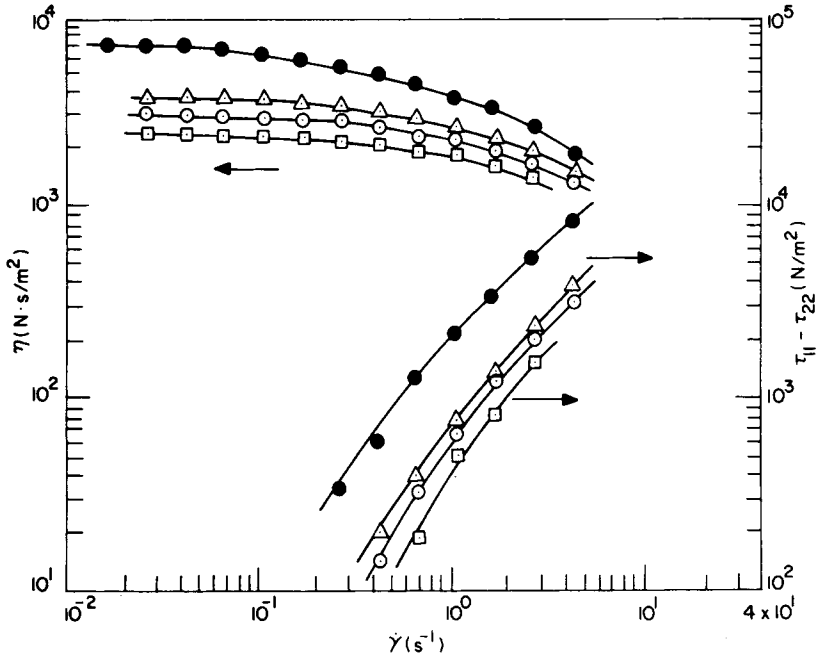


Fig. 7. η and $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ at 200°C: (●) virgin PP; (○) PP after extrusion; (△) PP/KR-TTS (0.3 wt %); (□) PP/KR-TTS (5.0 wt %).

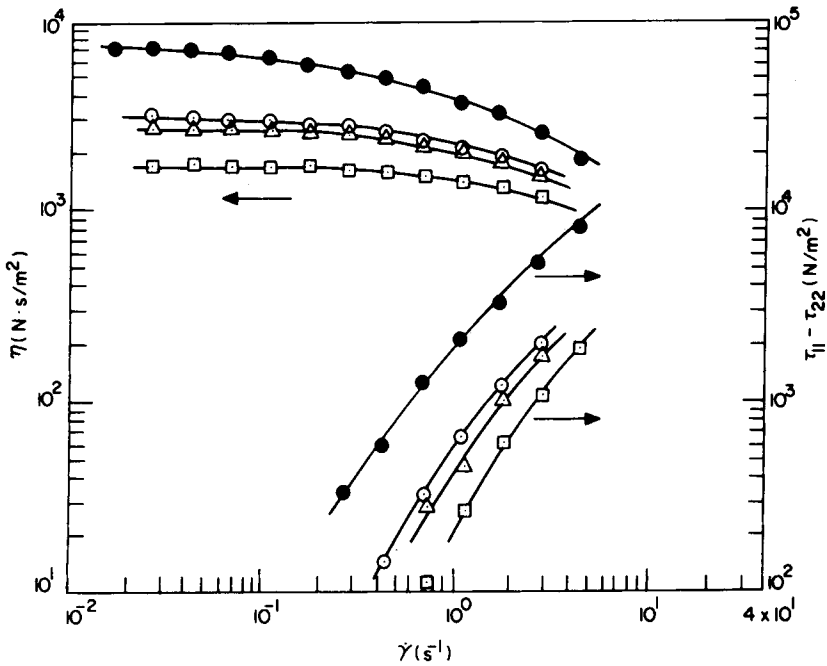


Fig. 8. η and $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ at 200°C: (●) virgin PP; (○) PP after extrusion; (△) PP/Y9187 (0.3 wt %); (□) PP/Y9187 (5.0 wt %).

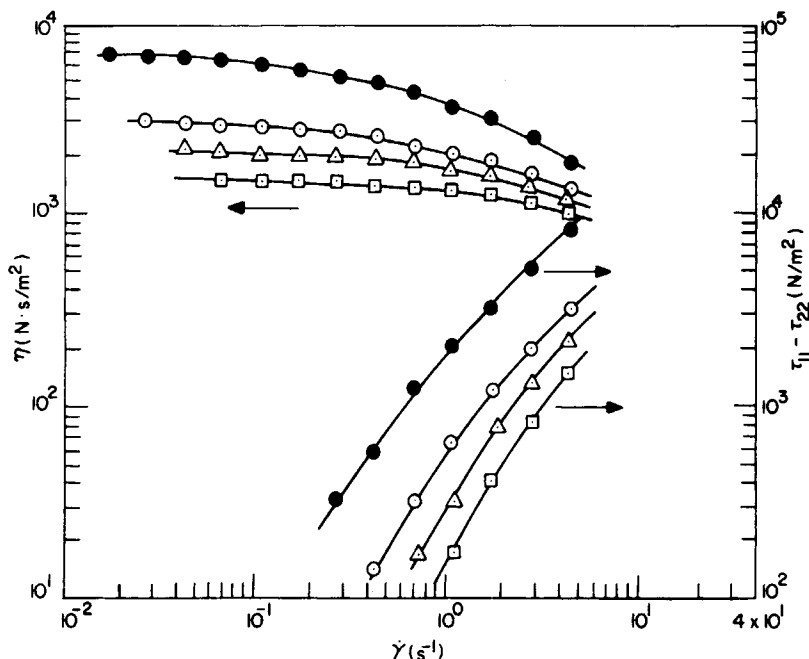


Fig. 9. η and $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ at 200°C: (●) virgin PP; (○) PP after extrusion; (△) PP/stearic acid (0.3 wt %); (□) PP/stearic acid (1.0 wt %).

influences the viscosity of the PP extruded. This then suggests that the coupling agent plays a chemical role, not a catalytic role.

A close examination of Figures 2, 4, 5, and 6 reveals that, using the *extruded* PP *without* coupling agent as a reference, the viscosity of the PP containing coupling agent goes through a maximum at 1.0 wt % coupling agent.

Stearic acid is long known as a lubricant in extrusion, and therefore we also used stearic acid to prepare a compound. Figure 9 gives plots of η and $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ for the PP containing stearic acid. It is seen that appreciable viscosity reduction occurs with increasing concentration of stearic acid. We therefore conclude that the mechanism causing the viscosity increase and/or decrease observed with the PP containing coupling agent is different from that observed with the PP containing stearic acid.

Table III describes a summary of the molecular weight measurements for the materials prepared in batch 2, and Figure 10 shows their molecular weight distribution curves. These measurements explain the cause of the observed reduction in melt viscosity, shown in Figures 6-9.

TABLE III

Summary of the Molecular Weight Measurements for the Materials Prepared in Batch 2

Material	Coupling agent concn (wt %)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_z \times 10^{-5}$	\bar{M}_w/\bar{M}_n
Virgin PP	—	7.39	4.80	15.39	6.50
PP/KR-TTS	5.0	5.43	4.93	23.42	9.08
PP/Y9187	5.0	5.22	3.67	11.98	7.03
PP/A1100	5.0	5.11	4.50	17.24	8.80
PP/Stearic acid	1.0	4.27	3.52	12.64	8.24

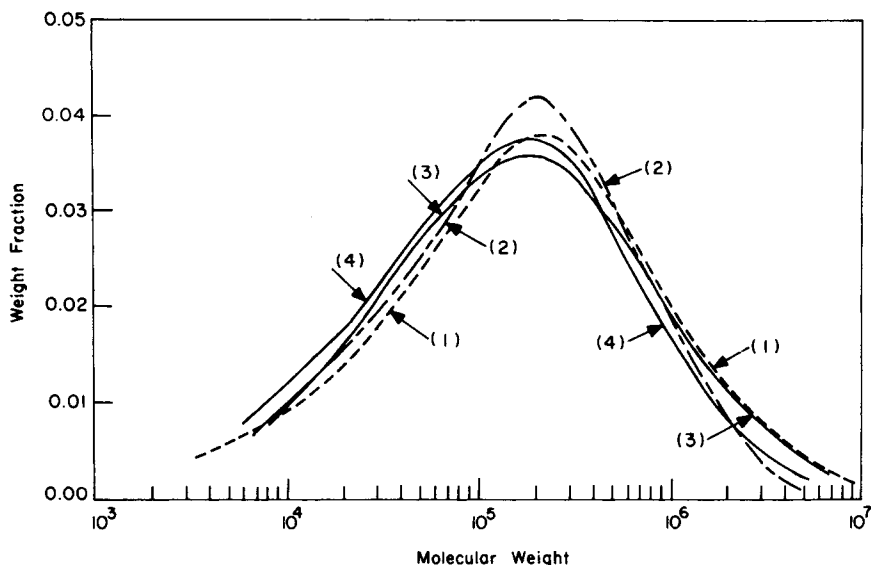


Fig. 10. Molecular weight distribution curves: (1) PP/KR-TTS (5.0 wt %); (2) PP/Y9187 (5.0 wt %); (3) PP/A1100 (5.0 wt %); (4) PP/stearic acid (1.0 wt %).

At this juncture, it is of interest to report that branched low-density polyethylene, when subjected to the same deformation and thermal histories, has exhibited little change in shear viscosity, as demonstrated in Table IV.

Elongational Viscosity and Melt Drawability. Figure 11 gives plots describing how the elongational viscosity (η_E) varies with time at various values of elongation rate as parameter, for the *virgin* PP and the *extruded* PP *with* and *without* coupling agent. Figures 12–14 give plots of η_E vs. elongation rate ($\dot{\gamma}_E$) for the PP/KR-KTTS, PP/Y9187, and PP/A1100 mixtures, at different values of coupling agent concentration. It is clear that 1.0 wt % coupling agent gives rise to η_E values lower than do 0.3 and 5.0 wt % of coupling agents, and that, in all cases, the *extruded* PP *without* coupling agent has a η_E value lower than that of the PP *with* coupling agent.

TABLE IV
Summary of the Viscosity Measurements for Low-Density Polyethylene

Shear rate (s ⁻¹)	Viscosity (N · s/m ²)	
	Virgin resin	Extruded resin
0.26	6.42 × 10 ³	6.42 × 10 ³
0.42	5.75 × 10 ³	5.67 × 10 ³
0.67	5.07 × 10 ³	4.97 × 10 ³
1.07	4.40 × 10 ³	4.33 × 10 ³
1.70	3.84 × 10 ³	3.65 × 10 ³
2.69	3.21 × 10 ³	3.09 × 10 ³
4.27	2.73 × 10 ³	2.65 × 10 ³
6.77	2.23 × 10 ³	2.09 × 10 ³
10.70	1.76 × 10 ³	1.67 × 10 ³

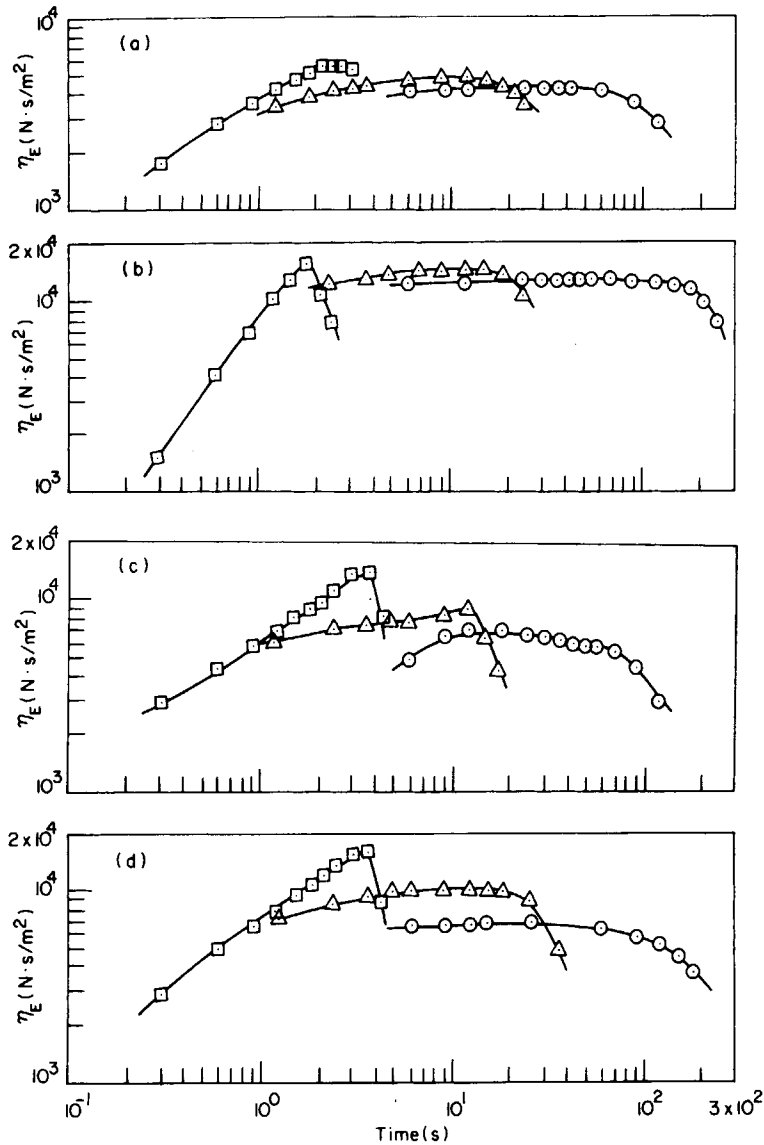


Fig. 11. η_E vs. time at 180°C for: (a) PP after extrusion; (b) PP/KR-TTS (1.0 wt %); (c) PP/Y9187 (1.0 wt %); (d) PP/A1100 (1.0 wt %); (○) 0.01 s⁻¹; (△) $\dot{\gamma}_E = 0.01$ s⁻¹; (□) $\dot{\gamma}_E = 1.0$ s⁻¹.

In order to correlate the elongational viscosity to processability, we conducted a simple melt drawability test (see Fig. 1), very similar to that described in our previous paper.¹⁰ Table V summarizes the results in terms of maximum draw-down ratio, $(V_L/V_0)_{\max}$. It is seen that $(V_L/V_0)_{\max}$ goes through a maximum at 1.0 wt % coupling agent concentration, and that, of the three specimens, the PP/KR-TTS mixture has the highest value of $(V_L/V_0)_{\max}$. Note further that the PP/Y9187 mixture has consistently higher values of $(V_L/V_0)_{\max}$ than the PP/A1100 mixture at all three levels of cou-

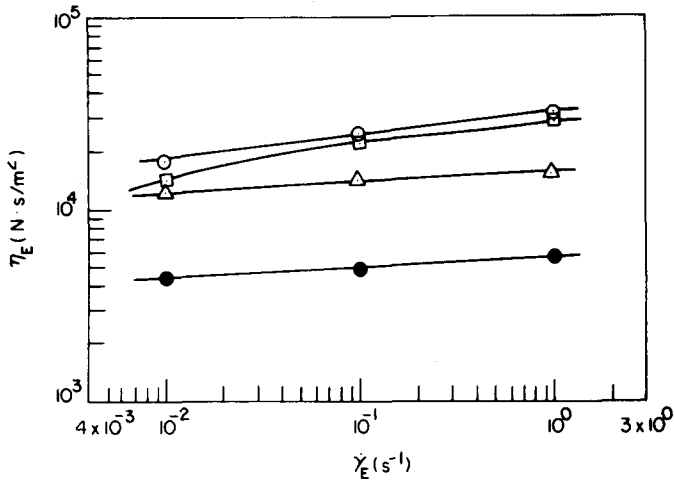


Fig. 12. η_E vs. $\dot{\gamma}_E$ at 180°C: (●) PP after extrusion; (○) PP/KR-TTS (0.3 wt %); (△) PP/KR-TTS (1.0 wt %); (□) PP/KR-TTS (5.0 wt %).

pling agent concentration investigated. We can regard the value of $(V_L/V_0)_{\text{max}}$ as a measure of melt drawability (or melt spinnability).

The Morphology of the Fracture Surface of Injection-Molded Specimens. In our previous paper,¹⁰ we reported evidence that both the titanate coupling agent KR-TTS and the silane coupling agents Y9187 and A1100, when added separately to the CaCO_3 -filled polypropylene, affected the morphological state of the PP phase. In that study, we examined photomicrographs of the tensile fracture surface of injection-molded specimens, using a scanning electron microscope. In the present study, we used the same procedure to investigate the morphology of the tensile fracture surface of the injection-molded specimens.

Figure 15 shows photomicrographs of the tensile fracture surface of the *virgin* PP and the PP *extruded* with sodium benzoate. It is well documented in the literature¹⁵ that sodium benzoate is an effective nucleating agent for

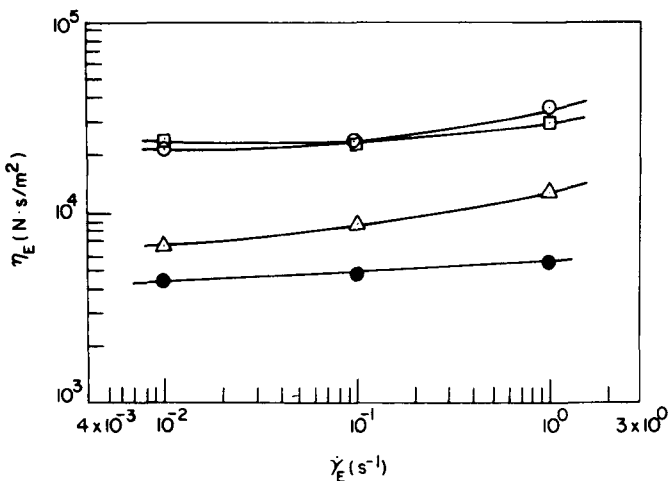


Fig. 13. η_E vs. $\dot{\gamma}_E$ at 180°C: (●) PP after extrusion; (○) PP/Y9187 (0.3 wt %); (△) PP/Y9187 (1.0 wt %); (□) PP/Y9187 (5.0 wt %).

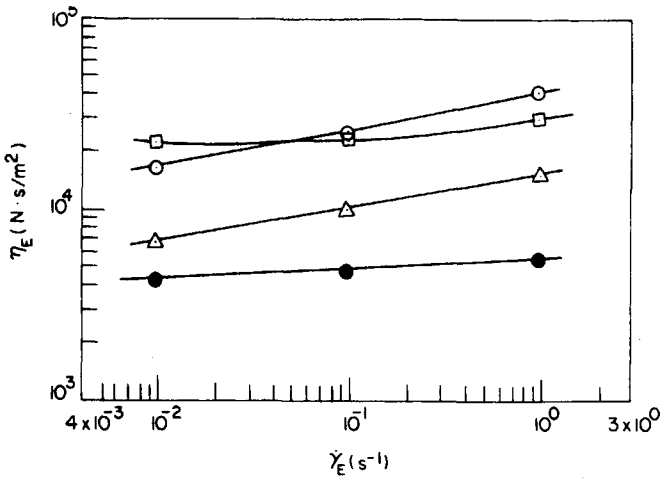


Fig. 14. η_E vs. $\dot{\gamma}_E$ at 180°C: (●) PP after extrusion; (○) PP/A1100 (0.3 wt %); (△) PP/A1100 (1.0 wt %); (□) PP/A1100 (5.0 wt %).

TABLE V
Summary of Melt Drawability Test

Coupling agent Concn (wt %)	Maximum draw-down ratio $(V_L/V_0)_{\max}^a$		
	PP/KR-TTS	PP/Y9187	PP/A1100
0.3	78	92	85
1.0	157	146	121
5.0	100	127	96

^a $(V_L/V_0)_{\max}$ for the extruded PP is 163.

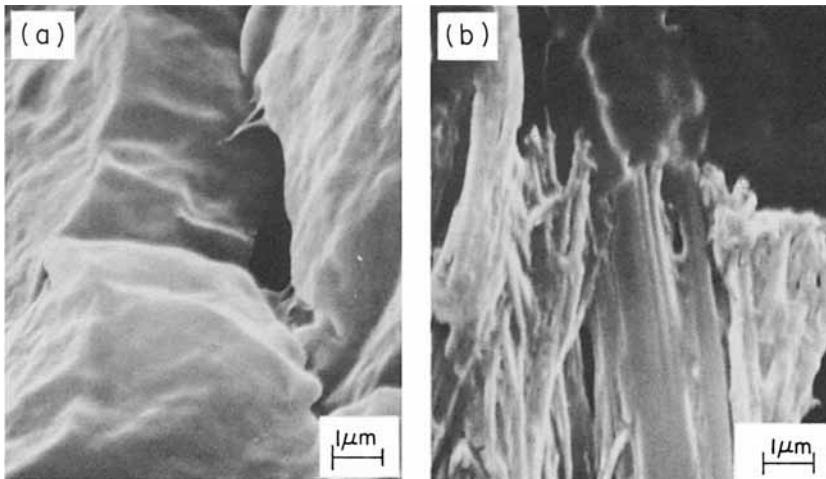


Fig. 15. Scanning electron micrographs of the tensile fracture surface: (a) virgin PP; (b) PP/sodium benzoate mixture.

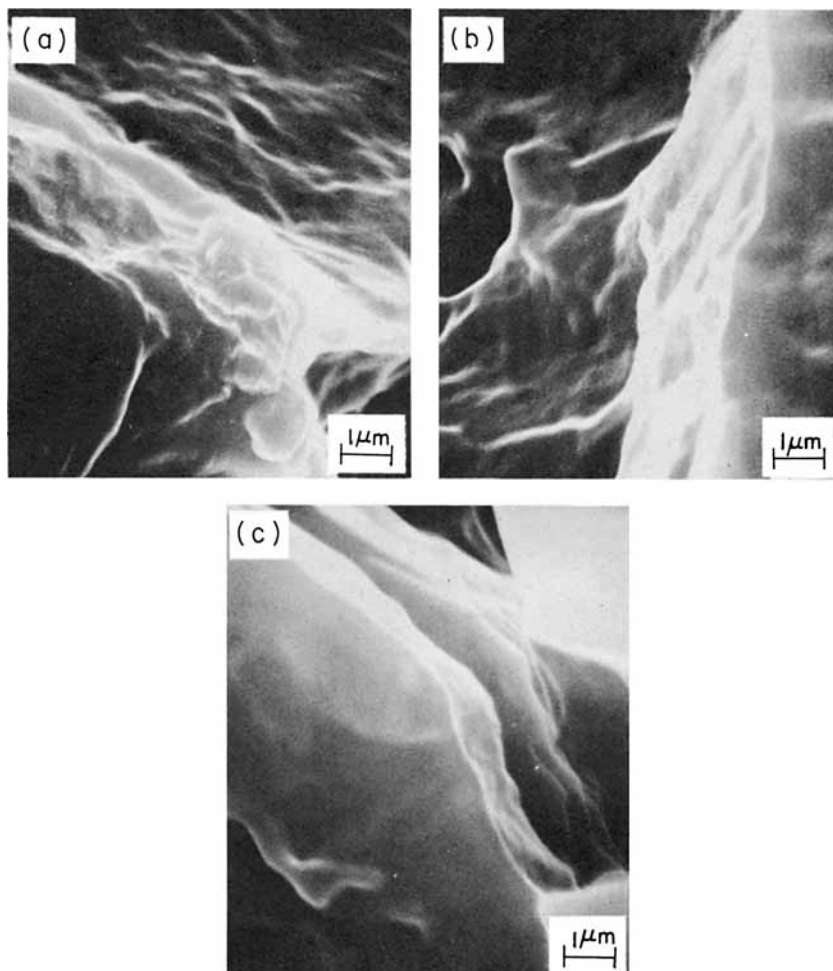


Fig. 16. Scanning electron micrographs of the tensile fracture surface: (a) PP/A1100 mixture; (b) PP/Y9187 mixture; (c) PP/KR-TTS mixture.

polypropylene. Indeed, it is seen in Figure 15 that the PP with sodium benzoate shows strong evidence of considerably enhanced crystalline structure, compared to the *virgin* PP. On the other hand, as may be seen in Figure 16, the PP with coupling agent has a tensile fracture surface indistinguishable from that of *virgin* PP [see Fig. 15(a)]. This indicates that the coupling agents, when added to PP, had *little* influence on the morphology of the PP phase. Our independent experiments confirmed that the degree of crystallinity and melting point were essentially the same for the PP *with* and *without* the coupling agents.

It should be remembered that, when CaCO_3 particles treated with coupling agents were added to PP and subsequently injection-molded, the morphological state of the PP phase was quite different from that of the PP/ CaCO_3 *without* coupling agent. In order to facilitate our discussion here, we have reproduced the photomicrographs reported in our previous publication¹⁰ and presented in Figure 17. Comparison of Figure 16 with

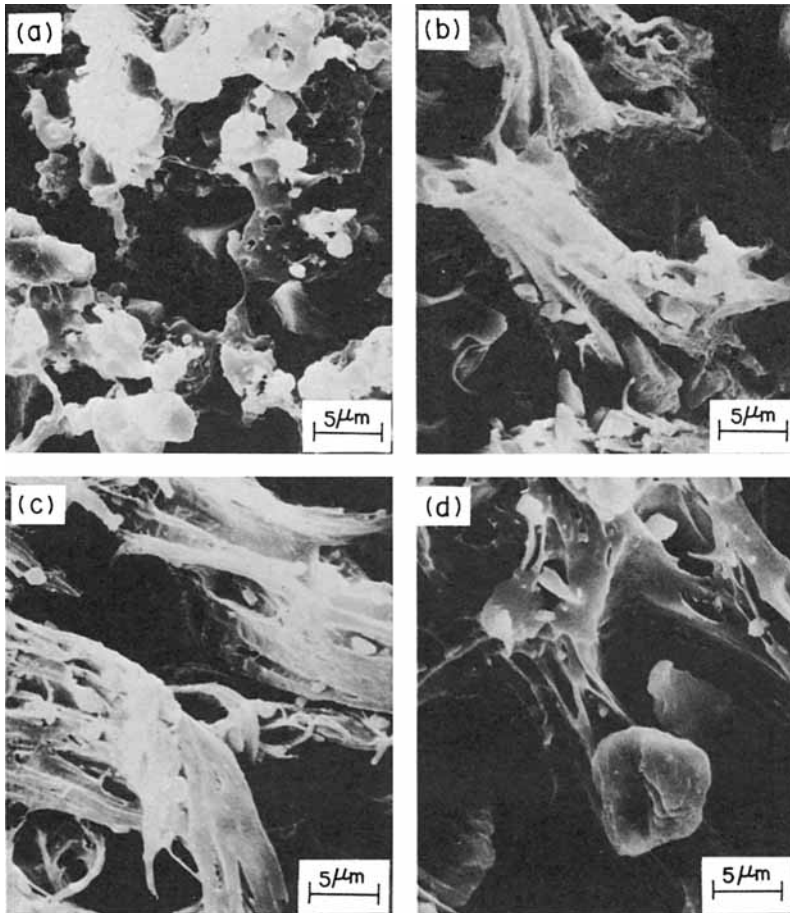


Fig. 17. Scanning electron micrographs of the tensile fracture surface¹⁰: (a) PP/CaCO₃; (b) PP/CaCO₃/KR-TTS; (c) PP/CaCO₃/Y9187; (d) PP/CaCO₃/A1100.

Figure 17 seems to suggest that the CaCO₃ particles somehow promote nucleation of the PP phase in the presence of coupling agents.

Fourier Transform Infrared (FT-IR) Spectroscopy. In order to have a better understanding of the interactions, if any, between the coupling agent and the PP and between the coupling agent and the PP/CaCO₃, we investigated the absorption characteristics of the ingredients involved, using FT-IR spectroscopy. More specifically stated, we attempted to obtain difference spectra between coupling agent and PP/coupling agent mixture, and then compare them with the IR spectra of coupling agents. We could not find evidence showing that any structural change occurred between the coupling agent and the PP.

According to the literature,^{9,16} improved mechanical properties of particulate-filled thermoplastic resins can be realized by mechanisms, such as through an interdiffusion between organofunctional coupling agent segments and thermoplastic matrix molecules. It is possible that the quantity

of coupling agent used in our sample preparation was not sufficient for us to detect the difference spectra, using FT-IR. Further efforts are needed to investigate the subject.

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