PP/PE Blends. IV. Characterization and Compatibilization of Blends of Postconsumer Resin with Virgin PP and HDPE

H. P. BLOM, J. W. TEH,* A. RUDIN

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

ABSTRACT: The mechanical properties of blends of isotactic polypropylene and high-density polyethylene with a postconsumer resin (recycled dairy containers) were investigated over the entire composition range. Modification of these blends with an ethylene/propylene/diene copolymer or an ethylene/vinyl acetate copolymer was also investigated. Isotactic polypropylene/postconsumer resin blends have satisfactory impact and tensile properties at postconsumer resin contents of less than 50% for certain applications. At higher postconsumer resin contents, the tensile properties were adversely affected. The impact properties remained satisfactory. Addition of an ethylene/propylene/diene copolymer improved the mechanical properties of these blends to levels equal to or greater than those for neat isotactic polypropylene. Ethylene/vinyl acetate copolymers were also able to improve the mechanical properties, but not as efficiently as did the ethylene/propylene/diene copolymer. Blends of high-density polyethylene and a postconsumer resin had poor impact and tensile properties. Although the ethylene/propylene/diene copolymer and ethylene/vinyl acetate copolymers were able to improve these properties, the improvement was insufficient for general recycling, except at lower ($\leq 25\%$) postconsumer resin contents. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2081–2095, 1998

Key words: polyethylene; polypropylene; blends; recycling

INTRODUCTION

The recycling of industrial plastic has been an ongoing practice in many industries. More recently, environmental, legislative, and consumer pressures have led to an increase in research directed toward the recycling of postconsumer plastic waste. Industrial scrap is relatively easy to deal with for the simple reason that contamina-

tion from other plastics is unlikely. This does not hold true for municipal plastic waste. Very often, this material is a mixture of several polymers, which has the result of making processing more difficult and of limiting the number of potential applications.

A number of approaches are currently being investigated for dealing with postconsumer resin.[1] Incineration, for the purpose of waste-to-energy recovery, is used in a number of countries. However, the standard reaction to this solution is the typical "not in my backyard" response, which usually arises from fears of pollution or increased traffic. Another solution that is currently being developed is pyrolysis. A number of companies are now introducing low levels of plastic waste into hydro crackers that produce syncrude or naphtha, which can then be used as part of a

Table I Properties and Molecular Weight Characteristics of Polymers Employed in This Investigation

Resin	M_n	M_w	M_z	MFI (dg/min)	ρ (g/cm^3)
PCR	9900	75,700	374,000	34	—
PP	21,700	166,000	509,000	20[a]	0.91
HDPE	16,000	72,600	256,000	5[b]	0.96
EPDM	65,700	165,000	379,000	50[c]	0.87
EVA-28	19,700	76,900	219,000	3[b]	0.95
EVA-33	12,200	53,400	167,000	43[b]	0.95

[a] ASTM D1238, 230°C, 2.16 kg.
[b] ASTM D1238, 190°C, 2.16 kg.
[c] Mooney viscosity (ASTM D6146) ML 1 + 8 (125°C).

feedstock for other applications, including polymerization. Yet another approach is the reduction of plastic required in articles like packages by down gauging. A popular solution in Europe is the reuse of plastic parts, such as poly(ethylene terephthalate) (PET) drinking bottles. Lastly, there is the approach of converting municipal plastic waste into resins which can be used to make new articles. For example, high-density polyethylene (HDPE) bottles for milk and water are currently reground and used to make oil and household chemical containers. Shopping bags, merchant bags, and dry-cleaning bags are being used to make trash bags and lawn and leaf bags.

It is this last solution, that of converting municipal plastic waste into new articles, that has had our attention. One of the major challenges facing this approach is that very often the material that emerges from a recycling facility is a blend of two or more homopolymers. This is due to several factors: One is that consumers do not exercise the required diligence in sorting the material that they place on the curb. Some facilities now have sortation equipment that can deal with these mixtures, but very often this significantly increases the final cost of the resin, which, in turn, discourages processors from purchasing these resins. Another factor that accounts for the existence of blends in the recycle stream is that articles are constructed from two (or more) different homopolymers. Examples of this include some detergent bottles [a body of HDPE and a spout or cap of polypropylene (PP)] or disposable diapers (PE outer liner and PP inner liner). It is physically impossible to separate these articles into their constituent components. Hence, municipal plastic waste often consists of polymer mixtures.

Nearly all polymer pairs are immiscible and incompatible. This results in materials which have poor mechanical properties and undergo phase separation. Consequently, these materials cannot be used alone or unmodified, but need to be mixed with a virgin polymer and compatibilized in some way.

In the first three parts of this series on PP/PE blends, we presented results on the characteriza-

Table II Composition of Blends Prepared in This Study

PCR (wt %)	*i*-PP (wt %)	HDPE (wt %)	Copolymer (wt %)
PP/PCR blends			
0	100	—	—
7.5	92.5	—	—
15	85	—	—
22.5	77.5	—	—
30	70	—	—
37.5	62.5	—	—
60	40	—	—
75	25	—	—
90	10	—	—
100	0	—	—
Compatibilization of PP/PCR blends			
23.8	71.2	—	5.0
47.5	47.5	—	5.0
71.2	23.8	—	5.0
HDPE/PCR blends			
0	—	100	—
25	—	75	—
50	—	50	—
75	—	5	—
100	—	0	—
Compatibilization of HDPE/PCR blends			
23.8	—	71.2	5.0
47.5	—	47.5	5.0
71.2	—	23.8	5.0

Figure 1   Variation of flexural modulus and impact strength with PCR content for PP/PCR blends.

tion of model blends of isotactic PP (*i*-PP) and two grades of HDPE. In part I,[2] in which we investigated *i*-PP/HDPE blends in which *i*-PP was the major phase, we showed that the addition of HDPE to *i*-PP resulted in a sharp drop in the elongation at break and in gate puncture strength. In the subsequent article,[3] we demonstrated that these *i*-PP-rich *i*-PP/HDPE blends (90/10 PP/HDPE) could be compatibilized with 1–5 wt % of the ethylene/propylene diene copolymer (EPDM) or the ethylene/vinyl acetate copolymer (EVA) and that the choice of compatibilizer should be determined by the desired mechanical properties. In the third installment,[4] we reported on our investigation into HDPE-rich *i*-PP/HDPE blends. We found that the addition of *i*-PP to HDPE adversely affected both the impact and the tensile properties of the HDPE. Compatibilization of the 10/90 PP/HDPE blend with EPDM was very effective in improving both of these properties to values approaching those for neat HDPE.

Our investigation into the recycling of polyolefin blends began with blends of virgin homopoly-

mers, because this afforded us greater control over what went into the blend. The actual grade of the homopolymer in a specific postconsumer resin is known at best only approximately, but this parameter is important in determining the final properties of the blend. These model blends gave us an indication of what could be done with PP/HDPE blends. This article outlines the result of our research aimed at transferring the knowledge gained from the model systems to actual postconsumer resins.

EXPERIMENTAL

Materials

The postconsumer resin (PCR) was supplied by Resource Plastics Corp. (Brampton, ON). This material consisted of municipal-sorted polyolefin tubs and lids and was made up of 1 part PP and 2 parts PE. The PE portion is a mixture of HDPE and linear low-density polyethylene (LLDPE).

Figure 2 Variation of tensile yield properties with PCR content for PP/PCR blends.

Virgin HDPE resin was supplied by NOVA Chemicals Ltd. (Calgary, AB). Virgin injection-molding grade *i*-PP was supplied by Montell Canada Inc. (Oakville, ON). The EPDM copolymer was supplied by Bayer Rubber Inc. (Sarnia, ON) and had an ethylene content of $\sim$ 80%, as determined by high-field NMR analysis. Two EVA copolymers were supplied by AT Plastics (Brampton, ON). EVA-28 has a vinyl acetate (VA) content of 28%, and EVA-33 has a VA content of 33%. Molecular weight data,[5] densities, and melt-flow properties are outlined in Table I.

Sample Preparation

Blending

All materials were tumble-blended prior to melt blending on a Buss KoKneader compounding extruder, Type PR 46. The extruder consisted of a kneading screw and an extruding screw at right angles to each other. The barrel temperature varied from 145°C at the feed port to 190°C at the final zone and 180°C at the die. The feed hopper auger speed setting was 6, the kneader screw

speed was set to 12, and the extruder screw speed was set between 7 and 9. The extruded strands were cooled in water ($\sim$ 5°C), air-dried, and pelletized. The compositions of the blends prepared in this study are listed in Table II. Compatibilization studies were conducted on blends containing 25, 50, and 75% PCR.

Injection Molding

Impact bars ($6.2 \times 12.7 \times 76$ mm^3) and dumbbell tensile specimens (ASTM D638—Type I) were injection-molded on a Battenfeld BSKM 50-ton press. The barrel temperature ranged from 190 to 210°C, the injection pressure was 3.22 MPa, the mold temperature was 40°C, and the injection time was 1.2 s. The impact specimens were notched (30°) to a depth of 2.0 mm the day they were molded. All samples were left in air at room temperature for 1 week prior to testing.

Annealing

Annealing was performed in a hot-air oven set at 75°C for 1 week. Impact specimens were notched

Figure 3   Effect of PCR content on the ultimate tensile properties of PP/PCR blends.

before annealing. These conditions were chosen to accelerate the aging process without melting the polymers. In this way, we hoped to assess, in a crude manner, the long-term properties of the materials.

Mechanical Testing

Impact testing was performed on an instrumented Charpy impact tester designed in our laboratory.[6] The results reported in this study were averages of 10 specimens. Impact strengths were calculated from the kinetic energy loss of the hammer during the impact event. Tensile testing was performed on an Instron tensile tester at a crosshead speed of 25.4 cm/min and an initial jaw separation of 10 cm. The results reported herein are averages of seven specimens.

RESULTS AND DISCUSSION

PP/PCR Blends

The PCR employed in this study is a ternary mixture of PP, HDPE, and LLDPE, in approxi-

mately equal amounts. Thus, when this material is blended with a virgin *i*-PP resin, the actual PP/PE ratio will not be the same as the PP/PCR ratio. In this article, we focused our attention on the PP/PCR ratio, since an important parameter in polymer recycling is the amount of virgin resin that must be added to a PCR to achieve desirable mechanical properties. The true PP/PE ratio for these PP/PCR blends varied from 100/0 PP/PE for the neat *i*-PP sample to 33/67 PP/PE for the neat PCR sample. The true PP/PE ratio will become important when comparisons are made with model blends.

The variation of impact properties with PCR content for blends of PP and PCR is shown in Figure 1. In this figure, 0% PCR corresponds to 100% *i*-PP. The flexural modulus of the PP dropped upon addition of 7.5% PCR, after which this property remained essentially constant over the remainder of the composition range. The impact strength, on the other hand, increased very sharply upon addition of 7.5–15% PCR. In fact, the addition of 7.5% PCR to *i*-PP increased the impact strength from 18.7 to 34.7 J/m. The impact strength in the PCR composition range of

Figure 4   Effect of the addition of EPDM or EVA on the flexural modulus of PP/PCR blends.

20–60% remained relatively constant at ∼ 27 J/m. The addition of more than 60% PCR to *i*-PP resulted in a decrease in the impact strength.

It is important to note that the impact strengths of all the blends presented in Figure 1 were higher than the values for neat *i*-PP and neat PCR. This positive deviation from strictly additive behavior was not seen for blends of virgin *i*-PP and HDPE.[2] Rather, these blends exhibited a negative deviation from additive behavior. In the present case, however, we are dealing with a more complex system, one in which the PE phase is itself a mixture of two PEs. It is not clear what effect the LLDPE will have on the mechanical

Figure 5   Effect of the addition of EPDM or EVA on the impact strength of PP/PCR blends.

Figure 6   Effect of the addition of EPDM or EVA on the yield stress of PP/PCR blends.

properties of the system, although it has been shown by DSC analysis that HDPE and LLDPE are themselves compatible.[7] However, no assumption was made in the present work regarding the compatibility of the materials investigated.

The tensile yield properties of blends of PP and PCR are shown in Figure 2. The first observation to note is that for blends containing more than

37.5% PCR no yield point was detected. In other words, the sample broke without yielding. At lower PCR contents, the yield strain remained constant and the yield stress decreased with increasing PCR content. The ultimate tensile properties are shown in Figure 3. It is clear that the PCR content had no effect on the ultimate tensile strength (UTS) for blends containing less than 60% PCR. At higher PCR contents, the UTS

Figure 7   Effect of the addition of EPDM or EVA on the yield strain of PP/PCR blends.

Figure 8   Effect of the addition of EPDM or EVA on the UTS of PP/PCR blends.

dropped slightly. The elongation at break, however, decreased in a monotonic fashion from the neat PP value to the neat PCR value. The only deviation from this trend is for the blend containing 7.5% PCR. The elongation at break for this sample increased significantly.

The tensile properties of the model blends[2] exhibited similar behavior to these i-PP/PCR blends. The tensile yield properties did not vary significantly with HDPE content, the UTS increased slightly, and the elongation at break decreased sharply.

The result of annealing of these blends is also shown in Figures 1–3. Annealing resulted in an increase in flexural modulus, yield stress, and UTS and a decrease in the impact strength and

Figure 9   Effect of the addition of EPDM or EVA on the elongation at break of PP/PCR blends.

Figure 10   Variation of impact properties with PCR content for HDPE/PCR blends.

elongation at break. The yield strain was unaffected. It should also be noted that annealing of the 40/60 PP/PCR blend resulted in a material that yielded before breaking. As was stated earlier, the fresh sample broke before yielding. These blends behaved similarly to the model i-PP/HDPE blends.

It is clear from the above data that the tensile properties of i-PP were adversely affected by the addition of PCR. The impact strength, on the other hand, was improved with the addition of PCR. Annealing did affect the mechanical properties, but not to such an extent as to render the materials unusable. Therefore, in applications in which impact properties comparable to neat i-PP are required and tensile properties are less critical, it would be possible to use neat PCR. However, if better tensile properties are required, a compatibilizer must be sought which will improve the elongation at break and the yield behavior of these blends.

The effect of EPDM and EVA on all the previously discussed properties are shown in Figures 4–9. In these figures, the properties of the PP/

PCR blends are indicated by the solid black bars. The samples modified with EPDM are represented by the bars with lines rising to the right, the samples modified with EVA-28 are represented by the bars with lines rising to the left, and those samples modified with EVA-33 are represented by the cross-hatched bars. The effect of annealing is not shown in these figures since this effect was quite small.

Figure 4 outlines the effect of EPDM and EVA on the flexural modulus of PP/PCR blends. It is clear that addition of these copolymers had little effect on this property, although EPDM did decrease this property slightly for each PP/PCR composition. In all cases, the blends are all slightly less stiff than the neat i-PP. The effect of these copolymers on the impact strength is shown in Figure 5. It has already been shown that all the PP/PCR blends had superior impact strength compared to the neat i-PP and neat PCR. Addition of 5% EPDM to these blends further improved the impact strength by 50–70%, compared to the respective PP/PCR blends. These PP/PCR/EPDM blends, therefore, had impact strengths

Figure 11   Effect of PCR content on the tensile yield properties of HDPE/PCR blends.

that were 110–150% higher than the neat *i*-PP. The EVAs also improved the impact strength of the PP/PCR blends, but only slightly. In all cases, the EVA-33 was better than the EVA-28.

Figures 6 and 7 outline the effect of the compatibilizer on the tensile yield properties. The yield stress (Fig. 6) was reduced slightly by the addition of either of the copolymers. Modification of the 25/75 PP/PCR blend (which did not have a yield point under tensile conditions) with either of the copolymers resulted in a material that did exhibit a yield point. The yield strain of the PP/PCR blends was increased slightly upon addition of EPDM or EVA.

Figure 8 shows the effect of the compatibilizer on the ultimate tensile properties of the PP/PCR blends. In all cases, addition of EPDM or EVA reduced this property to the level of neat PCR, which is ∼ 22% lower than the UTS for the neat *i*-PP. The elongation at break results are shown in Figure 9. This property reacted to the addition of EPDM or EVA in much the same way as did the impact strength. Addition of EPDM to the PP/ PCR blends increased the elongation at break

significantly at all PCR compositions. In fact, the 23.8/71.2/5.0 PP/PCR/EPDM blend had an elongation at break only 7% lower than that of neat *i*-PP, while at other PCR compositions, EPDM improved the elongation at break to levels greater than neat *i*-PP. The EVAs also improved this property, but, again, to a much lesser extent. However, at PCR contents less than 50%, both EVAs improved the elongation at break to the level of neat *i*-PP. It is interesting to note that the copolymers are more effective at enhancing the elongation at break at the 50/50 composition.

It has been shown[3] that compatibilization of the model blends of *i*-PP and HDPE could be achieved with EPDM and EVA. However, it was found that EPDM was more effective at improving the impact properties, while the EVAs were more effective at improving the tensile properties. In the present study, we found that EPDM was effective at improving both the impact and the tensile properties. The EVAs were also able to improve these properties, but to a lesser extent. An important factor that must be kept in mind concerning the *i*-PP/PCR blends is that the actual

Figure 12   Effect of PCR content on the ultimate tensile properties of HDPE/PCR blends.

PP/PE ratio of the compatibilized blend was approximately 85/15, compared to a 90/10 PP/PE ratio in the model blends. Also, the present blends contain LLDPE, which may affect the mechanical properties.

Annealing of the compatibilized PP/PCR blends displayed some interesting behaviors. In general, all the properties increased as a result of annealing, except the elongation at break. This differs from the model *i*-PP/HDPE blends,[2,3] where the impact strength also decreased upon annealing. In the case of the model blends, annealing resulted in an increase in the fleuxural modulus, the yield stress, and the UTS and a decrease in the impact strength, yield strain, and elongation at break. Normally, one would expect that an increase in the flexural modulus or UTS would be accompanied by a decrease in the impact strength and elongation at break, due to the increased crystallinity indicated by the UTS and flexural modulus. It must be borne in mind that we are not dealing with two-component model blends, but rather with four-component PCR sys-

tems. It is unclear at this time why the impact strength increased with annealing, and further work is being performed in order to more fully understand this phenomenon.

HDPE/PCR Blends

The true PP/PE content for these blends varies from 0/100 PP/PE for the neat HDPE to 33/67 PP/PE for the neat PCR. The impact properties of the HDPE/PCR blends are shown in Figure 10. The flexural modulus increased with increased PCR content, but the impact strength decreased drastically as the PCR content increased. Addition of 25% PCR to HDPE resulted in a decrease in the impact strength from 115 J/m for neat HDPE to 40.4 J/m for the 75/25 HDPE/PCR blend. This was not unexpected, since the impact strength of the neat PCR was 17.4 J/m. However, results for the blends are considerably below the straight line connecting the impact strength values of the neat HDPE and PCR.

The tensile yield properties (Fig. 11) did not change significantly with PCR content, except

Figure 13 Effect of addition of EPDM or EVA on the flexural modulus of HDPE/PCR blends.

that at high PCR contents (>50%) the material did not exhibit a yield point. The variation in ultimate tensile properties (Fig. 12) is, however, very significant. The UTS changed in a stepwise manner. The HDPE and the 75/25 HDPE/PCR blend have the same UTS, and the 50/50 and 25/75 HDPE/PCR blends and the neat PCR all have the same UTS value. The elongation at break decreased drastically with increased PCR content. This also was not unexpected, since the elongation at break of the neat HDPE is 41.3% and the elongation at break of the neat PCR is only 5.5%. The actual values for elongation at break for the blends were slightly below the straight line connecting the HDPE and PCR values. These results are in full agreement with the results obtained from the model blend study of HDPE-rich i-PP/HDPE blends.[2]

The effect of annealing on the blends of HDPE and PCR is shown in Figures 10–12. In general, all the properties are improved by annealing, except the elongation at break, for which the effect of annealing seems to be composition-dependent. This is consistent with the results from the model blend study of HDPE-rich i-PP/HDPE blends[2.]

The result of the addition of EPDM or EVA to these HDPE/PCR blends is shown in Figures 13–18. In Figure 13, it can be seen that all three copolymers reduced the flexural modulus of the blends. EPDM affected a larger reduction than

did either EVA. The net result was that the flexural modulus of the blends lies on the straight line connecting HDPE and PCR.

Addition of EPDM or EVA to the HDPE/PCR blends improved the impact strength of the blends, as seen in Figure 14. EPDM was more effective at improving the impact strength than were the EVAs. However, the impact strength of the compatibilized blends was still far below that of the neat HDPE. The best material, 71.2/23.8/5.0 HDPE/PCR/EPDM, had an impact strength that is ~ 40% lower than that for neat HDPE.

Once again, the tensile yield behavior (Figs. 15 and 16) is only slightly affected by the addition of EPDM or EVA. These copolymers reduced the yield stress slightly and improved the yield strain slightly. The most notable result is that EVA-33 improved the tensile properties of the 25/75 HDPE/PCR blend such that it had a yield point.

The variation of the UTS with PCR and the compatibilizer content is shown in Figure 17. The compatibilizers had only a small effect on the UTS at the extremes of the composition range, but reduced the UTS drastically at the midrange. The UTS dropped from 22.8 MN/m^2 for the 50/50 HDPE/PCR blend to ~ 11 MN/m^2 after addition of one of the copolymers, a drop of approximately 50%. The interesting aspect about this 50/50 HDPE/PCR system was that even though annealing generally has little effect on any of the me-

Figure 14   Effect of addition of EPDM or EVA on the impact strength of HDPE/PCR blends.

chanical properties annealing of the 47.5/47.5/5.0 HDPE/PCR/copolymer blends restored the UTS to the value of the fresh 50/50 HDPE/PCR blend.

The addition of compatibilizers to the HDPE/PCR blends resulted in an increase in the elongation at break (Fig. 18). At low PCR contents,

EPDM was the most effective at improving this property. The two EVAs also enhanced the elongation at break, but to a lesser extent, compared to EPDM. For the 50/50 HDPE/PCR blend, all three copolymers improved this property equally well. At high PCR contents, EPDM and EVA-28

Figure 15   Effect of addition of EPDM or EVA on the yield stress of HDPE/PCR blends.

Figure 16   Effect of addition of EPDM or EVA on the yield strain of HDPE/PCR blends.

left the elongation at break unchanged, while EVA-33 improved this property. It must be kept in mind here, however, that only the material containing 5% EVA-33 had a yield point. This observation accounts for the improved elongation at break. In the final analysis, however, only the 71.2/23.8/5.0 HDPE/PCR/EPDM blend had an elongation at break similar to that of the neat HDPE.

It has been shown that EPDM is an excellent compatibilizer for HDPE-rich i-PP/HDPE blends.[4] In the present study, we found that even though EPDM was found to be effective at improving the impact and tensile properties of the HDPE/PCR

Figure 17   Effect of addition of EDPM or EVA on the UTS of HDPE/PCR blends.

Figure 18   Effect of addition of EPDM or EVA on the elongation at break of HDPE/PCR blends.

blends it was unable to improve them to neat HDPE levels.

CONCLUSIONS

Addition of PCR to virgin *i*-PP resulted in a material with acceptable impact and tensile properties as long as the PCR content was less than 50%. At higher PCR contents, the blends had good impact properties but poor tensile properties. Compatibilization of these blends with EPDM and EVA was effective at improving the impact properties even further, as well as improving the elongation at break of the blends. In general, EVA was not as effective at improving the mechanical properties as was EPDM.

Addition of PCR to virgin HDPE resulted in a material with poor impact and tensile properties. Addition of EPDM to the 75/25 HDPE/PCR blend yielded a material with properties similar to those for neat HDPE, except for the impact strength, which was still well below this level. EVA was also able to improve the impact and tensile properties of these blends, but to a much lesser extent. At higher PCR contents, the compatibilized blends had mechanical properties that were very much inferior to the neat HDPE. However, the improvement that was realized points to the possibility of finding a more suitable compatibilizer for these HDPE/PCR systems.

REFERENCES

1. J. W. Ellis, *ANTEC,* **39,** 893 (1993).
2. H. P. Blom, J. W. Teh, and A. Rudin, *J. Appl. Polym. Sci.,* **58,** 995 (1995).
3. H. P. Blom, J. W. Teh, and A. Rudin, *J. Appl. Polym. Sci.,* **60,** 1405 (1996).
4. H. P. Blom, J. W. Teh, and A. Rudin, *J. Appl. Polym. Sci.,* **61,** 959 (1996).
5. S. Pang and A. Rudin, in *ACS Symposium Series 521, Chromatography of Polymers: Characterization by SEC and FFF,* Th. Provder, Ed., American Chemical Society, Washington, DC, 1993.
6. D. G. Cook, A. Rudin, and A. Plumtree, *Polym. Eng. Sci.,* **30,** 596 (1990).
7. N. K. Datta and A. W. Birley, *Plast. Rubb. Process. Appl.,* **2,** 237 (1982).