

# Evaluation of Recycled PP/Rubber/Talc Hybrids

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## SYNOPSIS

Mechanical properties of recycled PP/rubber/filler systems were studied and mechanisms were discussed on the basis of molar mass and molar mass distribution, morphologies, and thermal behavior. Characteristics of recycled PP/rubber/filler depend on degradation of PP and additional components. Recycling processes decreased impact strength, but it seemed not to affect tensile properties significantly. Aging with UV and moisture affected mechanical properties by some degree of PP chain scissions and ethylene chain crosslinking in EP rubber. Inorganic filler acted as a crack center and accelerated aging degradation. Paint decreased mechanical properties significantly by introducing stress concentrations. Recycle processing decreased the molar mass and increased the molar mass distribution of PP. Aging with UV decreased crystallization temperature and increased crystallization half-time by decreasing nucleation. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer waste is increasingly coming under the environmental spotlight,<sup>1</sup> and the major issue now centers on its disposal because of declining landfill capacity. On the other hand, auto manufacturers have increasingly turned to polymer materials as a mass reduction method.<sup>2</sup> There is now a growing realization that if polymer materials are to continue their expansion into the automotive industry they must ultimately be disposed of responsibly, be it by postmolding or after a second product life cycle. Among the plastic parts used in vehicles, PP bumpers have relatively simple material compositions and are estimated to grow at 12%/year through to 1996.<sup>3</sup> And, also, because of their large size, they have been targeted for recycling throughout the world. Information dealing with recycled bumpers is increasing, especially that related to methods of removing paint,<sup>4-6</sup> but some of the data are contrary. We have, therefore, reexamined the mechanical properties of recycled PP bumper bars in an attempt to reconcile these differences. Mechanisms of varied mechanical properties were studied on the basis of molar mass,

thermal behavior, and morphologies. The present article is part of such investigations and represents an introduction for the study of recycling PP/rubber/filler hybrids.

The degradation of pure PP has been widely studied.<sup>7-11</sup> However, there are few articles dealing with recycled PP/rubber/filler systems. Characteristics of recycled PP/rubber/filler depend not only on degradation of PP, but also on the additional components. In the three-component PP/rubber/filler systems, widely differing structure and, consequently, a wide range of properties has attracted more and more interest, because by the correct addition of both types of secondary components it is possible to obtain a variety of materials with targeted and optimal performance for the specific requirements of different applications. Recycling of three-component PP/rubber/filler systems has both scientific and commercial importance.

In this article the impact strength and tensile properties of recycled PP bumpers were used to evaluate their mechanical properties. The effect of paint, aging, and processing on the mechanical properties has been studied. A method for calculating the molar mass distribution from dynamic viscoelastic melt data was used to evaluate their molar mass ( $M$ ) and molar mass distribution ( $MD$ ). DSC was used to study their thermal behavior and

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**Table I** Materials Used in the Experiments

No.	Label	Years	Paint Colour	Formulation
1	Bumper-1	1981	—	PP base
2	Bumper-2	1984	—	PP base
3	Bumper-3	1988	white	PP base
4	Bumper-4	1992	red	PP base
5	Bumper-5	1993	white	PP base
5	Bumper-6	unused	—	PP base
6	Bumper-Ref		—	PP60/EP25/talc15

microstructure. Scanning electronic microscopy (SEM) was used to investigate morphologies of fracture and aged surfaces.

## MATERIALS AND EXPERIMENTAL

### Materials

A large number of bumper bars of different type/year were collected for these experiments. Table I lists several of them according to year of manufacture. Virgin PP (ICI Australia) and a PP/rubber/filler hybrid, PP 60/EPR 25/talc 15, with some carbon black and heat stabilizers, were used to as reference materials.

Various postconsumer bumper bars were washed with water to remove mud and rust, then dried in air. The cleaned bumpers were granulated to about 3.5 mm diameter, then extruded using a Haake twin screw extruder (diameter 42, diameter : length = 1 : 7). The test specimens were moulded using a Johns-600 injection molding machine. In this experiment, one full recycling means: 1—granulation, 2—extrusion, and 3— injection molding.

### Aging Experimental

Postconsumer PP bumper bars have been aged in the environment for varying periods. Virgin materials (Bumper-6) were aged in a QUV Accelerated Weathering Tester according to ASTM G-53. Table II gives the experimental conditions.

### Mechanical Property Testing

#### Testing of Impact Strength

The injection-molded test bars were notched according to ASTM D-256, using a milling machine. The notch had an included angle of 45°, a tip radius of 0.01 in., and a notch depth of 0.1 in. Davenport Izod Impact Test was used in this experiment. Width of the injection-molded specimens was 6 mm. The impact strength was measured at 20 ± 2°C and reported in Joule per meter of notch.

#### Testing of Tensile Properties

The specimens were injection molded according to ASTM Method D638 (width of narrow section = 10 mm, thickness = 4 mm, gauge length = 80 mm). Tensile tests were performed in accordance with this method on a Lloyd 200 apparatus using a crosshead speed of 50 mm/min. The tests were carried at 20 ± 2°C. All data were recorded and processed through a computer with Lloyd Instruments (V.2.01).

### Molar Mass (M) and Molar Mass Distribution (MD) Measurement

A method<sup>12,13</sup> for calculating the molar mass distribution from dynamic viscoelastic melt data was used in this work. The loss and storage shear moduli were measured on a Rheometrics Mechanical Spectrometer (RMS-605M). A plate diameter of 25 mm was employed to cover a frequency range 0.5 to 100 rad/s. The temperature range was 170 to 250°C. The

**Table II** Experimental Conditions for Aging

Light	Type UV-B	Peak Emission 313 nm	Low Cutoff (1%) 280 nm
Cycle	8 h UV at 50°C	4 h moisture (100%) at 50°C	Total 12 h

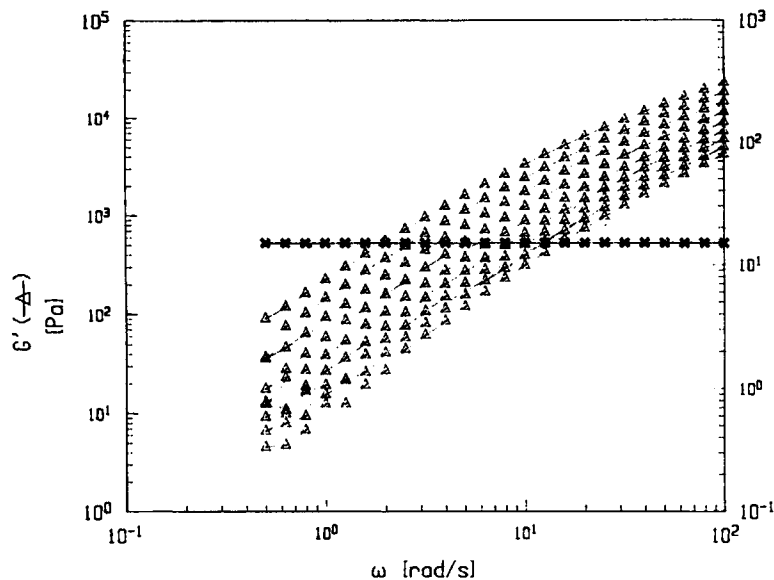


Figure 1 Measured storage modulus curves (pure PP).

complex shear modulus was shifted to a reference temperature and then molar mass distribution was calculated using Rheometrics RHECALC Software.

Figure 1 shows an example of measured storage modulus vs. various frequencies at different temperatures. The shape of all of the curves was similar, which meets the condition of two neighboring curves having the same shape. Figure 2 is the shifted storage molecular master curves from Figure 1. It is seen

that the master curve is smooth. From the master curve zero shear viscosity, molar mass and molar mass distribution were calculated. Figure 3 shows an example of apparent molar mass distribution.

**Thermal Behavior**

A Perkin-Elmer DSC7 Apparatus was used to study the thermal behavior and microstructure. Measure-

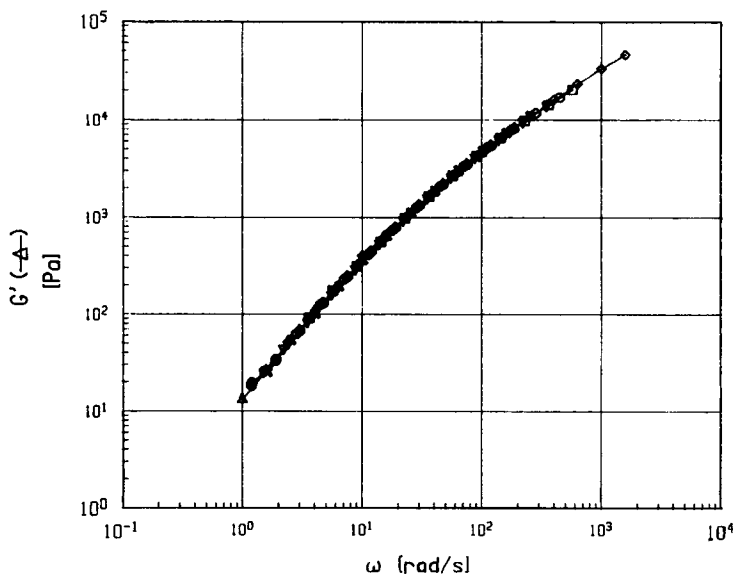


Figure 2 Shifted storage modulus master curve from Figure 1.

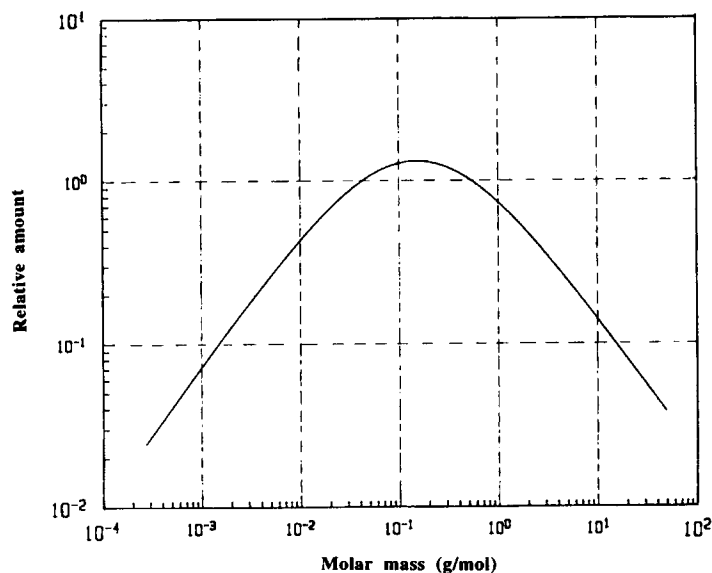


Figure 3 Calculated molar mass distribution from storage modulus.

ments were made on samples of approximately the same mass, which were cut from the surface of impact specimen bars with about 20  $\mu\text{m}$  thickness. Melting temperatures  $T_m$ , and crystallisation temperatures  $T_c$ , were obtained by heating and cooling samples at 20°C/min. For the aged samples, two types of DSC experiments were performed. In a first heating run, a sample consisting of a small piece of film cut from a surface (1 mg) was heated at 20°C/min from 40 to 200°C, left for 2 min at 200°C, and cooled at 20°C. The sample was then heated again at 20°C/min to 200°C; this constituted the second heating run. The first heating run was characteristic of the secondary "chemocrystallization" resulting from the aging. The second run and crystallization process are characteristic of crystallization and microstructure.

### Morphological Study

The fracture and aged surfaces were examined using a JEOL JSM-840A SEM after coating with gold-palladium alloy. In order to avoid distortion of the surface, the coating was applied for 10 s, then paused for 10 s, then the coating was repeated for a total of 100 s. Micrographs were obtained by collecting secondary electrons emitted upon bombarding the sample with 20 kV electrons. Micrographs were obtained at magnifications ranging from 1000 to 10,000 $\times$ .

## RESULTS AND DISCUSSION

### Mechanical Properties

#### *Mechanical Properties of Different Type/Year Bumper Bars*

Table III lists mechanical properties of some of collected bumpers and reference materials. Generally, the mechanical properties of different type/year bumper bars were significantly different. That was expected because their formulation and requirement for mechanical properties were different. This prevents any useful comparison between them to study the aging time on the mechanical properties.

#### *Effect of Paint on Mechanical Properties*

Figure 4 shows that the effect of paint on the tensile properties. It is seen that paint did not affect tensile properties significantly. However, the paint decreased impact strength significantly. Figure 5 shows the effect of paint on the impact strength. The impact strength decreased about 32--38% at room temperature. The paint particles were mainly cross-linked polyurethane, which has a poor interface with the PP matrix. The large size of the paint (about 2 ~ 3 mm) caused it to act as a stress concentration and weakness in PP matrix.

The paint on the surface of bumpers was removed by both chemical (phenol and dichloromethane) and

**Table III Mechanical Properties of Various Materials**

Materials	Yield Strength (N/mm <sup>2</sup> )	Modulus (MPa)	Elongation at Break	Impact (J/m)
Bumper-1	13.25 ± 0.12	437.7 ± 22.0	>100	544.17 ± 61.69
Bumper-2	14.44 ± 0.26	528.1 ± 71.3	47.8 ± 8.5	280.97 ± 11.84
Bumper-3	19.02 ± 0.59	457.9 ± 25.2	84.3 ± 13.6	335.69 ± 18.51
Bumper-4	14.54 ± 0.31	515.8 ± 7.96	42.8 ± 6.4	172.09 ± 14.31
Bumper-5	13.59 ± 0.22	509.1 ± 46.3	8.9 ± 0.76	219.98 ± 13.11
Bumper-6	14.64 ± 0.75	493.2 ± 34.9	56.1 ± 15	328.05 ± 12.1
Bumper-Ref	14.44 ± 0.26	528.1 ± 71.3	47.8 ± 8.5	280.97 ± 11.84

mechanical methods. There is no significant difference of mechanical properties between the materials in which paints were removed by different methods.

### Effect of Times Recycled on the Mechanical Properties

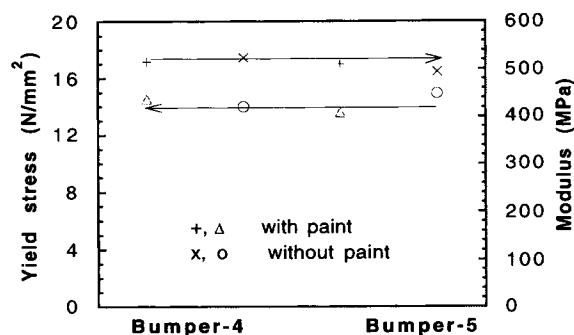
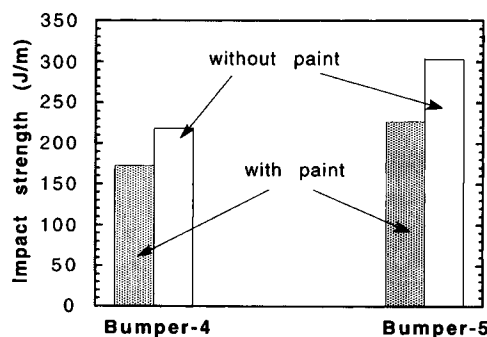
Table IV gives the effect of times recycled on the tensile strength. It is seen that the times recycled did not affect tensile strength significantly. Figure 6 shows the effect of times recycled on the impact strength. It is seen that the times recycled decreased impact strength. An interesting phenomenon is that the effect on the pure PP is not significant. This means that the effect of recycling processing may be mainly caused by the additional components.

There exist several types of degradation during processing. They are mechanical, thermal, chemical, and oxidation degradation.<sup>14-16</sup> There are two kinds of degradation for polymer chain: crosslinking and chain scission. Previous studies have shown that degradation of PP during processing is mainly chain scission.<sup>16-19</sup> This has explained the decrease of impact, and elongation in PP/rubber/filler systems was higher than that in pure PP. Furthermore, pre-

vious study has shown that below 310°C crosslinking was more important for the ethylene chain.<sup>20-24</sup> The crosslinking of ethylene in EP rubber reduced the efficiency of EP as a toughening agent in PP, which also resulted in decreasing the impact strength of PP. Results of PP chain scission and crosslinking of ethylene in EP have combined to not significantly change the tensile strength.

### Effect of Aging on Mechanical Properties

Table V shows the effect of aging on the mechanical properties. It is seen that impact strength decreased but yield strength and modulus increased. Interactions of photons with the polymer chain induce a complicated series of reactions. In the case of polyolefins, sufficiently detailed findings have been collected on photo-oxidative transformations of polymer chains.<sup>25</sup> For PP, crosslinking due to UV radiation is highly unlikely.<sup>25,26</sup> Degradation of PP by chain scission decreases impact strength. On the other hand, a secondary "chemocrystallization" of PP due to UV radiation has already been observed and discussed.<sup>7,26,27</sup> This was explained by assuming that chain segments resulting from photo-oxidative

**Figure 4** Effect of paint on the tensile properties.**Figure 5** Effect of paint on impact strength.

scissions of the chains that originally were present in amorphous regions can additionally crystallize owing to their sufficient mobility above 50°C during the exposure to the UV Accelerated Tester. Increasing crystallinity may result in an increase in tensile properties. Furthermore, the crosslinking of ethylene in EP rubber, as mentioned above, could increase tensile properties. The probability of the occurrence of these degradation sites is higher in the surface layer than the bulk, but such sites may also lie inside of materials.<sup>26,28</sup> Inorganic filler, similarly acts as an impurity and can accelerate aging degradation and play a role as a crack center.<sup>26</sup>

### Molar Mass (*M*) and Molar Mass Distribution (*MD*)

It is well known that for a polymer material it is not easy to calculate its actual molar mass and molar mass distribution and compare results between different methods. Furthermore, the method for calculating molar mass from zero shear modulus is only suitable for pure linear thermoplastic polymers. However, the aim of this work was to study the effect of recycle processing on the *M* and *MD*. Actual calculation of *M* and *MD* can be avoided and focus made on the change of them.

Figure 7 shows the effect of times recycled on the molar mass distribution of pure PP. It is seen that *MD* was increased by increasing times recycled. Molar mass was decreased by increasing the times recycled. Similar results were found for bumper bar materials. Table VI gives the effect of times recycled on the zero shear viscosity and molar mass distribution of pure PP and three components system, PP/rubber/filler, respectively. It is seen that zero shear viscosity was decreased and molar mass distribution increased with increasing times recycled. The results were used to explain the decrease of impact strength with times recycled.

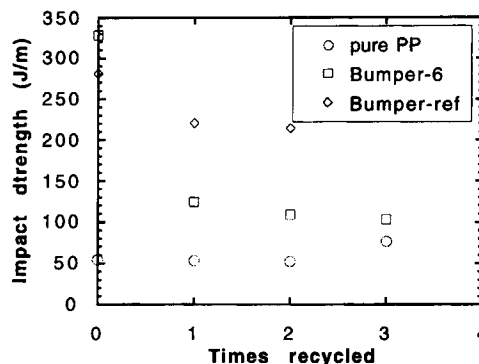


Figure 6 Effect of times recycled on impact strength.

It should be noticed that inorganic filler in bumper material increased the zero shear viscosity significantly, which affected the apparent molar mass determined from rheometry. Comparison of the results between pure and filled materials is not justified using this method.

### Thermal Behavior

Figure 8 shows DSC curves of the crystallization of polypropylene from virgin and aged materials for different times. It is seen that crystallization temperature decreased with increasing aging time. It is also seen that slope on the high temperature side of the curves decreased with increasing aging time. That means that overall crystallization growth decreased by the reduction of nucleation. The reason of the decreasing of nucleation can be explained by the different chemical structures of the aged materials:<sup>9</sup> the large amount of oxygenated groups gave rise to a polar polymer, which was incompatible with the nonpolar virgin PP. Details of crystallization kinetics of recycled PP/rubber/filler system and mechanisms will be discussed in a separate article.

Table IV Effect of Recycling Process on the Tensile Properties

Materials	Processing	Yield Strength (N/mm <sup>2</sup> )	Modulus (MPa)	Elongation at Break
PP-LZM197	Injection	23.49 ± 0.15	660.9 ± 21.4	29.9 ± 5.7
PP-LZM197	One recycle	23.88 ± 0.17	660.1 ± 21.6	24.3 ± 3.0
PP-LZM197	Two recycles	23.91 ± 0.24	668.0 ± 23.2	33.4 ± 4.5
Bumper-6	Cut from the bumper	14.64 ± 0.75	493.2 ± 34.9	56.1 ± 15
Bumper-6	One recycle	14.71 ± 0.12	565.0 ± 37.9	32.0 ± 8.3
Bumper-6	Two recycles	14.60 ± 0.21	584.8 ± 29.4	21.0 ± 7.6

**Table V Effect of Aging Time on the Mechanical Properties of Bumper-Ref Materials**

Materials	Virgin Materials	834 h <sup>a</sup>	1953 h <sup>a</sup>
Impact strength (J/m)	202.41	192.38	179.81
Modulus (Mpa)	641.9	685.2	730.2
Yield Strength (N/mm <sup>2</sup> )	14.27	14.54	15.03
Elongation (mm)	47.03	46.23	46.06

<sup>a</sup> Time ratio of UV to moisture is 2 : 1.

It is well known that melting enthalpy,  $\Delta H_m$ , is a quantity proportional to the heat of crystallization of a given sample and, thus, to its degree of crystallinity. Because the measurement on all the samples were done under identical instrument conditions, the variations of  $\Delta H_m$  may be taken to represent the variations of crystallinity. An increasing crystallinity has been reported for pure PP film that was due to cleaved chains in the amorphous phase, which could further crystallize.<sup>7,9</sup> Our experimental results for PP/rubber/filler systems did not show significant change.

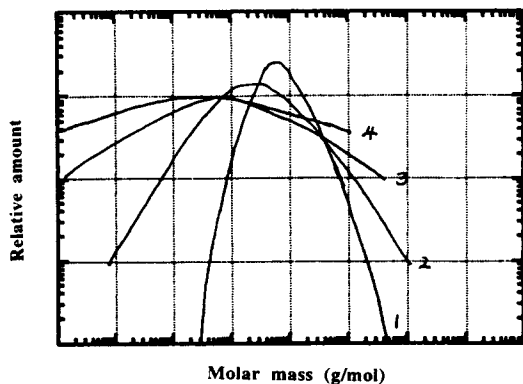
Table VII shows that the effect of aging time on the melting temperatures,  $T_m$ , and enthalpy,  $\Delta H_m$ . It is seen that for the first run  $T_m-1$  and  $\Delta H_m-1$  did not change significantly. However, for the second run, both melting temperature and enthalpy were significantly affected by the aging time.  $T_m-2$  and  $\Delta H_m-2$  decreased with increasing aging time. That indicates that "perfection" of crystal lamellar in PP has been destroyed. This is expected because incompatible polar groups in the aged materials could provide some defects in the PP spherulites. The results corresponded with crystallization temperature. The difference of melting temperature for run-1 and

run-2 was caused by the secondary crystallization of PP.

**Morphologies**

Examination of the fracture surfaces by SEM did not reveal any significant difference in fracture mechanisms except perhaps that the fracture was somewhat more fibrous, suggesting more matrix plastic flow in the virgin materials.

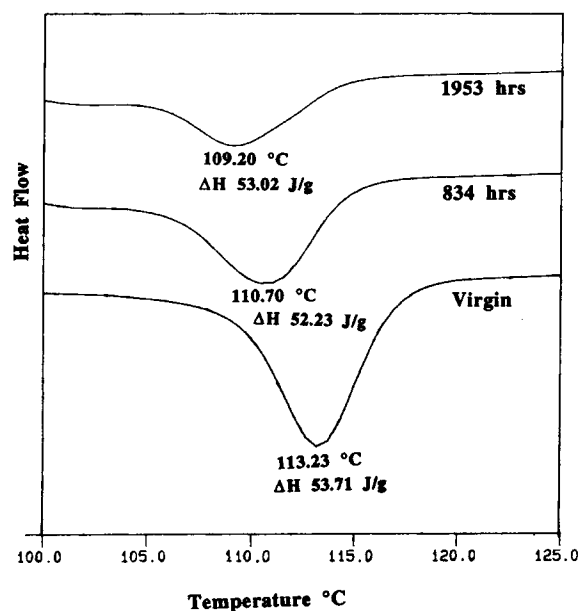
Examination of the surface given in Figure 9 clearly shows a difference in morphology. Figure 9(a) is the surface of a virgin material. It is seen that all the talc particles were covered by a PP matrix, although the talc particles can still be identified as gray regions. Figure 9(b) is the surface of a material aged for  $1 \times 10^3$  h. It is rather clear here that the PP film on the talc has been cracked. Talc particles appeared on the surface as bright areas. The varying of morphologies in pure PP film has been observed previously.<sup>7</sup> Mechanical properties of PP film were decreased significantly by UV aging.<sup>26</sup> That also explained the decreasing of mechanical properties of PP/rubber/filler hybrids. On the other hand, in the three-component PP/rubber/filler systems, talc and black carbon can act as a UV shield



**Figure 7** Molar mass distribution of recycled PP: 1—virgin PP, 2—one recycle, 3—two recycle, 4—three recycle.

**Table VI Effect of Recycle Processes on Zero Shear Viscosity and Mean MD**

Materials	Recycle Time	Relative $\eta_0$	Relative $M_w/M_n$
Pure PP	Virgin PP	1.00	1.00
	1	0.95	2.10
	2	0.88	2.36
	3	0.72	2.14
Bumper-6	Cut from bumper	1.00	1.00
	1	0.96	1.79
	2	0.89	2.17
	3	0.84	1.93



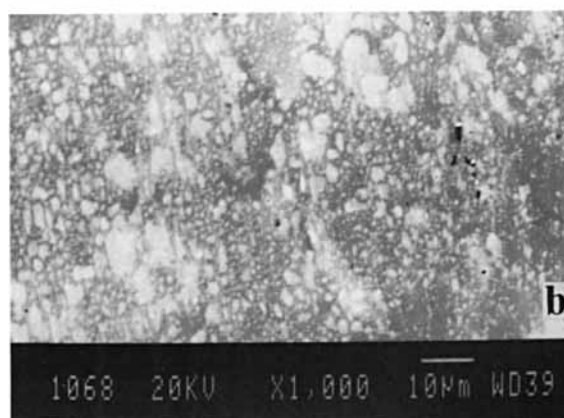
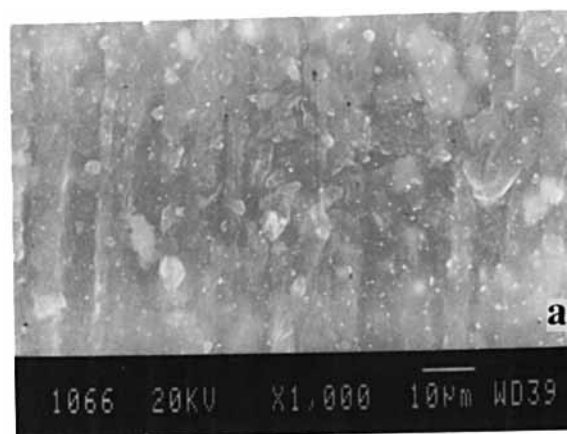
**Figure 8** Effect of aging time on the crystallization behavior.

to protect further aging. So the decrease was not as high as in the pure PP film.

## CONCLUSION

Characteristics of recycled PP/rubber/filler depend on degradation of PP and additional components. For example, degradation of ethylene in EP rubber is crosslinking, which results in decreasing efficiency of EP as a toughening agent. Inorganic filler can act as a crack center and accelerate aging degradation.

Recycle processing decreased impact strength, but it seemed not to affect the tensile properties significantly. Aging with UV and moisture affected mechanical properties to some degree by PP chain scissions and ethylene chain crosslinking in EPR rubber. The paint decreased mechanical properties



**Figure 9** Effect of aging on the surface morphologies. (a) virgin material; (b) aged for 1953 h.

significantly through introducing stress concentrations.

Recycle processing decreased the molar mass and increased the molar mass distribution of PP. Aging with UV decreased crystallization temperature and increased crystallization half-time by reducing nucleation in PP. Melting temperature and enthalpy

**Table VII** Crystallization Behavior of Aged Materials

Aging Time	Run-1		Run-2	
	$T_m-1$	$\Delta H_m-1$	$T_m-2$	$\Delta H_m-2$
Virgin materials	161.22	42.50	156.34	36.88
834 h <sup>a</sup>	161.13	42.71	155.31	32.93
1953 h <sup>a</sup>	160.96	41.76	153.11	29.22

<sup>a</sup> Time ratio of UV to moisture is 2 : 1.



of melting were decreased with aging time because oxygenated groups acted as defects in the PP spherulites. The photo-oxidized polypropylene changed the morphologies of the surface and introduced incompatible polar groups.

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