Toughening Polypropylene with Nanoscale Rubber Particles*

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SUMMARY: A new kind of powdered rubber, ultra-fine full-vulcanized powdered rubber (UFPR), was invented and used for toughening polypropylene. The UFPR dispersed well in the PP matrix on a nanoscale. Both toughness and stiffness of PP can be improved by toughening with UFPR. DSC data showed that UFPR has some nucleation effect on PP. When PP was toughened with UFPR and EPDM together, the impact strength showed a synergistic toughening effect.

Introduction

The rubber commonly used for PP toughening, such as EPDM, polybutadiene rubber, and SBR *etc.*, is usually in block or granular form and is non-crosslinked before blending. The size of rubber particles dispersed in a PP matrix is dependent on the viscosity ratio of PP to the rubber phase and the processing conditions such as screw speed *etc.* Therefore the particle size of the rubber phase in a PP matrix is uncontrollabe and is apt to change during melt processing.

In order to control the particle size of rubber in toughened plastics, we now use a new type of powdered rubber. It is a proprietary product (we call it ultra-fine full-vulcanized powdered rubber, UFPR; or elastomeric nano-particles, ENP), which has a highly crosslinking structure, and thus can prevent the rubber particles from sticking together. The UFPR is prepared by irradiating rubber latex and then spray drying.[1] The size of the UFPR is basically the same as that of the rubber latex, and can remain unchanged after blending with plastics. It is adjustable from 30nm to 2000nm, since the size of the rubber latex can be controlled by adjusting polymerization conditions. Our recent work[2] showed that UFPR has good and special toughening effects in different

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plastics. Its application in PP toughening will be discussed in this paper.

Results and Discussion

Table 1 shows the mechanical properties of PP toughened with modified styrene-butadiene UFPR. The toughness is greatly increased, compared with that of the neat PP, and at the same time the stiffness and heat resistance are also increased. This balance effect is impossible to achieve by using conventional rubber such as EPDM *etc.* Fig.1 shows that the UFPR particles with sizes less than 100nm dispersed very well in a PP matrix. This assures their good toughening effect in matrix.

Table 1 Mechanical properties of PP toughened by modified styrene-butadiene UFPR*

Sample	Tensile strength (MPa)	Notched Izod impact strength (J/m)	Flexural strength (MPa)	Flexural modulus (GPa)	Heat distortion temperature (°C)
Neat PP	34.9	99.7	34.3	1.49	113.6
1wt% UFPR	36.6	105	37.2	1.62	124.8
2wt% UFPR	37.0	265	38.0	1.65	126.8
5wt% UFPR	35.7	479	35.9	1.58	122.5

* The styrene-butadiene UPFR was modified by spray drying the UFPR latex together with dissolved sodium benzoate (10 phr based on dry latex). The neat PP is isotactic PP (B-200) made in SINOPEC Luoyang PetroChem. China

Table 2 shows the crystallization data of UFPR toughened PP. The cooling crystallization temperature of the PP sample toughened with modified UFPR is higher than that of neat PP. The absolute value of enthalpy change of PP during cooling crystallization increases after adding UFPR, which indicates that the crystallinity is increased. Under isothermal crystallization, the crystallization rate constant K of PP sample toughened with modified UFPR at 124□ is approximately 150 times higher than that of neat PP. Thus it can be concluded that the modified UFPR has a nucleation effect for PP crystallization, and increases both the crystallization temperature and crystallinity. This could be the reason why heat resistance and flexural modulus of PP were improved by using rubber as a toughener. For the modified UFPR, it is inferred that the sodium benzoate may locate on the surface of UFPR in nano scale and this special structure could be closely related to the excellent crystallization properties and to the simultaneous improvements in stiffness, toughness and heat resistance of the materials.

Table 2 Crystallization data of UFPR toughened PP *

Sample	non-isothermal**		isothermal***		
	T_c (°C)	ΔH_c (J/g)	T_c (°C)	n	K (min^{-n})
pure PP	111.9	-87.9	120	2.8	0.408
			124	2.7	0.043
toughened with 10 phr UFPR	119.6	-89.5	124	3.03	6.352
			126	3.2	1.164
			128	3.19	0.440

* determined on PE-7 DSC
** cooling rate 10 °C /min.
*** calculated with Avrami equation

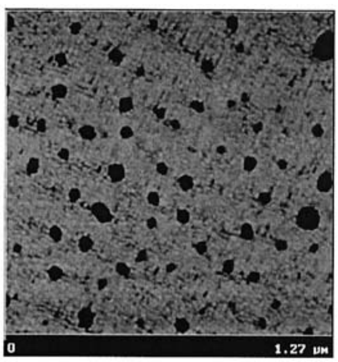

Fig.1 AFM micrograph of toughened PP using sodium benzoate modified styrene-butadiene UFPR.

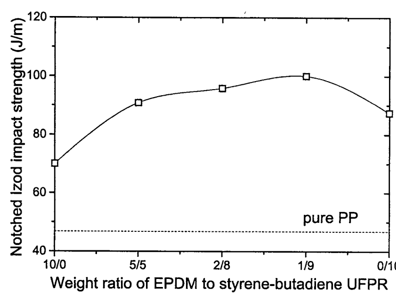

Fig.2 The effect of combined elastomer systems of styrene -butadiene UFPR and EPDM on the impact strength of PP.

UFPR has a small particle size, which is more suitable for toughening ductile plastics. Homopolymerized PP is brittle compared with some ductile plastics such as nylon and PET. According to the bimodal toughening model proposed by Y. Okamoto *et al.*[3] in an HIPS system, we combined UFPR and EPDM together to test whether they had a synergistic toughening effect in a PP system. The result is shown in Fig.2. The impact strength of PP toughened with UFPR was higher than with EPDM. A peak value was reached when the UFPR was dominant in the composition ratio and the content of EPDM was small. This result indicates that the best toughening effect can be obtained when UFPR and a small content of conventional rubber are added together into PP.

Conclusions

The modified UFPR can increase both toughness and stiffness of PP. It disperses uniformly in a PP matrix and has a nucleation effect in PP crystallization. The crystallization temperature and crystallinity of PP were increased, which resulted in the improvement of stiffness of PP. When UFPR was combined with EPDM, there is a synergistic effect in PP toughening. The peak value of impact strength appears at such a composition ratio in which UFPR is dominant.

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