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Unexpected Mechanical Properties of Functionalized Polypropylene: Tensile Test, Charpy Impact Tensile Test, DSC, and WAXD Analysis of Poly(5-hexen-1-ol-*co*-propylene)

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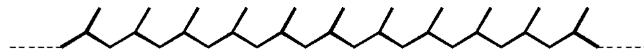
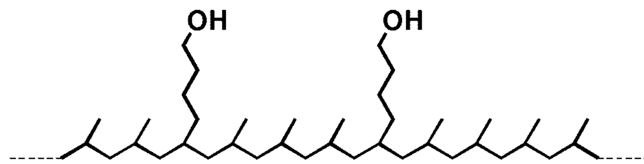
Isotactic polypropylene (PP) is one of the most important materials as hard plastics,[1−4] fire retardants,[5] and electrics,[6,7] and the demand has still been increasing. Recently, the copolymer of propylene and other olefins (ethylene or higher α-olefin) has been also developed as the thermoplastic elastomer. Invention of the homogeneous polymerization catalyst system like a metallocene/methylaluminoxane allows us to control the structure of copolymer easily. Thus, the various kinds of PP are available at present, from hard plastic to soft material. However, two important mechanical properties of the PP (elastic modulus and impact strength) are generally in the relation of the trade-off.[8,9] Introduction of the comonomer into PP decreases the elastic modulus, while the impact strength is improved.

We have developed the functionalized PP by means of copolymerization of propylene and α-olefin containing hydroxyl group so far.[10] In this paper, we will report and discuss the particular mechanical properties of the functionalized PP containing a hydroxyl group (PPOH), which shows the new relation of elastic modulus and impact strength that was out of the trade-off relation. Details of the PP and PPOH employed in the examination are as follows: PP: weight-average molecular weight (M_w) = 905 000, molecular weight distribution (M_w/M_n) = 2.15, isotactic triad (*mm*) = 98.6%; PPOH1.3: poly(5-hexen-1-ol-*co*-propylene), M_w = 503 000, M_w/M_n = 2.04, *mm* = 98.0%, content of comonomer = 1.3 mol %; PPOH6.4: poly(5-hexen-1-ol-*co*-propylene), M_w = 146 000, M_w/M_n = 1.90, *mm* = 98.4%, content of comonomer = 6.4 mol %. In addition, nonfunctionalized copolymer was also examined for comparison: PPH1.6: poly(1-hexene-*co*-propylene), M_w = 207 000, M_w/M_n = 2.62, *mm* = 98.4%, content of comonomer = 1.6 mol %; PPH6.5: poly(1-hexene-*co*-propylene), M_w = 227 000, M_w/M_n = 1.95, *mm* = 97.0%, content of comonomer = 6.5 mol %. Preparation of test peaces and measurement of physical properties were based on JIS K7113-1 (ISO 527-1) and JIS K7160 (ISO 8256) standard (see Supporting Information).

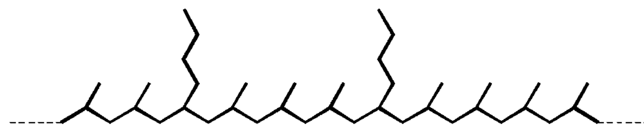
Figure 1 shows the stress−strain curves of tensile test. Surprisingly, it was found that the hydroxyl group incorporated copolymers exhibit a higher toughness trend than both pure PP and copolymer without a hydroxyl group. Table 1 also lists the results of the tensile test, Charpy impact tensile test, differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD). Regardless of the existence of a hydroxyl group, the introduction of comonomer improved the impact tensile strength drastically. Both PPOH6.4 and PPH6.5 showed the about 8 times



Polypropylene **[PP]**



Poly(5-hexen-1-ol-co-propylene) **[PPOH]**



Poly(1-hexene-co-propylene) **[PPH]**

high impact value in comparison with PP. Similar behavior was also observed on the elongation at break. These results seem to indicate that the incorporation of comonomer soften the PP. However, the tensile elongation modulus strongly depended on existence of the hydroxyl group. Although the incorporation of any comonomer decreased the modulus compared with PP, the PPOH6.4 exhibited 3 times higher modulus than the PPH6.5. Tensile strength (braking stress) also depended on the hydroxyl group. The PPOH1.3 and the PPOH6.4 were tougher than the others.

In order to interpret these unexpected phenomena, thermal property and crystalline structure were investigated by DSC and wide-angle X-ray diffraction (WAXD). Melting point (T_m) and heat of fusion (ΔH) decreased with introduction of any comonomer. The X-ray peaks were also broadened by the comonomer incorporation (it seemed to be like a mesophase polymer). The mesophase polymer is known to be softer material than crystalline polymer.[11,12] On the other hand, the hydroxyl group strongly influenced these values. The PPOH samples showed lower T_m and higher ΔH values than PPH. Crystallinity was estimated from the observed ΔH value using the standard enthalpy of fusion (ΔH_m = 164.9 J/g for isotactic PP).[13] It was revealed that the crystallinity of PPOH was much higher than that of PPH in spite of these samples contained similar amount of blanches, and the lower T_m implied the smaller crystal. The domain size of crystal was therefore estimated by the Hall equation using the bandwidth of the α-crystal (110) peak observed in WAXD.[14] With regard to DSC data, it was found that the PPOH6.4 has a smaller crystal domain than the PPH6.5.

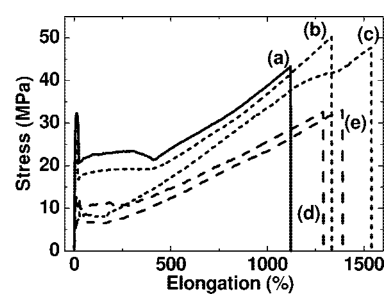


Figure 1. Stress−strain curves of functionalized PP: (a) PP, (b) PPOH1.3, (c) PPOH6.4, (d) PPH1.6, and (e) PPH6.5.

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Table 1. Mechanical Properties and High-Order Structure of Functionalized PP

sample	modulus[a] (MPa)	tensile strength[a] (MPa)	elongation at break[a] (%)	impact tensile strength[b] (kJ/m²)	T_m[c] (°C)	ΔH[c] (J/g)	crystallinity[d] (%)	fwhm[e] (deg)	domain size[f] (nm)
PP	619	43	950	95	160.8	78.6	47.7	0.63	13.3
PPOH1.3	419	50	1334	246	142.5	62.3	37.8	0.89	9.4
PPOH6.4	342	48	1539	803	111.1	38.6	23.4	2.86	2.9
PPH1.6	280	33	1290	308	131.9	30.7	18.6	1.75	4.8
PPH6.5	113	33	1390	779	132.5	21.7	13.1	1.62	5.2

[a] Determined by the tensile test. [b] Determined by the Charpy impact tensile test. [c] Heat of fusion (ΔH) determined by DSC. [d] Estimated by ΔH and ΔH_m (164.9 J/g for isotactic PP). [e] Half-bandwidth (fwhm) of α(110) crystal peak determined by WAXD. [f] Estimated by fwhm.

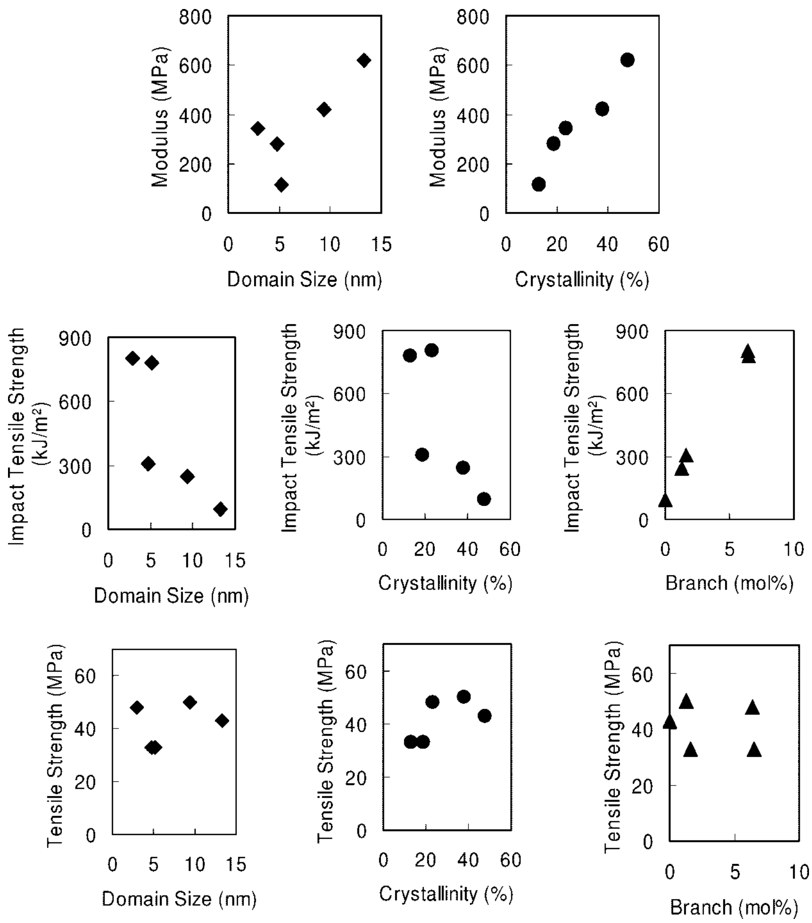

Figure 2. Relationship between mechanical property and structure of functionalized PP.

Consequently, the introduction of the hydroxyl group induced not only crystallization but also reduction of the crystal domain size.

The particular mechanical properties of the PPOH might be interpreted as follows. Figure 2 illustrates the relationship between each mechanical property and the structure of polymer sample. The modulus linearly increased with increasing crystallinity. It is indicated that the amount of rigid segment is the main factor for the elastic modulus. The impact tensile strength seems to be independent with both crystallinity and crystal domain size but depends on the number of branches. The impact tensile strength may relate to the character of amorphous segment. Assuming that the branches locate the amorphous part, thereby the elasticity of it should be elevated.[15−17] The tensile strength seems to be unrelated to any of crystal domain size, crystallinity, and number of branches. Although the details are not clear at present, intermolecular interaction by hydrogen bond formation can be pointed out as a plausible explanation. A similar phenomenon has been known in the ionomer, which is the copolymer of ethylene and polar monomer containing metal ion and is well-known as a highly tough resin.[18−22] On the other hand, Wu's review reported the brittle−ductile behavior of polymer is controlled by two chain parameters called entanglement density and characteristic ratio.[23] These parameters are influenced by the structure of polymer (chemical composition, branch, polar group, and so on). Accordingly, it is acceptable that the polar group affects the toughness of functionalized polypropylene.

So far, the functionalized polypropylene having a polar group has been expected as a surface modifier of PP in order to improve the dyeability and the adhesibility or the compatibilizer with polar materials. However, it is now revealed that PPOH can be used for the development of highly tough PP materials. In addition, it is also expected to be used as the physical modifier of the PP-based blend. The authors are continuing further investigation into the PPOH-based materials and will report all in good time.

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Supporting Information Available: Specific description for polymerization, analysis of first-order structure of polymer, ISO standard mechanical properties, DSC, and WAXD. This material is available free of charge via the Internet at http://pubs.acs.org.

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