Polypropylene Composites with Fine Particles of Poly(styrene-divinylbenzene)

YUKIO MIZUTANI, SATOSHI NAGO, MASARU SASAI

Tokuyama Corp., Tokuyama-city, 745-0053 Japan

ABSTRACT: Polypropylene composites were prepared by copolymerizing styrene and divinylbenzene in molten polypropylene by using an extruder. The resultant copolymers are of very fine particles uniformly dispersed in polypropylene phase with no aggregation. The properties of the resultant polypropylene composites were studied: crystalline structure, and mechanical, dynamic viscoelastic, and thermal properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1614–1620, 2000

Key words: polypropylene composite; polypropylene; copolymerization of styrene and divinylbenzene; extruder; mechanical properties; thermal properties; dynamic viscoelastic properties; crystalline structure

INTRODUCTION

We reported preparation of microporous sheets, which were prepared by biaxially stretching polypropylene (PP) sheets containing $CaCO_3$ filler.[1] Here, the PP phase is split and/or detouched at the periphery of the filler particles, so particle size of the filler is one of the most important factors. Also, it is elucidated that there is an inevitable limit regarding the pore size.[2] In order to prepare microporous sheets with relatively finer pore, the use of filler with relatively finer particle size is preferable. However, there is the well-known tendency in which the finer the particle size of the filler, the much more the particles tend to aggregate, and the size of the aggregated particle is effective to the pore formation. As a result, the smaller limit of the pore size is about 0.5 μm.

On the other hand, we reported preparation of ion exchange membranes by the paste method.[3] The paste consisting styrene (St), divinylbenzene (DVB), fine powder of polyvinylchloride (PVC),

dioctylphthalate (plasticizer), and benzoylperoxide is coated onto PVC cloth (reinforcing material) and the monomers are copolymerized to prepare base membrane, onto which ion exchange groups are introduced. Also, we elucidated the structure of the ion exchange membranes:[3] very fine particles of the ion exchange resin component are dispersed in the PVC substrate. This fact means that copolymerization of St-DVB in a PVC gel-phase results in a polymer composite, polymer alloy in other words, in which poly(St-DVB) particles of 0.01μm order are uniformly dispersed with no aggregation. In order to get rid of the limit described above, we considered that these fine particles could be useful as a kind of filler and tried to copolymerize St-DVB in molten PP.

We reported that PP composites are prepared by copolymerizing glycidylmethacrylate (GMA) or St with DVB in molten PP by using an extruder.[4,5] The copolymers are of fine particles (diameter, 0.01μm order), uniformly dispersed in the PP phase with no aggregation. GMA or St and DVB are compatible with molten PP, but the propagating polymer radicals of St or GMA are not and separate out of the molten PP phase. Furthermore, DVB promotes this phase-separation by forming crosslinkage. The mi-

Table I   Recipes

No.	PP (kg)	St (kg)	DVB (g)	1,1-bis(*t*-butylperoxy) cyclohexane (g)
1	20	0.92	80	50
2	20	0.92	80	100
3	20	1.84	80	100
4	20	1.84	80	150
5	20	2.76	160	200

gration of the monomers to the polymerization points is restricted owing to very viscous medium of molten PP. Accordingly, the copolymerization results in the fine particles of poly(GMA-DVB) or poly(St-DVB), uniformly dispersed in the PP phase with no aggregation, and these fine particles are effective to the micropore formation.

As described above, these polymer composites are novel as a polymer alloy. Therefore, we investigated some properties of the polymer composites with various poly(St-DVB) contents, as molding materials.

EXPERIMENTAL

Materials

PP was PN-18HG from Tokuyama Corp.[melt flow index, 43 g/10 min under a load of 2.16 kgf melt flow index (MFI)] . St and DVB were of commercial grade and the purity of DVB was 55 %. All the other reagents were of chemical grade.

Copolymerization of St and DVB

Various amounts of the St-DVB-initiator mixtures were well mixed with the PP powder by using a supermixer. The recipes of the mixtures were shown in Table I. The mixtures were extruded by using an extruder (78 m/m ϕ), equipped with twin screws, in order to copolymerize St-DVB, and pelletized. The pellets were cured at 80° C overnight under N_2 atmosphere.

Then the pellets were again extruded and pelletized with adding 2, 6-di-t-butyl-4-methylphenol (anti-oxidant, 1.2 % of PP). The St-unit content of the PP alloys were determined with the aid of an IR spectrometer, Perkin-Elmer 1600 Series by using the following wave lengths: PP, 973 cm^{-1} and polystyrene, 700 cm^{-1}. Densities of the resultant PP composites were measured by using Elec-

tric Densitometer ED-120T from A & D Company Ltd.

Mechanical Properties

Mechanical properties were estimated according to JIS as follows: tensile strength at yield (TS) and elongation to break (Eb) by using Strobograph AP from Toyo Seiki Seisakusho Ltd., JIS K-7113; Rockwell hardness (RH) by using Hardness Tester from Akashi Co., JIS K-7202; bending modulus (BM) and bending strength (BS) by using Bendgraph from Toyo Seisakusho Ltd., JIS K-7203; and Izod impact strength (IIS) by using CIB-401-AT from Orientec Ltd., JIS K-7110. All the test pieces are thermally pretreated at 130° C for 8 h under N_2 atmosphere. The number of the test pieces for the each measurement was 5, and the deviations were ± 5 %.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was carried out by using a differential scanning calorimeter (DSC, Model 6200R; Seiko Instruments). A thin film (about 0.2 mm thick) was punched to prepare a circular sample (about 6 mm in diameter and 5 mg), which was put into an Al pan. The temperature was first elevated to 230° C and after keeping for 10 min, was lowered down. Both the scanning speeds were 10° C/min.

Polarizing Microscopy

A small pellet was placed on a glass plate and melted at 230° C. Next, another glass plate was put on the molten polymer and pressed lightly to make the polymer thickness about 0.2 mm. Then, the sample was quenched very gradually. The prepared sample was observed under a Nicol prism by using a polarizing microscope (BH-2; Olympus Optical Co., Tokyo, Japan).

Dynamic Viscoelastic Properties

Test pieces were annealed at 155° C for 3 h and then gradually quenched under N_2 atmosphere. Dynamic viscoelastic properties were measured by using a dynamic viscoelastometer DMS200 from Seiko Instruments Inc. A frequency of 10 Hz was used from about − 100° C to melting point of the samples. The dimensions of test pieces were 20 mm long, 4 mm wide, and 0.4 ± 0.05 mm thick.

Transmission Electron Microscopy

The test piece was embedded in an epoxy resin and then treated with RuO_4 for 48 h after trimming.

Table II   Copolymerization Results

No.	Monomer Conversion (%)[a]	St-Unit Content (wt %)
1	24.0	1.2
2	40.0	2.0
3	34.4	3.3
4	60.4	5.8
5	60.3	8.8

[a] Calculated from the equation: [St-unit content (g)/(St + DVB) (g)] × 100.

The ultrathin sample was prepared using an ultra-microtome, Reichert-Nissei ULTRACUT-N from Leica AG (London, United Kingdom). The transmission electron microscope was JEM 200CX from JEOL (London, United Kingdom).

X-ray Diffraction

X-ray diffraction was measured by using nickel filtered Cu-Kα radiation with the aid of Rotaflex PU-200PL from Rigaku Denki Co. Ltd.

## RESULTS AND DISCUSSION

Copolymerization

Table II shows the copolymerization results. The retention times of the samples in the extruder (the copolymerization times) are not enough to obtain high monomer conversions, so the yields were rather low. The larger the monomer quantity, the higher the monomer conversion, which is expediently estimated from the St-unit content, neglecting the participation of the DVB component. It is noteworthy that the St-unit content is used as a measure of poly(St-DVB) content in this article. Also, it is elucidated that the initiator quantity is reasonably an effective factor in relation to the monomer conversion.

Figure 1 shows an example of transmission electron micrographs showing the dispersion state of the poly(St-DVB) particles in the PP phase. The very fine particles of poly(St-DVB) (diameter, 0.01μm) are uniformly dispersed with no aggregation. This is the feature of the crosslinking phase-separation copolymerization in the very viscous, molten PP phase.[4,5] Also, it was observed that the distribution density of the fine particles reasonably increases with increasing the St-unit content. Figure 2 shows the effects

Figure 1   Transmission electron micrograph of a PP composite.

of the St unit contents to MFI and density of the resultant polymer composites. The density increases with increasing the St-unit content, and there is an additivity between the densities of PP (0.91 g/cm^3) and poly-St (1.05 g/cm^3), regarding the densities of the PP composites. It is verified by the consistency of the plots with the linear line,
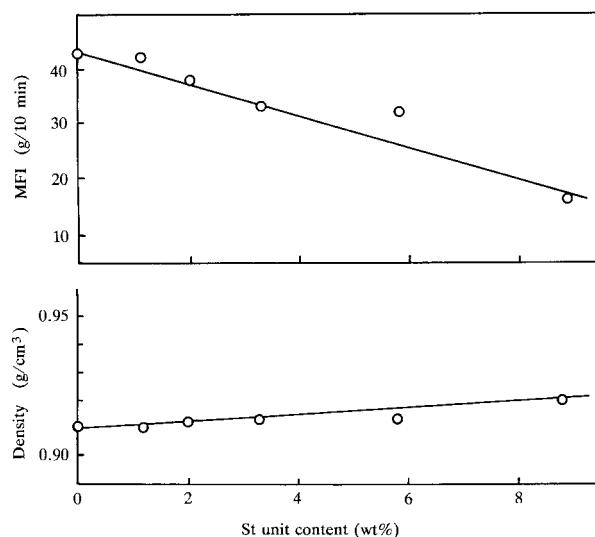
Figure 2   MFI and density versus St-unit content.

Table III   Mechanical Properties

No.	TS (MPa)	Eb (%)	RH	BM (MPa)	BS (MPa)	IIS (kJ/m^2)
PP	35	540	89	1600	50	1.7
1	40	40	101	2110	61	1.7
2	39	20	101	2050	59	1.7
3	40	20	103	2130	61	1.7
4	36	20	102	2150	62	1.8
5	40	20	102	2100	62	1.7

which is calculated by using the densities of PP and poly-St. The MFI decreases with increasing the St-unit content. It means that the presence of the fine particles of poly(St-DVB) suppresses the melt flowability of PP.

Mechanical Properties

Table III shows some mechanical properties of the PP composites. The TS, RH, BM, and BS of the PP composites are larger than those of PP, and the Eb of the PP composites is much smaller than PP. Also, the IIS of PP composites and PP are similar. This means that the crosslinking copolymerization of St and DVB in the molten PP makes the resultant PP composites harder than PP but does not make them any more brittle. These results suggest that the interpenetration of PP molecules and the three-dimensional polymer network of poly(St-DVB) (IPN structure) and/or graft polymerization of St and DVB molecules onto the PP molecules are probably concerned with. Here, the St-unit content are rather ineffective to the properties except Eb, and the details are obscure now.

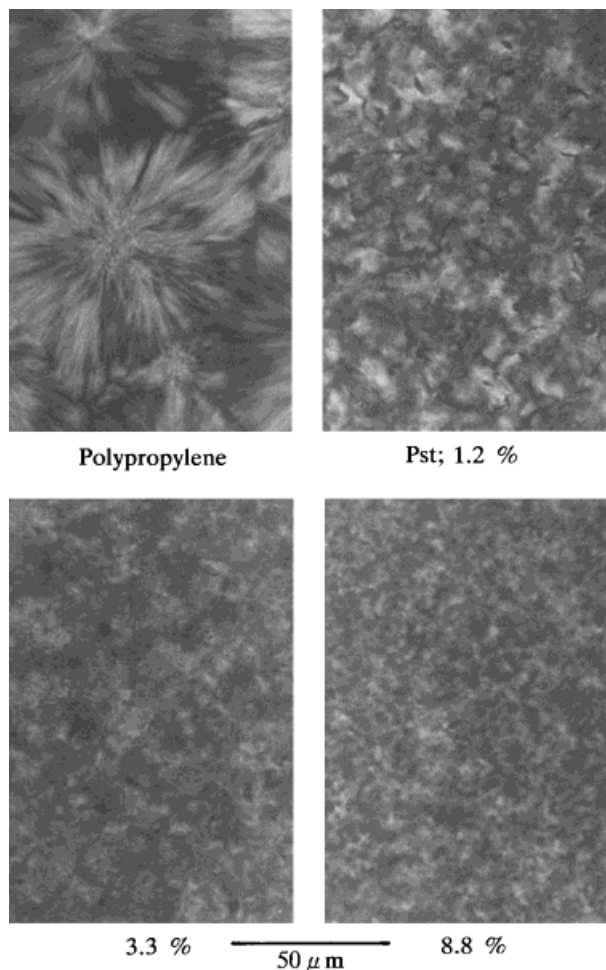## Differential Scanning Calorimetry

Figure 3 shows the DSC diagrams. Regarding the melting point, when the St-unit content is 1.2%, a small peak is observed at 149° C, which is assigned to the β phase of PP.[6] This peak becomes unclear, and the main peak broadens to the lower temperature side with increasing St-unit content, meaning that the poly(St-DVB) particles causes endothermic motion of the PP molecules at the lower temperature. Also, the peak top showing crystallization point evidently shifts to the higher temperature side with increasing St-unit content. This means that the fine particles of poly(St-DVB) are effective as a nucleating agent, as reported by Beck et al.[7]

Figure 4 shows dependencies of the melting
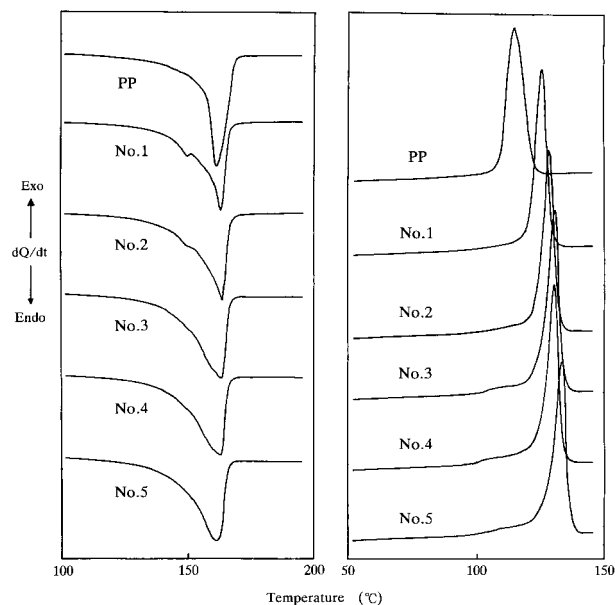
Figure 3   DSC diagrams.

and crystallization points onto the St-unit content. The melting point once increases and then decreases with increasing the St-unit content. This might be explicable as follows: the increase and the decrease are owing to the change in the balance of the nucleating effect of the fine parti-
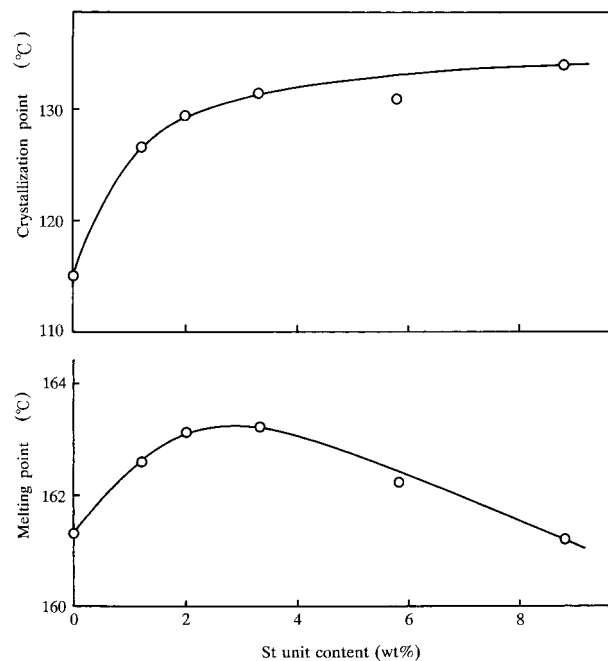
Figure 4   Crystallization and melting points versus St-unit content.

Figure 5 Polarizing micrographs of PP composites.

is reported that the peaks at Bragg angles (2θ) = 16 and 20° are assigned to β and γ phases of PP, respectively.[8] It is observed that PP composites contain γ phase but PP does not. It is also reported that the γ phase is contained in PP copolymers with ethylene,[9] which disturbs the crystallization of the propylene unit. Therefore, it is presumed that poly(St-DVB) particles behave similarly by forming the IPN structure and/or the graft polymer. Figure 7 shows relation between the crystallization degrees of the PP composites and the St-unit contents. The crystallization degree decreases with increasing the St-unit content. It is explicable by the increase of the noncrystalline component of poly(St-DVB). Then, the crystallization degrees of the PP components themselves were estimated, which linearly in-

cles of poly(St-DVB) and the participation effect of the IPN structure and/or the graft polymer, respectively. On the other hand, the crystallization point shown by the peak top becomes higher with increasing the St-unit content, probably owing to the nucleating effect of the fine particles of poly(St-DVB). However, the details should be studied further.

Polarizing Microscopy

Figure 5 shows polarizing micrographs showing spherulites of PP. The spherulites of PP are clearly observed and relatively larger. With increasing the St-unit content, the size of the spherulites becomes smaller. It means that the fine particles of poly(St-DVB) are effective as a nucleating agent.
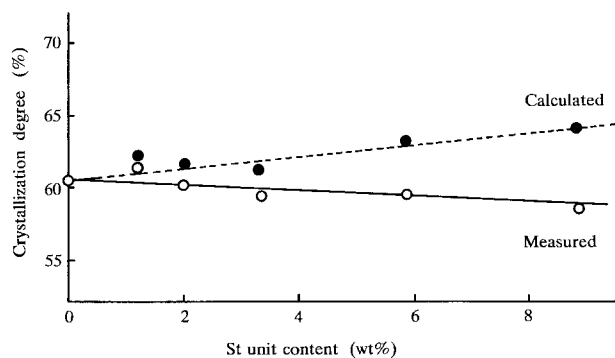
Crystalline Structure

Figure 6 shows the X-ray diffraction diagrams. It

**Figure 6** Diagrams of X-ray diffraction.

Figure 7 Crystallization versus St-unit content.

crease with increasing the St-unit content. This means that the fine particles of poly(St-DVB) are effective as a nucleating agent.
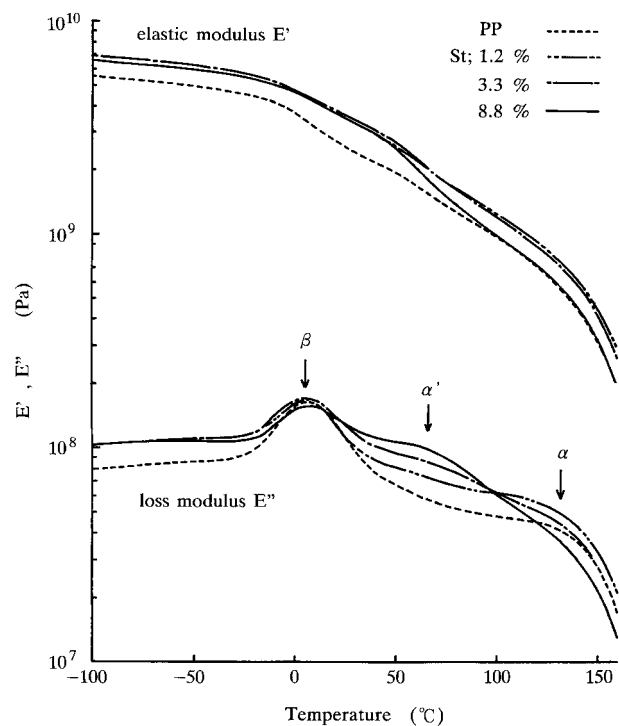
Dynamic Viscoelastic Properties

Figure 8 shows dependencies of tan δ onto temperature. It is known that in the case of oriented homo PP, which was cold-drawn at room temperature and then annealed, there are two dispersions, α and β dispersions at 130 and 7° C, respectively, which are assigned to molecular movement of crystalline and amorphous parts, respectively.[10] The curves of tan δ show a clear peak at 7° C, but no peaks at 130° C because of the premonitory molecular movement to melting.

The tan δ values of the PP composites at 7 and 130° C are smaller than that of PP. It means that
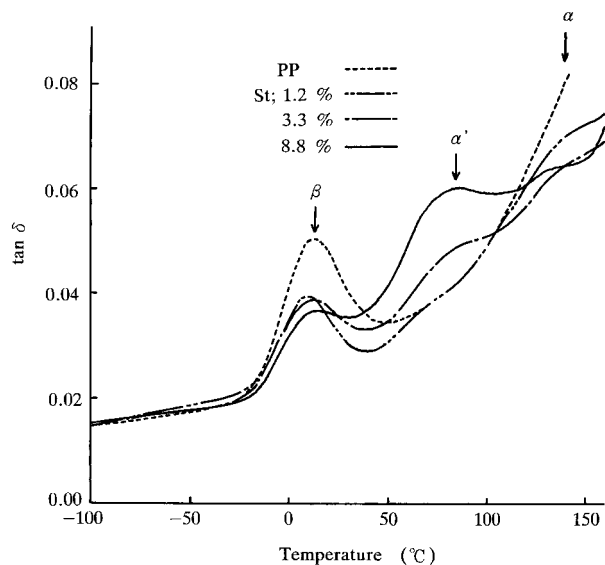
Figure 8 Dynamic viscoelastic behaviors of PP composites (tan δ).

Figure 9 Dynamic viscoelastic behaviors of PP composites (E′ and E″).

the molecular movement of PP molecules at about 7 and 130° C is restricted in the cases of PP composites in comparison with PP. Also, it is reported that poly(St-DVB) shows the dispersion at about 125° C.[11]

Accordingly, these broad peaks (α′ dispersion) show the presence of the IPN structure and/or the graft polymer containing the fine particles of poly(St-DVB). It means that the participation of the poly(St-DVB) component should make the molecular structure of the PP composites relatively more movable at this temperature region.

Figure 9 shows dependencies of elastic modulus (E′) and loss modulus (E″) on temperature. The E″ curves show the peaks of β dispersion and the clear peak in the case of the St-unit content of 8.8 %. On the other hand, the E′ curve decreases with increasing temperature. Figure 10 shows dependencies of E″ and tan δ onto the St-unit content. The tan δ values of α and β dispersions decrease with increasing the St-unit content. It means that the poly(St-DVB) component restricts the molecular movement of PP molecules. Contrarily, tan δ of α′ dispersion increases with increasing the St-unit content. It suggests the participation of the poly(St-DVB) component by forming the graft polymer and/or the IPN struc-
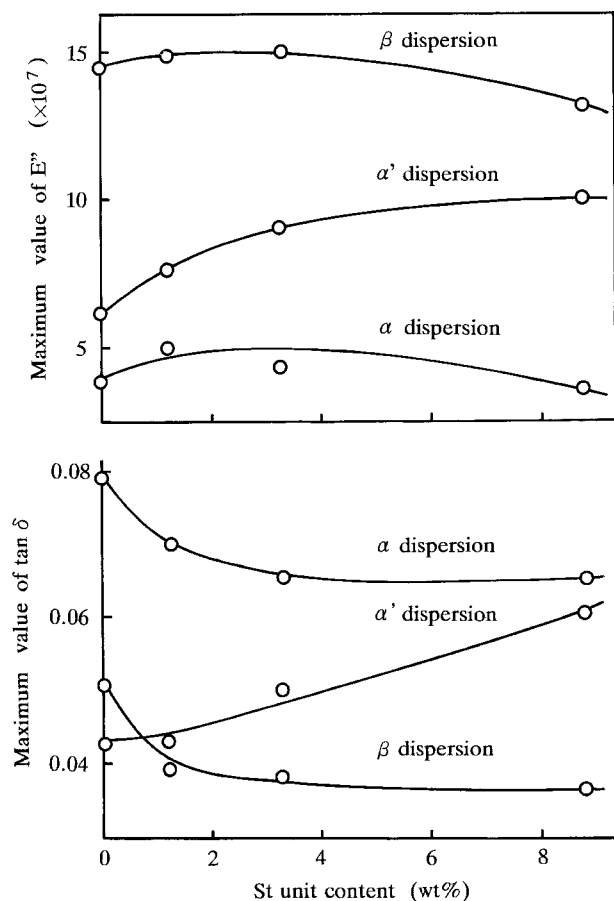
Figure 10   tan δ and E″ versus St-unit content.

CONCLUSION

St and DVB are copolymerized in molten PP phase by using an extruder. The resultant PP composites contain very fine particles of poly(St-DVB), uniformly dispersed in the PP phase with no aggregation. We studied mechanical, dynamic viscoelastic, and thermal properties and crystalline structure. The participation of poly(St-DVB) component makes the PP composite relatively harder and the fine particles of poly(St-DVB) are effective as a nucleating agent. Also, it is shown that the copolymerization of St-DVB in molten PP phase results in the graft polymer of St-DVB onto PP and/or the IPN structure of both the polymers, which affect the various properties of the PP composites. Accordingly, much more details should be investigated in the future.

ture. On the other hand, the E″ value of α' dispersion clearly increases with increasing the St-unit content, but the dependencies in the cases of α and β dispersions are rather delicate, showing slight decrease with increasing the St-unit content. These results also suggest the participation of the poly(St-DVB) component described above. These results, showing presence of the graft polymer and/or the IPN structure, should be meaningful to understand the results described above. However, the details should be studied further.

REFERENCES

1. Mizutani, Y.; Nakamura, S.; Kaneko, K. S.; Okamura, K. Ind Eng Chem Res 1993, 32, 221.
2. Nago, S.; Nakamura, S.; Mizutani, Y. Seikei Kako 1996, 8, 617.
3. Mizutani, Y. J. Memb Sci 1990, 49, 121.
4. Mizutani, Y. J Appl Polym Sci 1997, 63, 133.
5. Mizutani, Y.; Nago, S. J Appl Polym Sci 1999, 73, 1089.
6. Varga, J. J Appl Polym Sci 1989, 35, 1891.
7. Beck, H. N.; Ledbetter, H. D. J Appl Polym Sci 1965, 9.2131.
8. Morrow, D. R.; Newman, B. A. J Appl Phys 1968, 39, 4944.
9. Mezghani, K.; Phillips, P. J. Polymer 1995, 36, 2407.
10. Nago, S.; Azuma, K. J Macromol Sci Phys 1979, B16, 435.
11. Hayashi, T.; Ito, J.; Mitani, K.; Mizutani, Y. J Appl Polym Sci 1983, 28, 2880.