The Effect of Adding Polysilane on Heat Fusion Properties of Various Kinds of Polyethylene

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ABSTRACT: In this study, the affects that added polysilanes (PSis) (linear (M_w = 500–24,900, PMPS), cyclic (M_w = 900, PDPS), and networked (M_w = 1100, PPSi)) have on the heat-fusion properties of various types of polyethylene (PE) materials (HDPE, LDPE, LLDPE, and UHMWPE) were investigated. Addition of PM-5 (PMPS; M_w = 500) on the surface of PE films led to an increase in the peeling strength such that the modified films could not be peeled off even under the same conditions for which the PE films without PM-5. This result indicated that the modified film could be heat-fused at a much lower temperature than the neat sample. On addition of PDPS or PPSi of nearly the same molecular weight as PM-5 to the surface of PE films, the peeling strength decreased dramatically and the modified films could not be heat-fused any further than the neat PE samples under the same conditions. Moreover, for PMPSs of higher molecular weights, the peeling strength decreased dramatically with increasing molecular weight, and the modified PE films could not be heat-fused and thus were readily peeled off. Through evaluation of electron probe microanalysis measurements, it was found that only PM-5 (M_w = 500) can diffuse (migrate) into PE materials. Furthermore, the diffusion distance increased in the order LDPE, LLDPE, UHMWPE, and HDPE and corresponded to the intensity of the molecular motion in the amorphous region (β relaxation) of each PE material. Consequently, it was deduced that only PM-5 is compatible with PE and has the ability to migrate through the amorphous regions of PE materials, thus enabling this PSi to affect PE heat-fusion properties. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polysilane; polyethylene; heat-fusion; peeling energy; molecular motion

INTRODUCTION

‘The heat-fusion process is a widely used adhesion technique for polymer films and is particularly used for polyethylene (PE) because of its high processability and the reduced usage of chemicals to induce adhesion. Polymer films can wrinkle and shrink, however, in response to external heating during the heat-fusion process because the temperature is much higher than the glass-transition temperature or melting temperature of the polymers. Improvements in the heat-fusion process including lower temperatures and shorter exposure times are therefore necessary.

It has been found that polysilane (PSi) materials can be compatibilized with liner polyolefins (e.g., PE) and can improve the heat-fusion properties of PE materials.[1–4] PSi materials are remarkable polymers with a backbone comprised of Si–Si bonds and side chains formed from organic functional groups, and as a result they possess properties of both organic and inorganic materials.[5–10] The organic properties of PSis are what make them compatible with PE, while due to the Si–Si backbone, these polymers have photo- and electronic-properties similar to those of semiconductive silicones, such as photo-conductivity,[11,12] photoreactive properties,[13–15] high heat-resistance,[16,17] and nonlinear optical properties.[18–20] The mechanisms by which addition of Psi materials to the surface of PE films improves their heat-fusion properties and the nature of the interaction between PE and PSi at the heat-fusion boundary remain unclear, however.

In this article, we report the effects of adding PSis with different structures (currently PSi materials with linear, cyclic, and networked structures can be synthesized[21–27]) and molecular weights on the heat-fusion properties of different types of PE materials, including low density PE (LDPE), linear low density PE (LLDPE), high density PE (HDPE), and ultrahigh molecular weight PE (UHMWPE). PSi diffusion is also discussed.

EXPERIMENTAL

Materials

Three types of PSi materials were purchased from Osaka Gas Chemical Co., Japan; (1) linear (PMPS,

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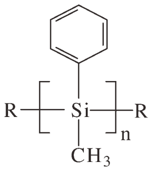
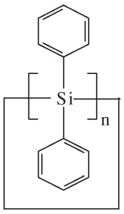
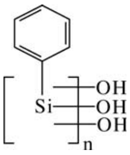
TABLE I
Characteristics of Polysilane Materials

	PMPS	PDPS	PPSi
Mn	440∼5,500	490	1,000
Mw	500∼24,900	900	1,100
			
	n = 4∼216 Linear structure	n = 5 Cyclic structure	n = 10 Networked structure

with M_w 500, 2500, 18,000, and 24,500); (2) cyclic (PDPS, $M_w = 900$); and (3) networked (PPSi, $M_w = 1100$) as listed in Table I. PE materials included LDPE ($M_w = 111{,}000$), LLDPE ($M_w = 89{,}000$, number of side chain carbons = 8), and HDPE ($M_w = 136{,}000$) from Idemitsu Petrochemical, Japan and UHMWPE ($M_w = 3{,}400{,}000$ from Mitsui Chemical, Japan (Table II).

Preparation of test specimens

PE film samples (HDPE, LDPE, and LLDPE) were prepared by hot-pressing under the conditions as follows: temperature was 180°C, soaking time was 13 min, and hot-pressing pressure was 10 MPa. UHMWPE films were also prepared by hot-pressing, but the conditions were as follows: temperature was 200°C, soaking time was 30 min, and hot-pressing pressure was 30 MPa. After hot-pressing, all the film samples were quenched in ice-water.

Peel test specimens were T-shaped films prepared by hot-pressing two PE films in piles. The heat-treated area was 10 mm in length and 5 mm in width, and pressing was controlled using a polyimide film (50 μm in thickness) as a spacer. PSis were added on the surface of the PE materials and the amount of PSi was 1.0 mg/cm^2. Then, they were hot-pressed under the conditions of each PE material (temperature and time) as listed in Table II. For example, LDPE films could be peeled off after heat-treatment at 110°C for 120 s, but after heat-treatment at the same temperature for 150 s, the films were completely heat-fused with each other such that they could not be peeled off. The hot-pressing pressure was 2 MPa.

Peel tests

Peel tests on PE films were performed using a tensile tester (KES G-1, KATO TECH, Japan) under tensile mode at ambient temperature according to JIS K 6854-3 (ISO 11339). Tensile head speed in the peel was set at 10 mm/min and the initial chuck distance was 10 mm. Peel tests were performed with at least five repetitions for each sample. Peeling energy can be calculated from the area under the stress-strain curves of the heat-fused PE films in the peel test. It should be noted that when PE films cannot be peeled off (i.e., they are heat-fused completely with each other), peeling energy cannot be calculated, and thus the maximum peeling energy within the measurable range is shown as the upper limit for the peeling energy.

Electron probe microanalysis measurements

Electron probe microanalysis (EPMA) measurements (JXA8900-RL, JEOL Co., Japan) were carried out to estimate the diffusion state of the Si atoms derived from the PSi added to the PE films. An acceleration voltage of 20 kV and an irradiation current of 1×10^{-7} A was used. Si atom mapping was achieved using a SiKα within 1 mm of the boundary of the heat-fused PE materials.

Dynamic mechanical measurements

Dynamic mechanical analyses (DMA) were performed using a dynamic viscoelastometer (Rheogel E-4000 (UBM Co., Japan) under tensile mode with an initial chuck distance of 20 mm at a frequency of 30 Hz and a heating rate of 2°C/min over the temperature range −150°C to 150°C. Test specimens were 0.4 mm in thickness, 3 mm in width, and 30 mm in length.

TABLE II
Characteristics of Polyethylene Materials

PE material	LDPE	LLDPE	HDPE	UHMWPE
Molecular weight/10^4	11.1	8.9	13.6	340
Melting Temp.(°C)	109.0	123.5	132.1	134.5
Degree of crystallinity (%)	26.2	38.5	52.6	39.4
Density (g/cm^3)	0.941	0.950	0.965	0.948
Heat fusion condition	110°C 120sec/150sec	125°C 210sec/240sec	130°C 270sec/300sec	170°C 900sec/1200sec

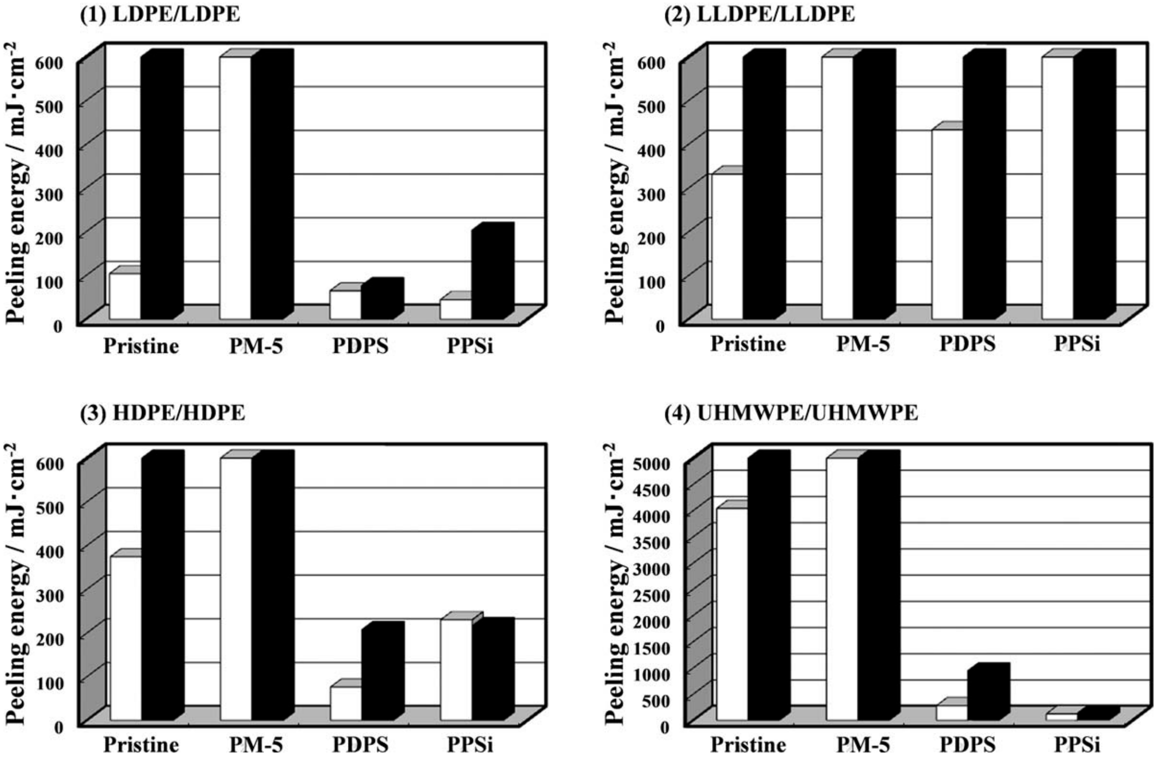


Figure 1 Effect of chemical structure of PSi on peeling energy of PE materials: (1) LDPE (110°C, left (white): 120 s, right (black) 150 s), (2) LLDPE (125°C, left (white): 210 s, right (black) 240 s), (3) HDPE (130°C, left (white): 270 s, right (black) 300 s), and (4) UHMWPE (170°C, left (white): 900 s, right (black) 1200 s).

RESULTS AND DISCUSSION

Effects of PSi chemical structure on the peeling energy of PE materials

In order to estimate the effects of the chemical structure of added PSi on the peeling energy of PE materials, three types of PSis: (a) linear PMPS, (b) cyclic PDPS ($M_w = 900$), and (c) networked PPSi ($M_w = 1100$) were used. To eliminate the effect of molecular weight, PM-5 ($M_w = 500$) was used as the linear PSi, PMPS. The peeling strength of each PE material with and without added PSis having different chemical structures is shown in Figure 1.

In the case of LDPE [Fig. 1(1)], neat LDPE films heat-treated at 110°C for 120 s could be peeled off and possessed a peeling energy of about 100 mJ/cm^2. The pristine heat-treated LDPE at 110°C for 150 s could not be peeled off, however, and exhibited a peeling energy of more than 600 mJ/cm^2. Notably, the LDPE films with added PM-5 were impossible to peel off even when they were heat-treated at 110°C for 120 s. There was also no significant change when the PM-5 modified LDPE was heat-treated at 110°C for 150 s using the same conditions under which neat LDPE did not peel off. Based on these results, it was deduced that PM-5 can modify the heat-fusion properties of LDPE. Moreover, despite the fact that PM-5 is thought to be viewed as a foreign substance by PE materials, it did not act as an inhibiter for the heat-fusion process, and as a result, LDPE with PM-5 can be completely heat-fused. The same behavior was observed for LLDPE, HDPE, and UHMWPE.

On the other hand, when adding PDPS and PPSi onto the surface of PE materials, their peeling energy changed dramatically, except for LLDPE. In the case of LDPE, HDPE, and UHMWPE, the PE films with PDPS and PPSi peeled off even when they were heat-treated under the same conditions under which the neat PE material was completely heat-fused. As a result, the peeling energy decreased considerably regardless of the heat-treatment conditions. In the case of LLDPE, however, such a remarkable change was not observed in the peeling energy when adding PDPS or PPSi onto the surface of the film, suggesting that some type of interaction between the PSi and LLDPE existed.

In any case, it was found that a linear PMPS can play an important role in improving the heat-fusion properties of PE materials.

Effect of the molecular weight of PMPS on the peeling energy of PE materials

Given that the molecular weight of PM-5 was somewhat lower than the molecular weights of the other PSis used in the above experiments, the effect of the

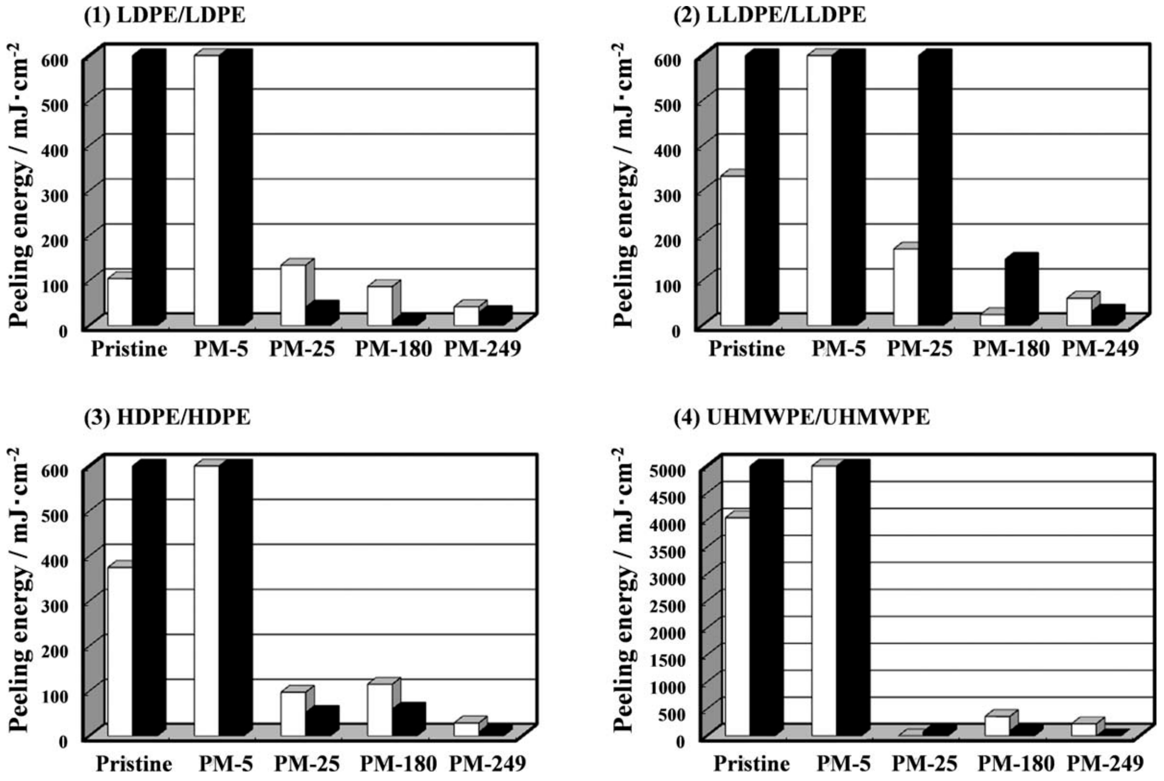


Figure 2 Effect of molecular weight of PMPS on peeling energy of PE materials: (1) LDPE (110°C, left (white): 120 s, right (black) 150 s), (2) LLDPE (125°C, left (white): 210 s, right (black) 240 s), (3) HDPE (130°C, left (white): 270 s, right (black) 300 s), and (4) UHMWPE (170°C, left (white): 900 s, right (black) 1200 s).

molecular weight of PMPS on the heat-fusion properties of PE materials was investigated. The variation in the peeling energy of various PE materials with different molecular weight PMPSs is depicted in Figure 2. For this experiment, PM-5 ($M_w = 500$), PM-25 ($M_w = 2500$), PM-180 ($M_w = 18{,}000$), and PM-249 ($M_w = 24{,}900$) were used. All of the PE films with PM-5 added onto the surface could not be peeled off and the boundary of each PE film was completely heat-fused. Addition of PMPSs with higher molecular weights onto the surface of PE materials, however, did not result in dramatic changes in the peeling energy.

For LDPE [Fig. 2(1)], the peeling energy decreased remarkably with an increase in the molecular weight of the PMPS. Moreover, when PMPSs having higher molecular weights than PM-5 were added, there was a tendency for the peeling energy of the modified LDPE that was heat-treated for 120 s (white bar) to be larger than that of the modified LDPE that was heat-treated for 150 s (black bar). It is possible, therefore, that PMPSs having high molecular weights act as inhibiters for the heat-fusion process of LDPE materials heat-treated at higher temperatures. A similar tendency was observed for HDPE and UHMWPE. Interestingly, for LLDPE, the peeling strength of LLDPE with PM-25 was still high and the value determined at the longer heating time is higher than that of the value measured at the shorter heating time up to a M_w of 180,000. As was seen previously, this result supports the notion that a different interaction between the PSi and LLDPE exists.

In general, though, it was confirmed that PMPSs having a molecular weight of about 500 play an important role in improving the heat-fusion properties of PE materials.

EPMA results near the heat-fusion boundary

Si-atom distribution maps indicating the Si concentration at the boundary of PE films obtained using EPMA measurements are shown in Figure 3. As can be seen, there are remarkable differences between the cases where PM-249 [Fig. 3(a)] and PM-5 [Fig. 3(b)] were added to LDPE.

When PM-249 ($M_w = 24{,}900$) was added at the boundary of LDPE films, a small amount of Si atoms was distributed in the LDPE materials but most of the Si atoms were observed near the boundary (designated by a dotted line in the picture). On the other hand, when adding PM-5 ($M_w = 500$) at the boundary of PE films, a large amount of Si atoms was observed in the LDPE, indicating that PM-5 can diffuse into PE materials. Considering that LDPE films with added PM-249 were peeled off and those with added PM-5 were not, it can be concluded that the

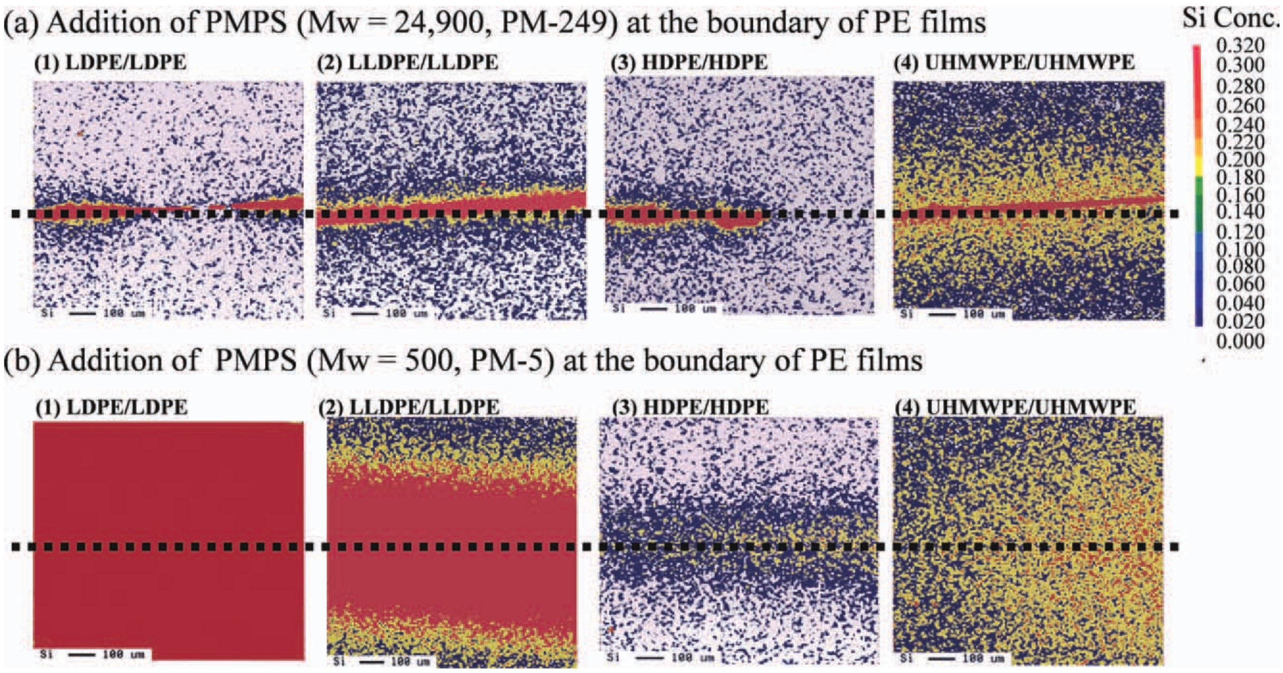


Figure 3 EPMA results of Si atom distribution at the boundary of PE materials by addition of PMPS with different molecular weight: (a) PM-249 (M_w = 24,900) and (b) PM-249 (M_w = 500) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

diffusion process of PMPSs was the most important factor for improving the heat-fusion properties of LDPE. A similar tendency was also observed for LLDPE, HDPE, and UHMWPE. Based on these results, it appears likely that only the low-molecular weight PMPS (PM-5) can allow a much stronger heat-fusion state to form at the boundary of PE films because it can diffuse into PE materials and interact strongly with the PE molecules.

To gain further insight, the Si-atom distribution distance from the boundaries of PE films with added PM-5 was also measured; the results are shown in Figure 4. It was found that the Si atoms diffused over a long distance from the boundary of the LDPE films. Interestingly, the diffusion range of Si atoms in LLDPE was narrow in comparison to that for LDPE, and it became much narrower for HDPE and UHMWPE. From these results, it was deduced that the distribution conditions for the Si atoms derived from PM-5 were affected by the molecular motions and/or higher-order structure of the PE materials.

DMA results for PE materials

To confirm this theory, we next investigated the molecular motions of the PE materials used in these experiments. Because PM-5 cannot diffuse through the crystalline regions of PE, it must pass through the amorphous regions. As a result, a good relationship between the β relaxation intensity corresponding to molecular motions in the amorphous region and the diffusion distance of Si atoms in each PE sample might be expected. DMA measurements were used to estimate molecular motion; the variation of loss modulus (E'') as a function of reciprocal temperature ($1/T$) for the 4 PE films is shown in Figure 5. In the high-temperature region, the α relaxation around 120°C corresponding to molecular relaxation by thermal vibration in a crystal phase[28] is observed, whereas in the low-temperature region, the β relaxation around 40°C corresponding to local main chain relaxation in the amorphous region is seen.[28] Based on these results, it appears that the intensity of the β relaxation of PE materials does indeed have some correlation with the distribution conditions for the Si atoms derived from PM-5. That

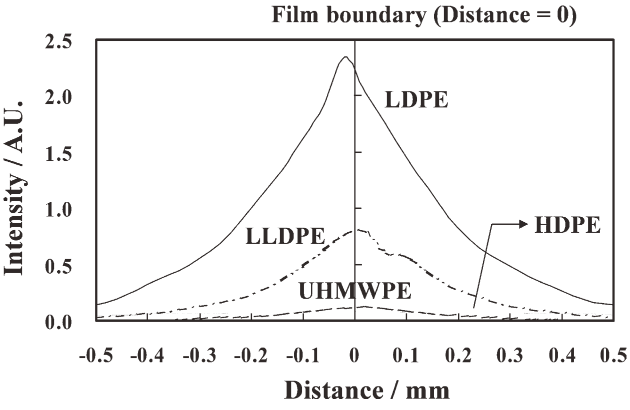


Figure 4 Si atom diffusion distance from the boundary of PE materials by addition of PMPS (M_w = 500).

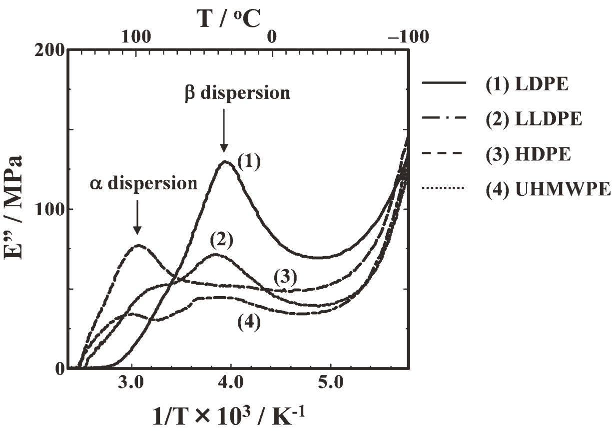


Figure 5 Variation of loss modulus (E'') with temperature of PE materials: (1) LDPE, (2) LLDPE, (3) HDPE, and (4) UHMWPE.

is, PM-5 can diffuse into LDPE over a longer distance because it has the highest β relaxation intensity. In addition, because LLDPE has a relatively high β relaxation intensity compared to HDPE and UHMWPE, PM-5 can diffuse to some extent within LLDPE. In both HDPE and UHMWPE, which have low-intensity β relaxations, however, long range distribution of the Si atoms derived from PM-5 is not observed. Therefore, we propose that PM-5 can diffuse over a long distance into PE materials that exhibit a high-intensity β relaxation. Furthermore, PSi materials having a bulky cyclic or networked structure and/or a higher molecular weight (even in the case of PSis with a linear structure) cannot pass through the amorphous region of PE because the activation energy to diffuse into PE materials was relatively high due to their steric hindrance. Consequently, no significant effect on the heat-fusion properties of PE was observed when using PDPD, PPSi, and PMPSs having molecular weights higher than that of PM-5.

CONCLUSIONS

In this article, the effect of adding PSis having different chemical structures (linear, cyclic, and networked) and linear PSis with different molecular weights on the heat-fusion properties of various PE materials was investigated, and the results were discussed as follows:

a. When using PSi materials with different chemical structures that have similar molecular weights, it was found that a linear PSi, PM-5, can affect the heat-fusion properties of all PE materials. PE films with added PM-5 could not be peeled off even when they were heat-treated under the same condition for which neat PE could be peeled off.
b. When using linear PSi materials with different molecular weights, the low molecular weight PSi, PM-5, had an optimum influence on the heat-fusion properties of all PE materials. That is, there was a tendency for the peeling strength of PE films to markedly decrease with increasing molecular weight of the PSi. When PM-249 ($M_w = 24{,}900$) was added onto the surface of PE films, they could be easily peeled off.
c. To compare the characteristics of PM-5 and PM-249 in PE films, Si atom distribution conditions were measured using EPMA. PM-5 was found to diffuse into PE materials, whereas PM-249 did not. Furthermore, it was found that the Si atom distribution distance was different for different PE materials in the order LDPE, LLDPE, UHMWPE, and HDPE.
d. It was determined from DMA results that the intensity of the β relaxation of PE materials has some correlation with the distribution conditions of the Si atoms derived from PM-5. First, PM-5 diffused over the longest distance in LDPE, which has the highest β relaxation intensity. Second, in LLDPE, PM-5 diffused to some extent because it had the next highest β relaxation intensity. Third, in HDPE and UHMWPE, PM-5 diffused only slightly because of the low intensity of the β relaxation. Therefore, we propose that PM-5 can diffuse through the amorphous regions of PE materials over a long distance.

This study did not determine, however, what type of interactions exist between the PSi and PE materials. Because elemental Si belongs to the Carbon group in the periodic table, there is the possibility that PSis having organic functional groups as side chains have a good affinity with organic materials. Further investigation is required to confirm this assumption.

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