Effect of Adding Polysilane on Melt-Flow Properties of Ultra-High Molecular Weight PE

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ABSTRACT: The effects of polysilane addition on the melt-flow and mechanical properties of ultra-high molecular weight polyethylene (UHMWPE) were investigated. The kneading torque during melt process of pure UHMWPE without polysilane increased significantly with time and reached a constant value after 100 min. However, the kneading torque did not increase by addition of polysilane materials into UHMWPE, which indicates that all the polysilane materials suppress an increase in the kneading torque during melt process of UHMWPE at 200°C, especially a linear polysilane (PMPS) and a networked structure polysilane (PPSi). When using linear polysilane materials with different molecular weights, the low molecular weight polysilane (PM-5, $M_w = 500$ Da) had the most dominant effect on the heat-flow and mechanical properties of UHMWPE. UHMWPE with PM-5 could be elongated over 1000% strain, which was the similar to the case for pure UHMWPE, although the elongation at break of UHMWPE with additions of different molecular weight PMPS was significantly decreased with increasing molecular weight of PMPS. Furthermore, the kneading torque during melt process of UHMWPE decreased with increase in the amount of PM-5 addition, from 1 to 5 wt %. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polysilane; ultra-high molecular weight polyethylene; melt-flow properties; viscoelasticity

INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) has a molecular weight that is 10–100 times higher than that of conventional high-density polyethylene (HDPE), and it exhibits prominent chemical and mechanical properties, such as high impact strength, high wear-resistance, and excellent mechanical properties at low temperatures. However, it is difficult to mold UHMWPE, because its high molecular weight results in high viscosity even under melt-flow conditions around 200°C. Therefore, it is difficult to apply conventional processing techniques to UHMWPE, except for compression molding and ram extrusion.[1,2] Much effort has been extended to reduce the viscosity of UHMWPE by solution or gel processing.[3–6] An alternative technique to reduce the melt viscosity of UHMWPE is dilution with conventional PE[7–9] or PP,[10,11] which has a relatively lower molecular weight, or by the addition of lubricants such as calcium stearate,[12] mineral oil,[13] and poly(ethylene glycol).[14,15] However, effective amounts of these agents cause a marked decrease in some of the most desirable properties of UHMWPE. The present study is aimed at investigating a method for modification of the melt-flow properties of UHMWPE by the addition of polysilane with various chemical structures. The effect of adding various amounts of a linear structured polysilane with different molecular weights to UHMWPE on the melt-flow and mechanical properties was then investigated. The change in the morphology and molecular motion of UHMWPE by the addition of polysilanes was investigated by thermal analysis, optical microscopy, and mechanical (dynamic and static) measurements.
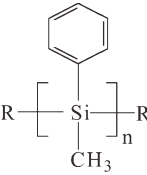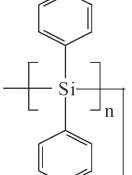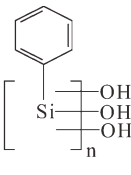
EXPERIMENTAL

Materials

UHMWPE ($M_W = 3,400,000$ Da, Code: 340M) manufactured by Mitsui Chemical Co., LTD., Japan was used. Three types of polysilanes were purchased from Osaka Gas Chemical Co., Japan: (1) linear (PMPS, with $M_w = 500$, 2500, and 24,900 Da); (2) cyclic (PDPS, $M_w = 900$ Da); and (3) networked (PPSi, $M_w = 1100$ Da), as listed in Table I.

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TABLE I
Characteristics of Polysilane Materials

	PMPS	PDPS	PPSi
M_n	400–5,500	490	1,000
M_w	500–24,900	900	1,000

n=4 ∼ 216   n=5   n=10

Linear structure   Cyclic structure   Networked structure

Preparation method of UHMWPE with polysilanes

After a given proportion by weight of polysilane was added to UHMWPE, melt mixing was carried out with a LABO PLASTOMILL 100MR (Toyo Seiki Co., Japan) at 200°C for 100 min at a constant rotation rate of 10 rpm.

Film samples were prepared using a hot-press under the following conditions: temperature 493 K, soaking time 20 min, and pressure 10 MPa. The prepared films were 0.4 mm thick.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was carried out in the temperature range 10–200°C at heating rate of 10 °C/min in an N_2 atmosphere, using a DSC-7 (Perkin Elmer, Japan Co.) instrument.

Polarized optical microscope observation

Polarized optical microscope observation was carried out with an OPTIPHOT2-POL (Nikon Co., Japan) microscope under the crossed nicols condition.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out at a frequency of 30 Hz and heating rate 2 °C/min over the temperature range −150 to 300°C, using a dynamic viscoelastometer (Rheogel E-4000 (UBM Co., Japan) in tensile mode, with an initial chuck distance of 20 mm. Test specimens were 0.4 mm thick, 3 mm wide, and 30 mm long.

Static mechanical measurements

Stress–strain curves were determined with an EZ-TEST (Shimadzu Co., Japan) tensile tester in tensile mode, with initial chuck distance of 10 mm and strain rate of 0.5 mm/s at ambient temperature.

Viscoelastic measurements

Shear storage (G') and loss (G'') moduli were measured using a CVO-50 (Bohlin Instrument Co., Japan) rheometer with parallel plate, at 20°C temperature intervals in the temperature range 200–340°C. The frequency range was 0.01–30 Hz.

Coefficient of friction measurements

Static (μ_S) and dynamic (μ_D) coefficients of friction were measured using the EZ-TEST (Shimadzu Co., Japan) tensile tester, according to the JIS K7125 standard. Test specimens were 80 mm in width and 200 mm long, and the loaded weight was 9.8 N.

RESULTS AND DISCUSSION

Effect of chemical structure of polysilane on the melt-flow and mechanical properties of UHMWPE

Figure 1 shows the variation of kneading torque with time for UHMWPE with addition of 5 wt % polysilanes with differing chemical structure. For the neat UHMWPE without any polysilane (designated "Pristine" in the Figure), the initial torque was about 30 N m, and it began to increase rapidly after 40 min, finally reaching a constant value of about 130 N m within 100 min. Addition of 5 wt % PMPS or PPSi to UHMWPE did not change the torque, which reached a constant value of about 40 N m after 50 min. The torque increased by only 10 N m and was about one-tenth that of neat UHMWPE. However, for the blend of UHMWPE with 5 wt % PDPS the torque began to increase after 60 min, and reached a constant value around 80 N m, which was about
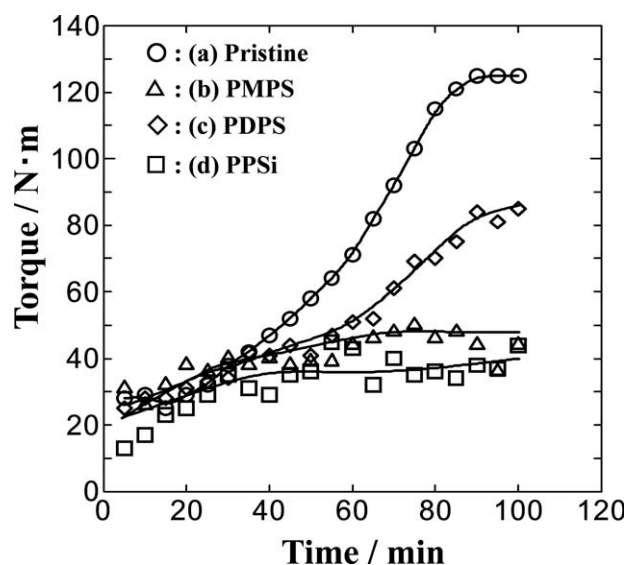

Figure 1 Variation of kneading torque of UHMWPE with different chemical structure polysilane: (a) Pristine, (b) PMPS, (c) PDPS, and (d) PPSi.
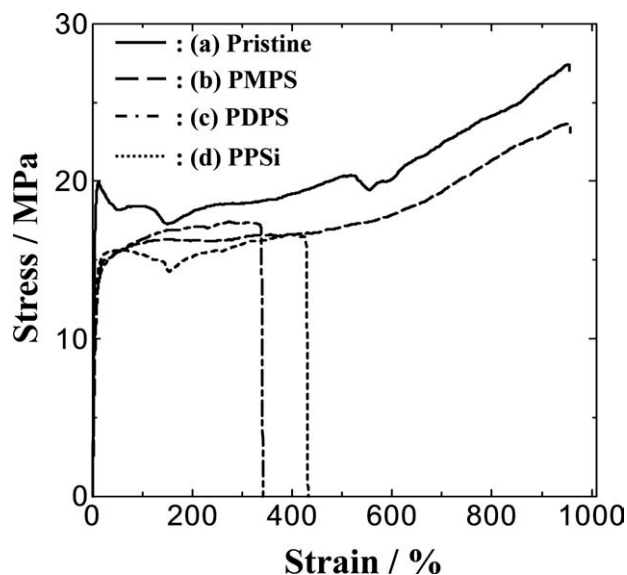
Figure 2 Stress–strain curves of UHMWPE with different chemical structure polysilane: (a) Pristine, (b) PMPS, (c) PDPS, and (d) PPSi.

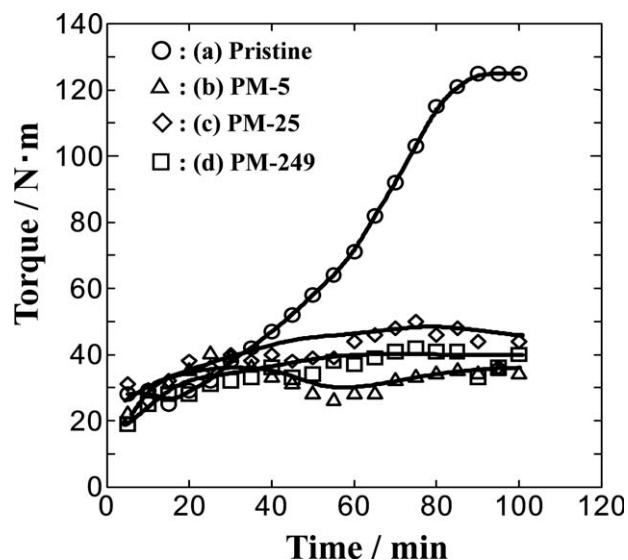**Figure 3** Variation of kneading torque of UHMWPE with different weights of PMPS: (a) Pristine, (b) PM-5, (c) PM-25, and (d) PM-249.

two-thirds of that of neat UHMWPE. Thus, the polysilanes suppressed the torque increment during melt process of UHMWPE at 200°C.

Figure 2 shows stress–strain curves of UHMWPE with and without addition of polysilanes with varying chemical structures. On addition of 5 wt % PMPS to UHMWPE, the specimen could be elongated, as for UHMWPE, to >1000% strain, which was the measurement limit. On addition of 5 wt % PDPS or PPSi to UHMWPE, the elongation at break was reduced to about 400%, indicating that a phase separation at an intermediate of UHMWPE matrix and dispersed polysilane phase occurred. From Figure 2, Young's modulus and yield stress values for UHMWPE with and without polysilanes were obtained; the data are given in Table II. Addition of 5 wt % of the polysilanes with differing chemical structure (PMPS, PDPS, and PPSi), to UHMWPE resulted in Young's modulus and yield stress becoming smaller than the values for neat UHMWPE. Young's modulus of UHMWPE with PMPS (linear structure) was the smallest and that of PPSi (networked structure) was the highest for the UHMWPE/polysilane blends. Although Young's modulus of neat polysilanes could not be measured because their molecular weights were too small to fabricate film specimens, it was thought that PPSi had a higher modulus due to its networked structure

and PMPS had a smaller modulus due to its linear structure.

These results indicate that PMPS is a promising candidate for modification of the melt-flow properties of UHMWPE, while maintaining the mechanical properties, especially the high elongation at break of UHMWPE.

Effect of the molecular weight of PMPS on the melt-flow and mechanical properties of UHMWPE

The effect of the molecular weight of PMPS on the melt-flow properties of UHMWPE was investigated.
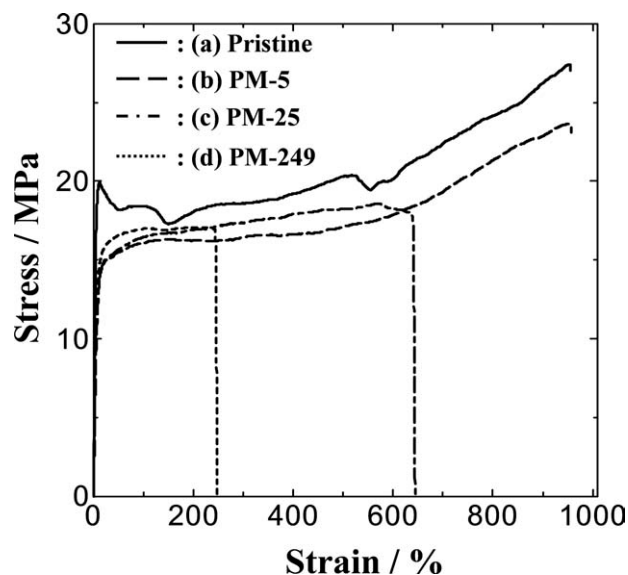

Figure 4 Stress–strain curves of UHMWPE with different molecular weight PMPSs: (a) Pristine, (b) PM-5, (c) PM-25, and (d) PM-249.

TABLE II
Young's Modulus and Yield Stress of UHMWPE with Different Chemical Structure Polysilane

	Pristine	PMPS	PDPS	PPSi
Young's modulus (MPa)	387	200	241	254
Yield stress (MPa)	19.9	15.1	14.9	15.7

Young's Modulus and Yield Stress of UHMWPE with Different Molecular Weight PMPSs

	Pristine	PM-5	PM-25	PM-180	PM-249
Young's modulus (MPa)	387	200	241	248	292
Yield stress (MPa)	19.9	15.1	15.1	16.2	16.7

The variation in the kneading torque of UHMWPE with different molecular weight PMPSs is depicted in Figure 3. For this experiment, PM-5 (M_w = 500 Da), PM-25 (M_w = 2500 Da), and PM-249 (M_w = 24,900 Da) were used. Addition of PMPSs with higher molecular weights to UHMWPE had the effect of suppressing the kneading torque increment during melt process of UHMWPE. The kneading torque did not increase within 100 min, whereas the torque for pristine UHMWPE increased and reached a constant value within that time.

Figure 4 shows stress–strain curves of UHMWPE and blends of UHMWPE with 5 wt % PMPSs with differing molecular weights, namely PM-5, PM-25, and PM-249. It was found that the higher the molecular weight of PMPS was, the smaller the elongation at break of the UHMWPE/PMPS blend. As is often the case with polymer blends, miscibility or compatibility of different polymers deteriorates with increase of the molecular weights of the blend components, in accordance with the Flory–Huggins theory. Thus it is suggested that a phase separation occurred in the UHMWPE blends with high molecular weight PMPSs. Young's modulus and the yield stress of the blends of UHMWPE with PMPSs of differing molecular weight are given in Table III. Although Young's
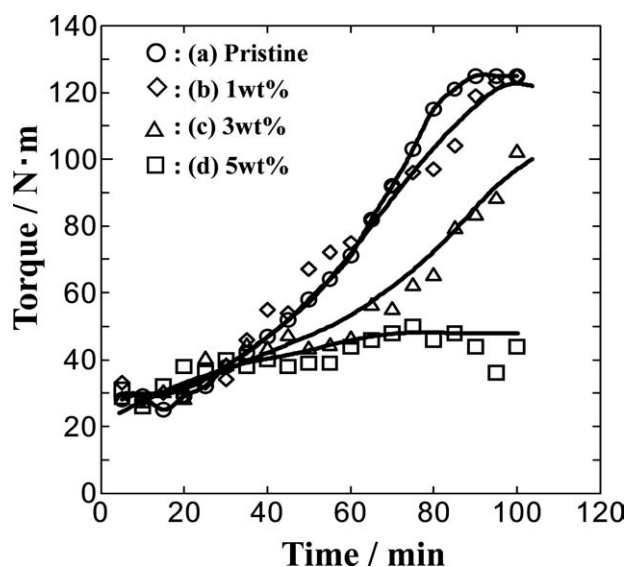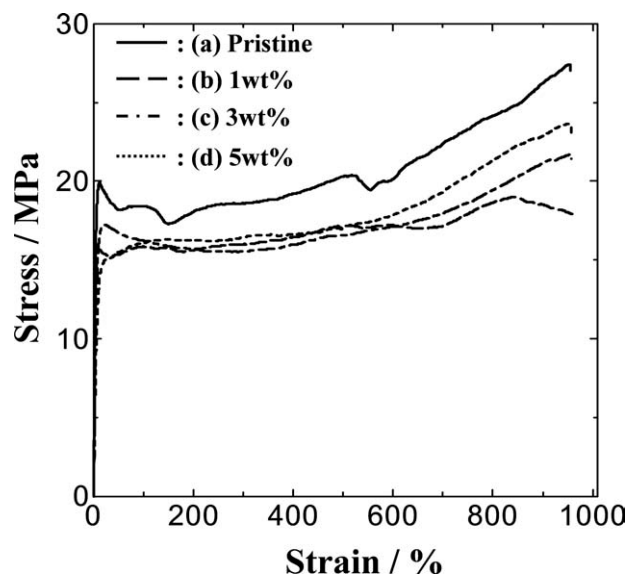

Figure 6 Stress–strain curves of UHMWPE with different amount of PM-5: (a) Pristine, (b) 1 wt %, (c) 3 wt %, and (d) 5 wt %.

modulus and yield stress were smaller than those of neat UHMWPE, there was a tendency for those values to increase with increase of the molecular weight of the PMPS blended with UHMWPE.

In general, though, it was confirmed that PMPSs with molecular weight about 500 Da played an important role in improving the heat-flow properties of UHMWPE and maintaining the mechanical properties, especially the high elongation at break of UHMWPE.

Effect of the PM-5 content on the melt-flow and mechanical properties of UHMWPE/PM-5 blends

In this section, the effect of the weight of added PM-5 on the melt-flow and mechanical properties of UHMWPE was investigated. As shown in Figure 5, addition of 1 wt % PM-5 to UHMWPE caused the kneading torque to increase with time, and it showed a similar tendency to that of neat UHMWPE. On addition of 3 wt % PM-5 to UHMWPE, the kneading torque increased slightly with time, and the increment within 100 min was almost halfway between the increments for 1 wt % and 5 wt % PM-5. Consequently, it is thought that an additive relationship holds for the melt-flow properties of UHMWPE/PM-5 blends.

Figure 5 Variation of kneading torque of UHMWPE with different amount of PM-5: (a) Pristine, (b) 1 wt %, (c) 3 wt %, and (d) 5 wt %.

Young's Modulus and Yield Stress of UHMWPE with Different Amount of PM-5

	Pristine	PM-5		
		1 wt %	3 wt %	5 wt %
Young's modulus (MPa)	387	337	263	200
Yield stress (MPa)	19.9	15.7	17.3	15.1

	Pristine	PM-5		
		1 wt %	3 wt %	5 wt %
Degree of crystallinity (%)	48.1	47.2	45.1	39.4
Melting temperature (°C)	128.6	129.6	129.5	129.0
Density (kg/m^3)	927	931	938	939

Figure 6 shows stress–strain curves of UHMWPE and its blends with 1, 3, and 5 wt % PM-5. UHMWPE with up to 5 wt % PM-5 could be elongated to >1000% strain. Hence PM-5 did not induce phase separation in the UHMWPE matrix while retaining its effect of modifying the melt-flow properties of UHMWPE. In Table IV, Young's modulus and yield stress of UHMWPE and its blends with different proportions of PM-5 are summarized. Although the modulus decreased with increase of the proportion of PM-5, the yield stress was almost independent of the amount of PM-5.

In Table V, the degree of crystallinity, melting temperature, and density of UHMWPE and its blends with varying proportions of PM-5 are summarized. The degree of crystallinity decreased with the proportion of PM-5, which is similar to the trend of Young's modulus. The density of UHMWPE with varying proportions of PM-5 increased with increase of the amount of PM-5 because the density of PM-5 is larger than the density of UHMWPE. Polarized optical microscope images of UHMWPE with varying proportions of PM-5 are shown in Figure 7. There was a tend-
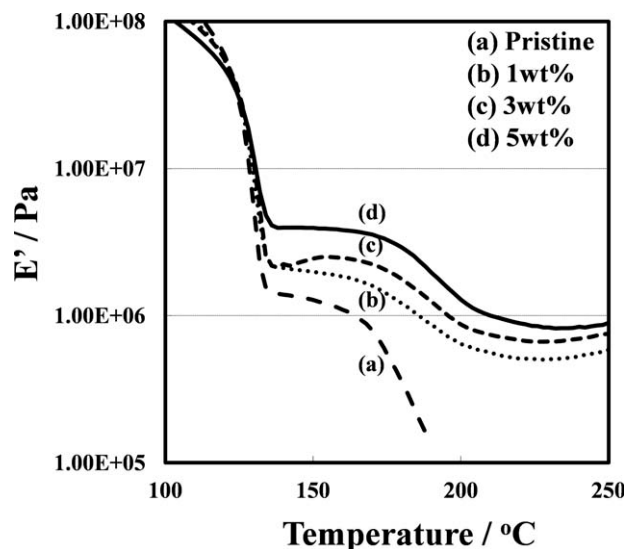

Figure 8 Variation of storage modulus (E') of UHMWPE with different amount of PM-5: (a) Pristine, (b) 1 wt %, (c) 3 wt %, and (d) 5 wt %.

ency for the size of UHMWPE crystallites to decrease with increasing proportion of PM-5, similar to the trend of decreasing crystallinity. This result indicated that PM-5 tended to be an inhibiter for crystallization in UHMWPE because PM-5 was compatible with polyethylene molecules, but they could not co-crystallize in the polyethylene crystals. In the melt-flow state, it was considered that PM-5 could exist neat the polyethylene molecules and it reduced the friction between the polyethylene molecules, resulting in decrease of kneading torque during melt process of UHMWPE.
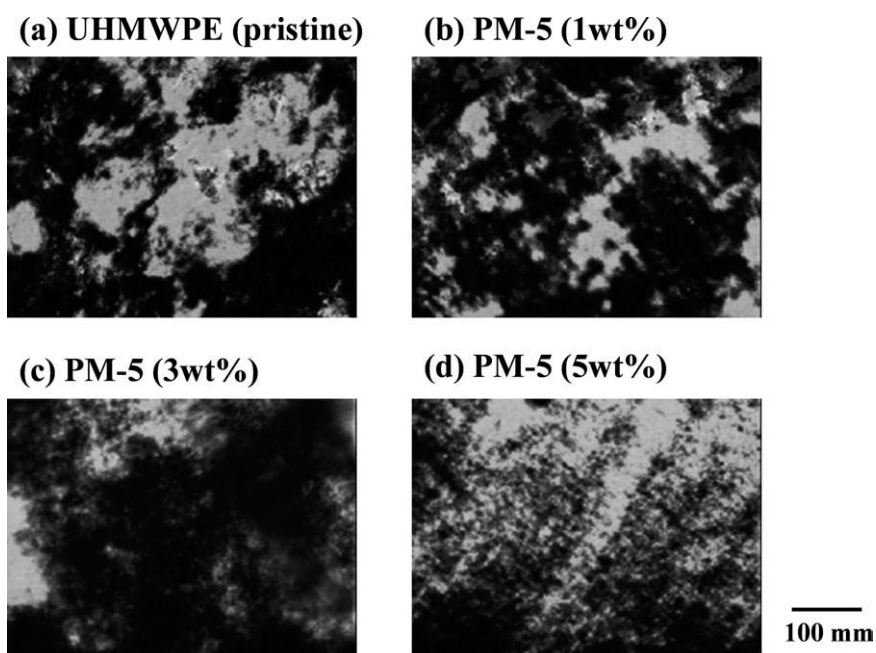

Figure 7 Polarized optical microscope observation results of UHMWPE with different amount of PM-5: (a) Pristine, (b) 1 wt %, (c) 3 wt %, and (d) 5 wt %.
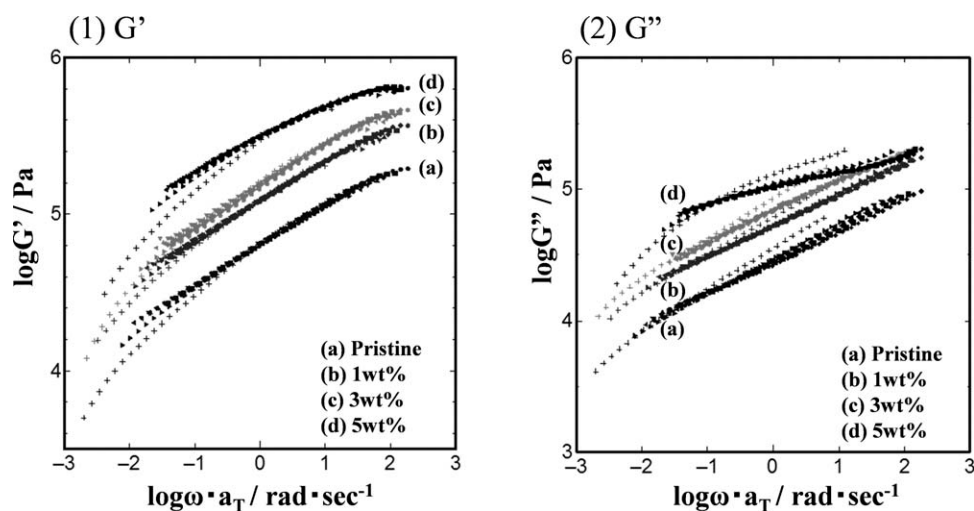
Figure 9 Variation of (1) storage shear modulus (G') and (2) loss shear modulus (G'') of UHMWPE with different amount of PM-5: (a) Pristine, (b) 1 wt %, (c) 3 wt %, and (d) 5 wt %.

DMA was carried out to quantify the molecular motions of UHMWPE blends with different proportions of PM-5. The variation of storage modulus (E') with temperature is shown in Figure 8. The rubber-like plateau region was observed for all UHMWPE samples and the values of E' increased with increase of the proportion of PM-5 in the blend. In addition, a second plateau region at higher temperature was observed. In general terms, these phenomena are thought to be associated with the development of a networked structure in UHMWPE. To confirm these phenomena, viscoelastic measurements were used to estimate molecular motion in the melt-flow state of UHMWPE. The variation of shear storage (G') and loss (G'') moduli as a function of frequency is shown in Figure 9 (1) and (2), respectively. The values of G' and G'' for the blends were larger than those of neat UHMWPE, and the shift ratio also increased with increasing proportion of PM-5 in the blends. These results are thought to indicate formation of a particular structure and/or a particular interaction between UHMWPE and PM-5.

Finally, we measured the coefficient of friction of UHMWPE blends with varying proportions of PM-5, because UHMWPE is widely used as a low friction material in applications such as tribological parts under non-lubricant conditions. The static (μ_S) and dynamic (μ_D) coefficients of friction are given in Table VI. With addition of PM-5 each coefficient of friction tended to increase slightly. As a result, UHMWPE with addition of PM-5 up to 5 wt % can be used as a tribological material in an industrial field.

CONCLUSIONS

In this article, the effect of adding polysilanes with different chemical structures (linear, cyclic, and net-worked), linear polysilanes with different molecular weights, and varying proportions of a fairly low molecular weight linear silane on the melt-flow properties of UHMWPE was investigated. The principal observations were as follows.

(a) Polysilanes with different chemical structures but similar molecular weights suppressed the torque increment during melt process of UHMWPE at 200°C. The linear silane PM-5, and network structured silane PPSi showed the largest effects. In terms of tensile properties, UHMWPE with added PM-5 could be elongated to >1000% strain, which was similar to neat UHMWPE, but UHMWPE with added PPSi and PDPS fractured at about 400% strain. On those grounds it is thought that the miscibility of UHMWPE and PPSi, and UHMWPE and PDPS, are poorer than the miscibility of UHMWPE and PM-5.

(b) Of the linear polysilane materials with different molecular weights, the low molecular weight polysilane PM-5 had the largest influence on the melt-flow and mechanical properties of UHMWPE. Thus there was a tendency for the elongation at break of UHMWPE blends to markedly decrease with increasing molecular

TABLE VI
Static and Dynamic Coefficient of Friction of UHMWPE with Different Amount of PM-5

	Pristine	PM-5		
		1 wt %	3 wt %	5 wt %
Static coefficient of friction ($/10^{-2}$)	7.37	11.20	7.10	10.00
Dynamic coefficient of friction ($/10^{-2}$)	3.12	3.14	3.53	4.20

weight of the polysilane component. Blends of UHMWPE and PM-249 (M_w = 24,900 Da) were easily broken at about 200% strain.

(c) The kneading torque during melt process of blends of UHMWPE with PM-5 decreased as the proportion of PM-5 increased from 1, 3, and 5 wt %. The implication is that the melt-flow properties of the blends are additive, i.e., melt-flow properties vary linearly with the proportion of PM-5. The degree of crystallinity decreased with increasing proportion of PM-5, and was similar to the trend of Young's modulus. Thus PM-5 is a promising candidate for modifying the melt-flow properties of UHMWPE, but also plays the role of an interfering substance when UHMWPE crystallizes.

(d) DMA data showed that the rubber-like plateau region was observed for all UHMWPE samples with added PM-5, and the values of E' increased with increasing proportion of PM-5. Moreover, the shear moduli G' and G'' also increased with increase of the proportion of PM-5. From these results, PM-5 is believed to form a particular structure and/or induce a particular interaction in UHMWPE/PM-5 blends.

(e) The static (μ_S) and dynamic (μ_D) coefficients of friction increased slightly with addition of PM-5 to UHMWPE. As a result, UHMWPE with up to 5 wt % added to PM-5 can also be used as a tribological material in an industrial field.

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