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SHORT COMMUNICATION

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Miscibility and gas permeability of poly(ethylene-co-5,4 mol% 3,5,5-trimethylhexyl methacrylate)-polydimethyl-siloxane blends

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Abstract Blends of poly(ethylene-co-5.4 mol% 3,5,5-trimethylhexyl methacrylate) (PE-TMHM) with poly(dimethylsiloxane) (PDMS) were prepared in the PDMS content range from 0 to 20%. The miscibility was studied for PE-TMHM–PDMS blends by DSC, dynamic mechanical and microscopic spectroscopy, and the gas permeability was measured for O_2, N_2 and CO_2 as function of PDMS content. PE-TMHM and PDMS were partially miscible with each other below 20 wt% of PDMS content. The permeability coefficients (P) for O_2, N_2 and CO_2 were increased by the blending of PDMS to PE-TMHM. The change of P for O_2 with PDMS content well reflected the partially miscible phase separation behavior.

Key words Poly(ethylene-co-5.4 mol% 3,5,5-trimethylhexyl methacrythlate) – poly(dimethylsiloxane) – miscibility – permeability – dynamic elastic measurement – DSC

Introduction

To date, scientific and industrial studies have been extensively made on polyethylenes modified with a small amount of functional moiety, such as branched alkyl groups and olefin rings (norbornene, etc.), to improve the physical properties [1, 2]. In the preceding work [3], we synthesized poly(ethylene-co-5.4 mol% branched alkyl methacrylate)s (PE-BAM). In PE-BAM, the highly branched alkyl methacrylate moiety was found to decrease the crystallinity in polyethylene region and increase T_g even at the low content of 5.4 mol%.

Recently, Hirose et al. [4] found that poly(dimethylsiloxane) (PDMS) is soluble in several highly branched alkyl alkanoates, such as 3,5,5-trimethylhexyl ester of nonanoic acid. This finding motivated us to investigate the miscibility of PDMS with PE-BAM because polyethylene is known to be scarcely miscible to PDMS. On the other hand, silicone resins such as PDMS commonly have a large gas permeability [5], and therefore it is worthwhile to study gas permeability in blends of PE-BAM with PDMS. The present paper reports miscibility and gas permeability for blends of poly(ethylene-co-5.4 mol% 3,5,5-trimethylhexyl methacrylate) (PE-TMHM) with PDMS.

CPS 750

Experimental

PE-TMHM was prepared with a dehydrogenchloride reaction of poly(ethylene-co-5.4 mol% methacrylic acid chloride) with 3,5,5-trimethylhexyl alcohol. Poly(ethylene-co-5.4 mol% methacrylic acid) (PEMA) is NUCREL (N-1560) of Mitsui-DuPont Polychemicals Co., which is a random copolymer and has apparent molecular weight of about 19 200 in number average and about 94 500 in weight average, and 3,5,5-trimethylhexyl alcohol was supplied from Nisshin Oil Mills Ltd.: A mixture of PEMA (100 g), thionyl chloride (250 ml) and benzene (750 ml) was stirred for 5 h at 323 K, and the acid chloride of PEMA was obtained by fully evaporating the solvent and remaining thionyl chloride. The acid chloride obtained was dissolved in benzene (550 ml), and 3,5,5-trimethylhexyl alcohol (1.5 mol) was added to the acid chloride/benzene solution, and then the solution was refluxed for 8 h at 338 K. The crude PE-TMHM was obtained by pouring the reaction mixture into acetone, and was thoroughly purified by several precipitations using acetone as precipitant. PEMA was judged to be fully esterified with 3,5,5-trimethylhexyl alcohol by IR spectra; the peak near 1700 $\mathrm{cm^{-1}}$ and a broad peak at 2500 ~ 3000 $\mathrm{cm^{-1}}$, which are attributed, respectively, to stretching vibration of C=O and OH in dimeric COOH groups, disappeared by the esterification, while a peak appeared near 1730 $\mathrm{cm^{-1}}$ which is attributed to C=O stretching vibration of the ester.

PE-TMHM–PDMS blends were prepared by fully mixing PE-TMHM with PDMS for more than 30 min at 423 K in a Brabender extruder, until the torque viscosity reaches a constant value. PDMS is TSE 200A of Toshiba Silicone Co., and has a kinematic viscosity of more than 1 $\mathrm{m^2\,s^{-1}}$. The blends for measurements were prepared by compression-molding into sheets of 100 to 170 μm thick at 423 K under 100 $\mathrm{kg/cm^2}$. The sheets obtained were confirmed to be uniformly mixed with each other on microscopic observation. The blend sheets with more than 20 wt% of PDMS content could not be produced because PDMS is a viscous liquid at room temperature.

Dynamic mechanical measurements were carried out with a Toyo-Seiki Reographsolid S-1 at 10 Hz at the heating rate of about 3 K/min in the temperature range from 103 to 293 K. Thermal measurements were made by use of a Seiko-Denshi DSC 220C calorimeter at the heating rate of 10 K/min in the temperature range from 133 to 423 K. The microscopic photographs for the blends were taken by optical microscopy (Nikon, Optiphoto-pol. XTP-11) at room temperature. Gas permeability was measured for O_2, N_2 and CO_2 in the temperature range from 277 to 315 K by using the vacuum time lag method as described previously [6, 7].

Results and discussion

Figure 1 shows DSC heating curves for PE-TMHM–PDMS blends. In PE-TMHM, there is a bend near 227 K and two peaks around 313 ~ 333 and 355 K, which are assigned, respectively, to T_g and two melting points for semi-crystalline and crystalline polyethylene regions. In the blends, T_g and two melting peaks are also observed, but another peak appears around 233 K. The 233 K small peak is not seen, when PDMS content in the blends (y) is 2 wt%, but as y increases above 2%, appears and increases in intensity. PDMS ($y = 100\%$) shows a large and sharp peak near 228 K which is clearly assigned to the melting point of PDMS crystallites. Therefore, the 233 K peak for the blends is assigned to the melting of their PDMS crystalline region. Thermal data for PE-TMHM–PDMS blends are listed in Table 1. As y increases, T_g somewhat descends but the degree of crystallinity for PE-TMHM region $[X_c/(1 - y/100)]$ is around 19% and is not so much changed with y. The melting point of PDMS crystalline region $[T_m(\mathrm{PDMS})]$ is almost unchanged with y, but it is noted that the melting enthalpy change of PDMS crystalline region $[\Delta H(\mathrm{PDMS})]$ is very small, compared with that of PDMS ($y = 100\%$). We calculated $\Delta H_n(\mathrm{PDMS})$ normalized to 100% of y, where $\Delta H_n(\mathrm{PDMS}) = \Delta H(\mathrm{PDMS}) \cdot (100/y)$. $\Delta H_n(\mathrm{PDMS})$ shows the extremely small values from 4.8 J/g in the $y = 5$ wt% blend to 6.5 J/g in the $y = 20$ wt% blend, which are, respectively, equal to the amount from 3/20 to 1/5 of PDMS blended. These

Fig. 1 DSC 2nd heating curves for PE-TMHM–PDMS blends. y: PDMS content (wt%), T_g: glass transition temperature of PE-TMHM amorphous region, T_m(PDMS): melting point of PDMS crystalline region, T_m(PE-TMHM): melting point of PE-TMHM crystalline region. A: $y = 100\%$, B: $y = 20\%$, C: $y = 10\%$, D: $y = 5\%$, E: $y = 2\%$, F: PE-TMHM ($y = 0\%$)

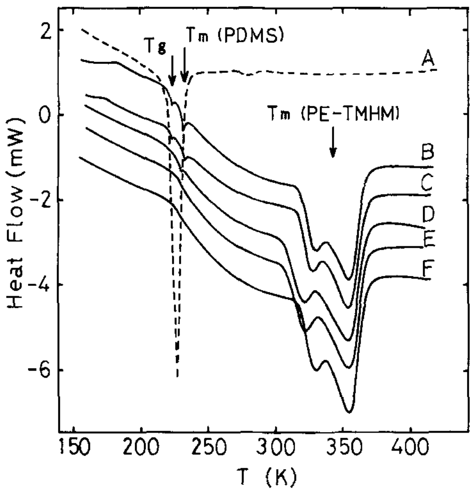

Table 1 Thermal data for PE-TMHM–PDMS blends

PDMS content (y, wt%)	0	2	5	10	20	100
T_g (PE-TMHM) (K)	227	227	227	222	222	–
T_m (PDMS)[a] (K)	–	–	233	234	234	228
ΔH(PDMS) (J/g)	–	–	0.2	0.5	1.3	33
ΔH_n(PDMS)[b] (J/g)	–	–	4.8	5.0	6.5	33
ΔH(PE-TMHM) (J/g)	53	56	55	50	43	–
X_c(PE-TMHM)[c] (%)	18	19	19	17	15	–
$X_c/(1 - y/100)$ (%)	18	20	20	19	19	–

[a] Melting point of PDMS crystalline region.

[b] $\Delta H_n(\mathrm{PDMS}) = \Delta H(\mathrm{PDMS}) \cdot (100/y)$.

[c] Degree of crystallinity was calculated assuming that the melting enthalpy of polyethylene crystallite is about 290 J/g.

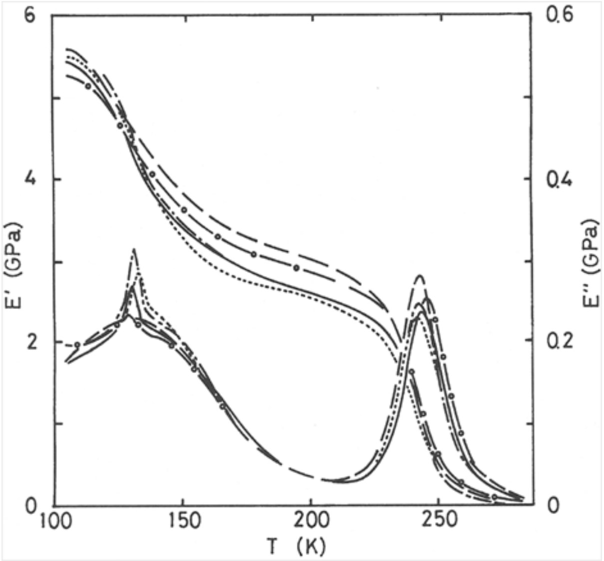

Fig. 2 Temperature dependencies of elastic constant (E') and the loss (E'') for PE-TMHM–PDMS blends at 10 Hz. - -: PE-TMHM ($y = 0$), -o-: $y = 2$ wt%, ——: $y = 5$ wt%, —·—: $y = 10$ wt%, -----: $y = 20$ wt%

Table 2 Relaxation temperatures (T_{max}/K) at 10 Hz for the blends

y (wt%)	α relaxation	β relaxation	α' relaxation
0	241	137	–
2	244	137	127
5	243	139	130
10	242	141	131
20	241	142	133

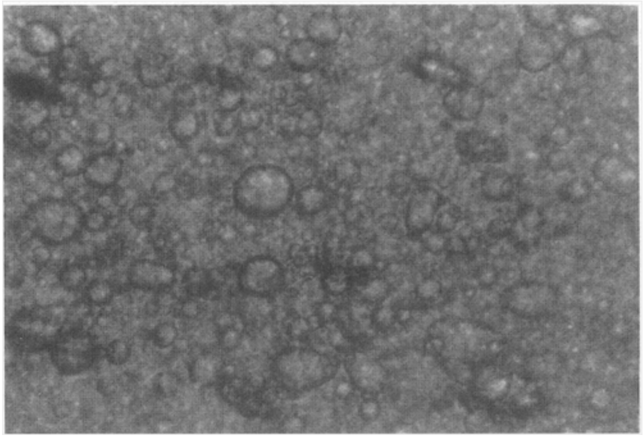

Fig. 3 A photograph of PE-TMHM–PDMS blends ($y = 20$ wt%) [× 100]

small values of ΔH_n(PDMS), of course, result from the decrease of PDMS crystalline region, which may be caused by either the decrease of crystallinity in PDMS rich phase due to hindrance of crystallization with other high melting components (i.e. PE-TMHM) or the decrease of PDMS phase due to dissolution of PDMS to PE-TMHM rich phase. Consequently, it is deduced that PDMS is partially miscible with PE-TMHM system, which was also supported by the following mechanical and gas permeability results.

Temperature dependences of dynamic elastic constant (E') and the loss (E'') are shown for PE-TMHM–PDMS blends in Fig. 2. In E''-temperature plots, PE-TMHM shows two relaxations, α around 241 K and β around 137 K, which are related to reorientational molecular motion of long segments above T_g and local molecular motion of short segments below T_g, respectively. In PE-TMHM–PDMS blends, the addition of PDMS slightly shifts α relaxation to lower temperatures and somewhat decreases the intensity. It is noted that a sharp peak in E'' appears near 137 K, superposing on the β relaxation, and is strengthened with increasing y. Clearly, this sharp peak may be related to T_g of PDMS (146 K [5]) and is hereafter denoted as α' relaxation. The dynamic mechanical data are listed in Table 2. The α' relaxation is not seen in PE-TMHM but appears in the blends, and this result indicates that PDMS is phase-separated in the blends. Figure 3 shows a typical microscopic photograph for PE-TMHM–PDMS ($y = 20\%$) blends. In the blends, there are seen the phase-separated PDMS rich particles whose diameters are in the order of 10^{-5} m.

Figure 4 shows temperature dependence of gas permeability coefficients (P) for N_2, O_2 and CO_2. In PE-TMHM, the values of P are about 3.7×10^{-10}, 1.1×10^{-9} and 5.9×10^{-9} cm^3 (STP) cm/cm$^2 \cdot$ s $\cdot$ cmHg at 298 K for N_2, O_2 and CO_2, respectively, where cm^3 (STP) means volume at standard temperature (273 K) and pressure (1 atm). The values of P for PE-TMHM–PDMS blend

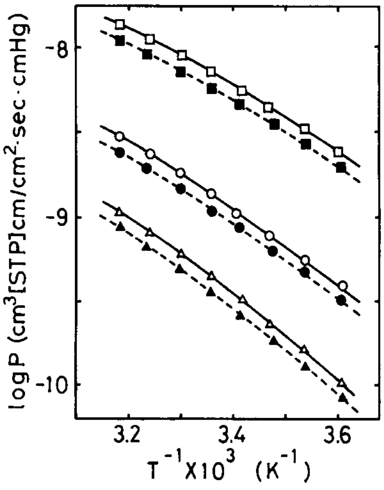

Fig. 4 Temperature dependencies of permeability coefficient (P) for O_2, N_2 and CO_2. closed symbols: PE-TMHM ($y = 0\%$), open symbols: blends ($y = 20\%$), ○ ●: O_2, △ ▲: N_2, □ ■: CO_2

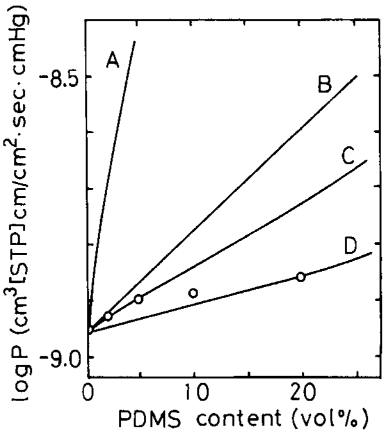

Fig. 5 Change of permeability coefficient (P) with PDMS content (vol%) in PE-TMHM–PDMS blends at 298 K. A) parallel model, B) miscible model, C) Maxwell model, D) series model

($y = 20$ wt%) increase by the presence of PDMS. The values of P increase with increasing temperature for all the gases and the plots of log P versus reciprocal of temperature ($1/T$) show no inflection point, which means that any phase transition does not exist in this temperature range between 277 and 315 K.

To elucidate the mechanism of gas permeation in the present PE-TMHM–PDMS systems, the permeability coefficients (P) were measured for O_2 as function of PDMS content (y) at 298 K. The data are plotted in Fig. 5. In general, gas permeability through blends is sensitively dependent on the composite geometry [8]. When the two components of polymer blends are completely miscible, the relation of log P with y shows a straight line,

$$\log P = \phi_1 \log P_1 + \phi_2 \log P_2 \tag{1}$$

where P is the permeability coefficient of the blends, P_1 and P_2 are the permeability coefficients for the respective phases, and ϕ_1 and ϕ_2 are their volume fractions, but when the two components are not miscible, the change of P with y is complicated and is essentially governed by the composite geometry, e.g., as successfully summarized by Robeson et al. [8, 9] based on the pioneering work of Maxwell [8, 10]. In the simple series laminates for two component systems,

$$P = P_1 P_2/(\phi_1 P_2 + \phi_2 P_1) \tag{2}$$

while

$$P = \phi_1 P_1 + \phi_2 P_2 \tag{3}$$

for the parallel laminate model. For the dispersed system, in which the spherical particles are dispersed in the continuous matrix phase, P satisfies the Maxwell equation,

$$P = P_m[P_d + 2P_m - 2\phi_d(P_m - P_d)] / [P_d + 2P_m + \phi_d(P_m - P_d)] \tag{4}$$

where m and d refer to the continuous matrix phase and dispersed phase, respectively.

We calculated the theoretical curves for the change of P with PDMS content in the present blends from Eqs. (1) ~ (4), where we used 6.0×10^{-8} cm^3 (STP) cm/cm^2·s·cmHg as P of PDMS [6, 7] and assumed that the volume fractions (ϕ_1, ϕ_2) for the two phases in Eqs. (1) ~ (4) are almost equal to the weight fractions (y, $1 - y$). The theoretical curves are expressed by the solid lines in Fig. 5. As PDMS content increases above 2%, the experimental data deviate downward and approaches the series model at 20%.

Conclusion

PE-TMHM and PDMS were partially miscible with each other in the PDMS content range below 20 wt%. The change of P with PDMS content faithfully reflected the partially miscible phase separation behavior. The present work certainly affords a way to make an olefinic polymer membrane having a large gas permeability. It should be one of the important subjects to investigate miscibility and gas permeability of blends of various poly(ethylene-co-branched alkyl methacrylate)s with polysiloxane.

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