Annealing of Polypropylene–Poly(ethylene-co-propylene) Blends. I. Thermal and Physical Properties of Blends

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Synopsis

Annealing of polypropylene and blends of polypropylene and poly(ethylene-co-propylene) was studied. The structural and physical properties were determined from thermal, mechanical, physicochemical, and spectral investigations. The particular emphasis was on the characteristics of structure and thermal properties of relatively amorphous components segregated from the crystalline region by annealing. Annealing of polypropylene induced an increase in crystallinity resulting in a decrease in impact strength. In contrast, by annealing a blend of polypropylene and poly(ethylene-co-propylene), the impact strength and rigidity were significantly improved with an increase in annealing temperature. The effect of annealing in a binary system was ascribed to the formation of a thicker transitional layer at the interface of the two polymers owing to the increased mobility of amorphous polymer segments. The results of tensile impact strength and brittle temperature were correlated with a deformational mechanism involving the crazing of the matrix.

INTRODUCTION

In view of the commercial importance of polypropylene (PP), a large amount of research has been directed toward the detailed characterization of its microstructure and microcrystalline structure and ways to improve its inherently poor impact strength at low temperature. A multicomponent polyblend is one means of achieving certain specific properties which are difficult to obtain from any one of the simple components alone. A majority of PP blends are concerned with the modification of impact strength. The presence of elastomer averts brittle failure and permits enhanced energy absorption by facilitating the orientation and cold drawing of the glassy PP phase to form crazes. The size and special distribution of the dispersed elastomer are critical to impact behavior. The morphology of a polyblend is often altered by processing and thermal history due to the fact that polymeric materials are usually incompatible and blends are thermodynamically unstable because of the lack of a significant entropic contribution to the free energy.

Some papers[1-6] and patents[7,8] have already reported the effect of annealing on PP and commercial block PP. However, any investigations of the effect of annealing on the blends of the crystalline polymer like the blend of PP and poly(ethylene-co-propylene) (PEP) have scarcely been undertaken. The crystallinity and the crystalline size of PP increase during annealing up to the melting point. It was observed in this work that annealing of PP–PEP blend improves not only the hardness and the tensile strength, but also the impact

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strength and the brittleness at low temperature. The particular emphasis was on the characteristics of microstructure and physical properties of the interface between two dynamically incompatible components, which can be controlled by the thermal treatment inducing the change in deformational mechanism of the matrix.

The present paper deals with the microstructures and properties of annealed PP and PP–PEP blends. First, the physical properties and viscoelastic behavior of annealed samples were correlated with molecular weight of PP and the annealing condition. Second, the microstructure and thermal property of the n-heptane soluble fraction of annealed PP–PEP blend were investigated in order to clarify the property of the transitional layer at the interface of the two polymers. Finally, a deformational mechanism was proposed for the annealed PP–PEP blends.

EXPERIMENTAL

Commercial grade PP (Tokuyama Soda Co., Ltd.) and PEP random copolymers (Mitsui Petrochemical Ind., Ltd) were used throughout this work. Their characteristics were presented in Table I. The melt flow index (MFI) was measured at 230°C under a 2.16-kg load according to ASTM-D1238. Molecular weight was measured in o-dichlorobenzene (o-DCB) at 135°C with a gel permeation chromatograph (Waters Company, Model GPC-200). Ethylene content of PEP was determined with ^{13}C-NMR. The glass transition temperature (T_g) of PEP was determined as the temperature at the peak of tan δ measured with a dynamic viscoelastometer.

Polymer blends were prepared on a differential two-roll mill at 180°C for 5 min and compression-molded within a plaque at 220°C under a pressure of 10 kg/cm^2 for 10 min of melt resistance time, followed by cooling to room temperature at a cooling rate of about 35°C/min.

Annealing of the samples was carried out in an evacuated vessel. All specimens were stored at 23°C and 50% humidity for 48 h in a temperature-controlled room prior to testing. Brittle temperature (T_b) and tensile impact strength (TIS) were estimated according to ASTM-D746 and ASTM-D1822, respectively. Tensile test was carried out at 23°C with a dumbbell test piece of L type in ASTM-

TABLE I
Analysis of Polymers

PP	MFI (g/10 min)	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
PP-1	2.3	42.5	4.9
PP-2	4.5	28.1	4.8
PP-3	13	22.0	4.8

PEP	MFI (g/10 min)	Ethylene content (mol %)	$\Delta H_{PE}/\Delta H_{PP}^a$ (cal/g)	T_g (°C)
PEP-1	0.74	78	0.0/0.0	−41
PEP-2	5.8	80	0.0/0.0	−38
PEP-3	0.58	80	0.1/0.0	−41

[a] ΔH_{PE} and ΔH_{PP} are the heat of fusion of PE and PP in a PEP, respectively.

D1822-68 by Tensile Testing Instrument, Model UTM-5T (Toyo Baldwin Co.).

Thermal analysis was performed in nitrogen at a heating rate of 10°C/min by using a differential scanning calorimeter (Perkin-Elmer Co., Model DSC-1B). The samples for the thermal analysis were thermally treated by cooling at a rate of 2.5°C/min after melting at 200°C for 15 min prior to annealing.

Dynamic mechanical measurements were carried out at 110 Hz with a Rheo-Vibron viscoelastometer (Toyo Baldwin Co., Model DVV-II) over the temperature range of −130°C to 160°C, at a heating rate of 1°C/min. The storage modulus E', the loss modulus E'', and the loss tangent tan δ were recorded.

Crystallinity of PP was obtained by means of X-ray diffraction.

RESULTS AND DISCUSSION

Annealing Phenomena of PP–PEP Blends

Some papers[3,4] report that recrystallization and migration of amorphous PP simultaneously occur in the crystalline areas by annealing. The recrystallization increases the polymer density and hardness of PP. On the other hand, the migration of amorphous PP contributed to a decrease in T_b, because of the thermodynamic mobility of amorphous polymer segments rejected out of the crystalline region.

Figure 1 plots TIS and the crystallinity of PP against the annealing time as a function of annealing temperature. Both TIS and crystallinity reach the equilibrium state in 3 h by annealing at each temperature of 120°C and 130°C. The equilibrium value of crystallinity increased with annealing temperature, while the equilibrium value of TIS decreased. Because of the similarity in annealing temperature dependence of both crystallinity and TIS, it was suggested that the fracture mechanism evaluated by the TIS test was closely related to crystallinity. Considerable changes in some important mechanical properties such as crystallinity and impact strength must occur within 3 h at these temperatures.

Table II shows the mechanical properties of annealed PP and annealed PP–PEP blend. The change in stress–strain mechanical properties of PP–PEP
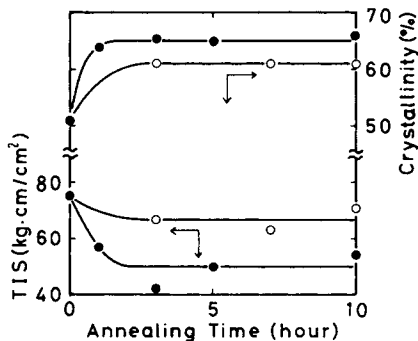

Fig. 1. Dependence of TIS and crystallinity of PP-2 sample on annealing time: (O) annealed at 120°C; (●) annealed at 130°C.

TABLE II
Effect of Annealing on Mechanical Properties of PP and PP–PEP Blend

Sample	YS^a (kg/cm²)	TS^a (kg/cm²)	Elongation (%)	$E^a \times 10^{-3}$ (kg/cm²)	H_R^a	TIS (kg·cm/cm²)	T_b (°C)
Unannealed PP-2	281	441	1030	3.6	93	62 ± 3	29
Annealed PP-2 110°C, 3 h	305	445	980	3.7	—	47 ± 2	—
Annealed PP-2 140°C, 3 h	320	370	750	4.0	96	34 ± 1	16
Unannealed Blend PEP-1/PP-2(20/80)^b	224	286	860	2.7	67	101 ± 4	−31
Annealed Blend PEP-1/PP-2(20/80)^b 140°C, 3 h	218	236	580	2.9	70	148 ± 5	< −40

ᵃ YS = yield strength, TS = tensile strength, E = Young's modulus, H_R = Rockwell hardness.
ᵇ Wt %.

blend by annealing is similar to those of PP; T_b is also improved in both samples. The most surprising feature of the present study is the unexpected effectiveness of PEP as a toughening agent for PP during annealing. In contrast to the decrease in TIS of PP by annealing, annealing of PP–PEP blend significantly improves TIS, in spite of the fact that the latter has the continuous PP phase and its TIS decreases with annealing. The fact that PEP actually increases the impact resistance of the annealed sample suggests that the elastomer has a dominant effect as an energy absorber at the interface between the continuous and dispersed phases. Therefore, we deduce that there are mainly two different morphological changes in PP and the PP–PEP interface in the annealed PP–PEP blend system; that is, in the continuous PP phase the migration of amorphous PP from the crystallizing part will occur during the recrystallization by annealing, and in the dispersed PEP phase the blending of PEP and amorphous PP will be facilitated by annealing at their interface.

Figure 2 shows the effect of annealing on the dynamic storage modulus E', the dynamic loss modulus E'', and the mechanical loss tangent tan δ, respectively, for PP, PEP, and PP–PEP blend before and after annealing. Annealing resulted in a shift of T_g and also a change in the peak height. There are two peaks of tan δ curves for PP, corresponding to α-relaxation at about 120°C and β-relaxation at about 15°C. The α-relaxation is ascribed to the segment motion of amorphous part restricted in crystalline region, and the β-relaxation is related to the relaxation associated with the glass transition. PEP also has two peaks at −110°C and −60°C. The peak at −110°C is possibly attributed to the local mode motion and the peak at −60°C is related to the relaxation due to the glass transition of PEP.

Annealing at 140°C for 3 h causes the shift of those peaks and the change of peak height on the dynamic mechanical properties of PP and PEP; that is, the temperature shifts of β-relaxation of PP and the principal relaxation of PEP toward lower temperatures, and the shift of α-relaxation of PP toward higher temperatures, and the increase of E'. The amorphous composition rejected from crystalline regions by annealing will cause the shift in the glass transition temperature of the system toward lower temperatures.
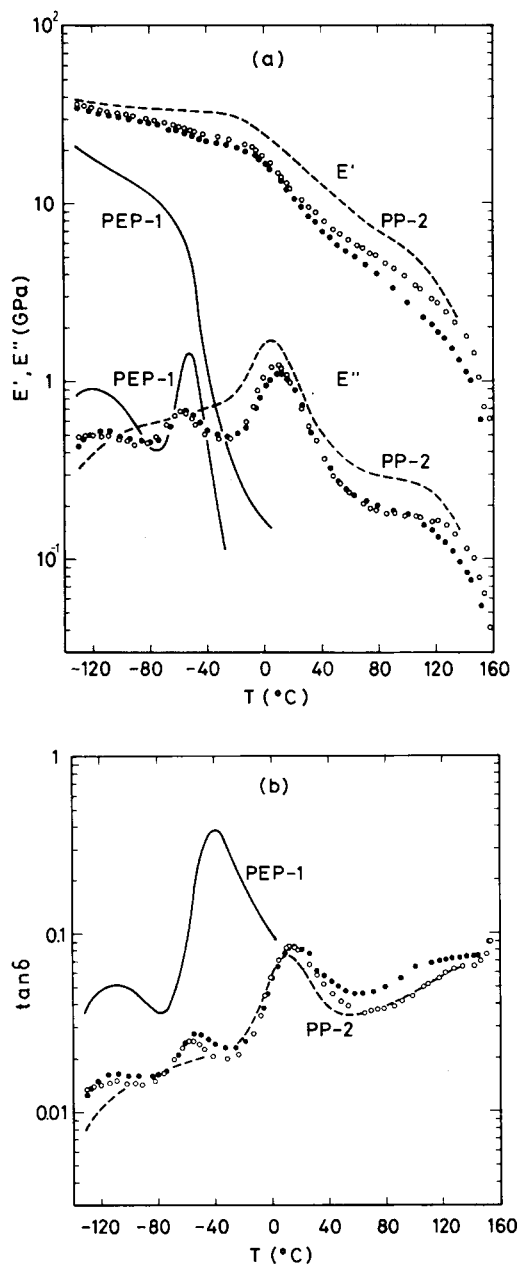
Fig. 2. Dynamic mechanical properties of PP-2,PEP-1, unannealed PEP-1/PP-2(20/80) blend, and annealed PEP-1/PP-2 (20/80) blend: (a) dynamic storage modulus E' and dynamic loss modulus E''; (b) mechanical loss tangent tan δ; (- - -) PP-2; (——) PEP-1; (●) unannealed PEP-1/PP-2(20/80) blend; (○) PEP-1/PP-2(20/80) blend annealed at 140°C for 3 h.

The normalized DSC curves (Fig. 3) for the unannealed and the annealed PP shows that annealing causes the variation of the crystalline structure, especially the lamella thickness, and that annealing at higher temperature produces the thicker lamella structure. Thus, the enhancement of mobility of amorphous
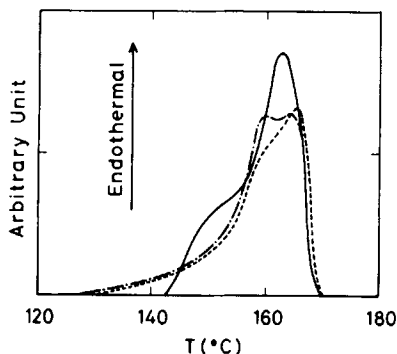
Fig. 3. Normalized DSC curves of PP-2 sample: (- - -) unannealed; (- · - ·) annealed at 110°C for 5 h; (——) annealed at 140°C for 5 h. The heats of fusion for these samples are 20.4 cal/g, 20.1 cal/g, and 22.8 cal/g, respectively.

PP segment rejected from the crystalline region by annealing may improve the brittleness of the specimen. The improvement of T_b by annealing (Table II) is in agreement with the results reported in the other papers,[3–5] but those papers have not elucidated the effect for TIS by annealing.

The fracture of PP–PEP blends was assumed to occur as follows: the intercrystalline region of PP matrix, the PP–PEP interface, and the dispersed PEP domain in the PP–PEP blend. Evidently, the considerable alternations of the crystalline region and the interface in an annealed PP–PEP blend have a bearing on the impact strength. Especially, we should note the interface of the dispersed PEP particles and PP matrix to understand the improved TIS in the blends by annealing. Therefore, we tried to evaluate the interface change in the annealed blends.

First, the tensile shear strength was measured to directly evaluate the strength of the PP–PEP interface with a single lap joint,[9] (Fig. 4), for the unannealed and the annealed samples. Annealing at 140°C for 4 h caused improvement in about 30% bonding strength between PP and PEP at their interface. The transitional
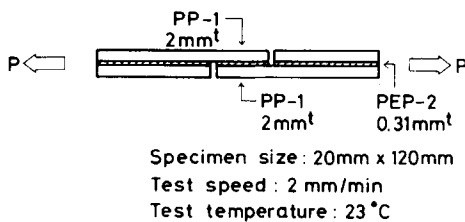
Fig. 4. Specimen for measurement and results of tensile shear strength.

layer of PP and PEP may be formed by annealing at the interface, for example, as observed in a blend of polyoxymethylene and low density polyethylene.[10]

Second, if the transitional layer is formed at the interfacial zone of the annealed PP–PEP system, the PEP part diffused into the semicrystalline region of PP matrix may be extracted with some difficulty. On the basis of this assumption, the following extraction was carried out.

PEP-1 and the residual part of PP-2 after extraction with n-heptane were blended on the two-roll mixer. TIS values of samples unannealed and annealed at 140°C for 4 h were 125 kg·cm/cm^2 and 147 kg·cm/cm^2, respectively. The enhancement of TIS was also observed in the annealed sample. The unannealed and annealed TIS specimens were extracted with n-heptane for 10 h after grinding to a powder less than 50 mesh. The extracted polymers were analyzed (Table III). A part of the unannealed sample was extracted with 15.8 wt %, whereas the annealed sample was extracted with 10.9 wt %. Because the ethylene content of PEP-1 is 78 mol % (Table I), the compositions of PEP-1 and PP-2 extracted from each sample can be calculated from the ethylene content of the extracted polymer. The difference in PEP-1 content of polymers extracted from the unannealed sample and from the annealed sample was 3.5 wt %, and this was substantial. Therefore, a part of PEP was diffused through annealing into the semicrystalline region of PP which was extracted with difficulty using n-heptane.

The normalized DSC curves of the n-heptane-soluble fractions in both unannealed and annealed samples are shown in Figure 5. The polymer extracted from the annealed sample has little crystallinity of polypropylene due to the recrystallization of PP-2 by annealing.

These data support the assumption of the formation of the transitional layer in PP-PEP blend systems.

Third, we calculated the thickness of the interfacial zone between two polymer phases with the aid of Helfand and Tagami's theory.[11] Stehling and co-workers have mentioned that the interfacial thickness should be greater than 30 Å to produce good impact strength in polymer blends.[12] According to the calculated solubility parameters on the basis of Hoy's equation,[13] the difference in a solubility parameter between PP and PEP used in this work is 0.61 (cal/cc)$^{1/2}$. Therefore, assuming molecular weight of 10^5 and temperature of 25°C, the thickness of PP–PEP interface before annealing is 20 Å. It is predicted that its

TABLE III
Influence of Annealing on Extraction Efficiency and Properties of n-Heptane Soluble Fraction
of PEP-1/PP-2(20/80) Blend[a]

| | Extracted part per whole polymer[b] (wt%) | | | Ethylene content (mol %) | ΔH (cal/g) |
	PEP-1	PP-2	Total		
Unannealed	13.0	2.8	15.8	67	3.3
Annealed 140°C, 4 h	9.5	1.4	10.9	70	0.3

[a] The insoluble fraction of PP-2 after extraction with n-heptane for 12 h was used for blending. The amount of soluble fraction was 5.0 wt % of whole polymer.

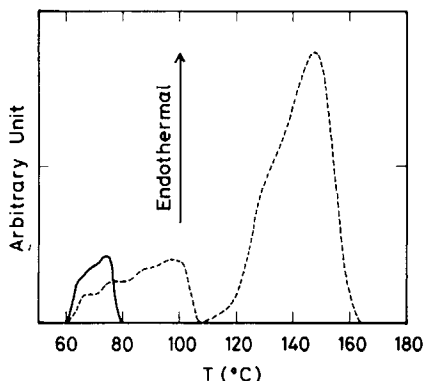[b] Calculated from ethylene contents of both extracted fractions and PEP-1.

Fig. 5. Normalized DSC curves of n-heptane soluble fraction of PEP-1/PP-2(20/80) blend sample: (- - -) unannealed; (——) annealed at 140°C for 4 h.

thickness will grow by increasing the annealing temperature, but it is impossible under the present status of thermodynamic theory of polymers to calculate the thickness after annealing. However, it is expected that the thickness of the interfacial zone (the transitional layer) will become 30 Å or greater by annealing.

Effect of Annealing on TIS and Tb

As described above, the mechanism of improvement of TIS by annealing was different from that for T_b. Although there are many methods to evaluate impact strength, no clear relationship has been obtained from their data; therefore, we can not explain the effect of annealing on TIS and T_b clearly. If the mechanism of effect of annealing in the studied system becomes clear, it will be very helpful to consider the phenomenon of the impact fracture on the measurements of TIS and T_b applied in the present study and to design the polymer structure to improve the impact strength.

Figure 6 shows the dependence of the annealing effects of TIS and T_b on the molecular weight of PP and PEP. The degree of improvement of T_b for PP by annealing is similar to that for the PP–PEP blends. It shows that the phenomenon to improve the brittle property for both annealed PP and annealed PP–PEP blends occurs in the amorphous part of PP matrix, which is a common component in each system. The molecular weight of PEP does not seem to influence preferentially the effect of annealing on T_b in PP–PEP blend systems. The PEP component of a blend does not contribute to the improvement of T_b by annealing.

The variation of TIS (Fig. 6) in the annealed blends appears to be very complex. Because TIS of the unannealed PP reduces with decreasing molecular weight and increasing annealing temperature [Fig. 6(c)], the morphology of the PP matrix must change to decrease TIS by annealing. On the other hand, TIS of the blend systems tend to improve with higher molecular weight PP and lower molecular weight PEP by annealing. Assuming that TIS will be affected by both changes of the PP matrix and the interfacial zone between the PP matrix and the dispersed PEP particles, the complex behavior of TIS in the annealed systems

may be distinctly explicable.   Namely, although the transitional layer between PP and PEP grows through annealing to improve the adhesion strength in most cases.   Figure 6(d) shows that the mechanisms of fracture on TIS test of the PP–PEP blend systems will be affected by each molecular weight of PP and PEP and also by the annealing temperature.
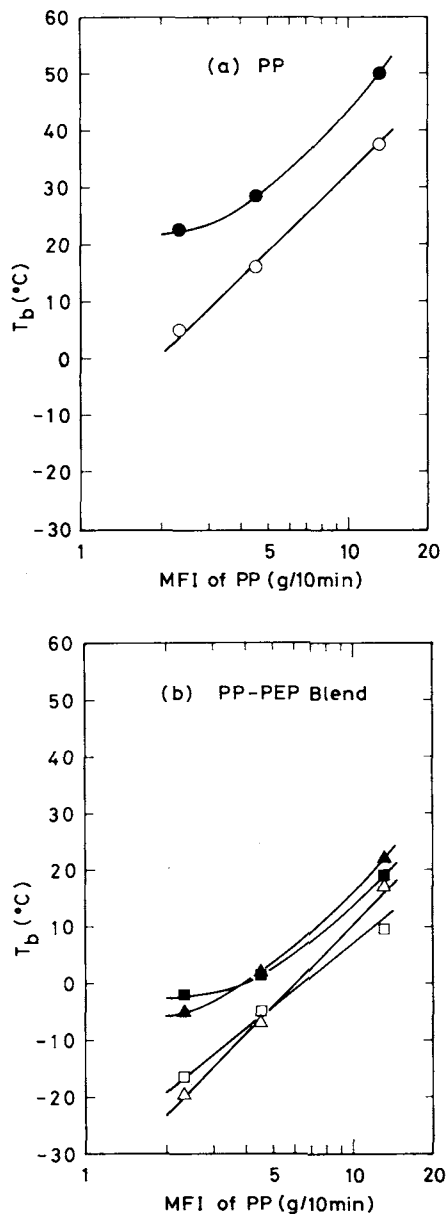

Fig. 6. Dependence of TIS and T_b for PP and PEP/PP blend samples on MFI of PP.   Unannealed: (●) PP; (▲) PEP-3/PP(10/90) blend; (■) PEP-2/PP(10/90) blend.   Annealed at 110°C for 5 h: (Φ) PP; (∇) PEP-3/PP(10/90) blend; (◇) PEP-2/PP (10/90) blend.   Annealed at 140°C for 5 h: (○) PP; (△) PEP-3/PP(10/90) blend; (□) PEP-2/PP(10/90) blend.
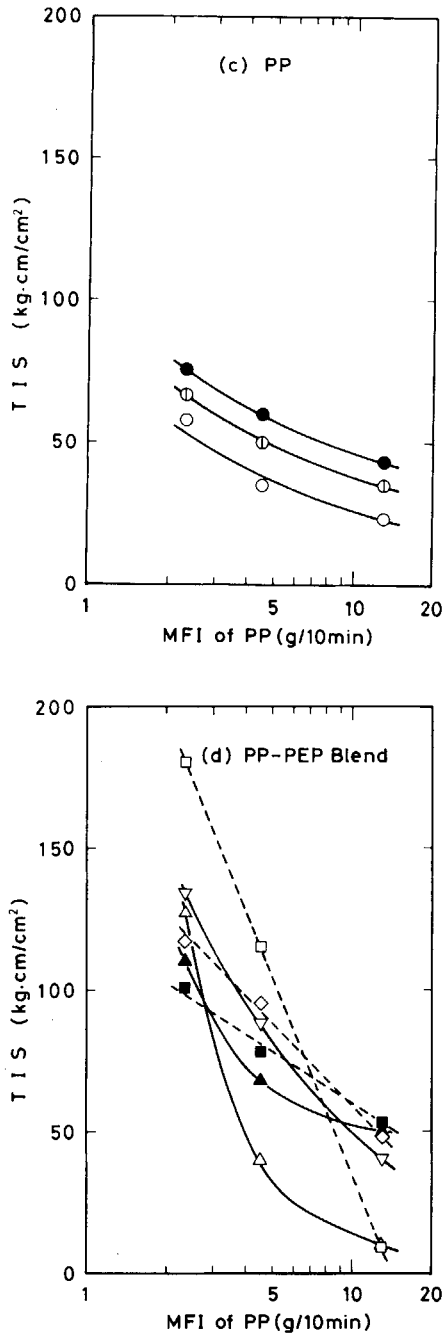
Fig. 6. (*Continued from the previous page.*)

As can be seen from the dependence of heat of fusion for the unannealed and annealed PP on molecular weight (Fig. 7), the amount of amorphous composition in PP matrix increases with the molecular weight of PP, regardless of the annealing temperature. The formation of the thicker transitional layer at the
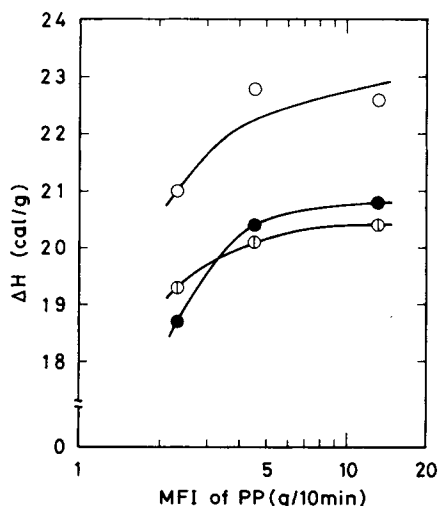
Fig. 7. Dependence of heat of fusion of PP samples on MFI: (●) unannealed; (◐) annealed at 110°C for 5 h; (○) annealed at 140°C for 5 h.

PP–PEP interface will be achieved in the annealed PP–PEP blend systems with PP containing more amorphous PP, because the transitional layer of PP–PEP must be composed of PEP and amorphous PP rejected from the semicrystalline region of PP, causing significant improvement of TIS in these samples.

A fracture model (Fig. 8) explains semiquantitatively the effect of annealing on TIS and T_b for PP and PP–PEP blend. The impact force W_b may be divided into three elements as follows:
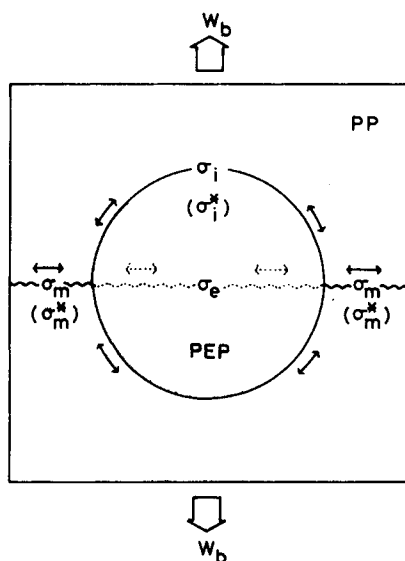
$$W_b = \sigma_m + \sigma_i + \sigma_e \tag{1}$$

Fig. 8. Fracture model for effect of annealing on TIS and Tb for PP and PEP/PP blend. Arrows show the growth of crazing.

where σ_m is the energy used mainly for the intercrystalline fracture in PP matrix, σ_i is the energy used to cause the interfacial crack between PP matrix and dispersed PEP domain, and σ_e is the energy stored by the dispersed PEP domain. Therefore, $\sigma_i = \sigma_e = 0$ in the fracture of PP. When TIS is applied W_b represents the total energy abstracted from the pendulum of the testing instrument, that is, it is equal to the peak value of energy stored in a specimen. Since the brittle temperature (T_b) is equal to the temperature at which brittle fracture occurs in a half probability, following Gaussian distribution, W_b indicates the constant energy transmitted from the hammer to a specimen. When eq. (1) is applied to T_b, each element of σ_m, σ_i, and σ_e represents the relaxation energy at the temperature of T_b in PP matrix, PP–PEP interface, and dispersed PEP domain, respectively. Therefore, T_b will be improved since the relaxation energy is greater at low temperatures.

Developing eq. (1), the annealing effect as discussed above will be expressed in the following equation:

$$W_b = (\sigma_m + \sigma_m^*) + (\sigma_i + \sigma_i^*) + \sigma_e \quad \text{for annealed system} \qquad (2)$$

where σ_m^* and σ_i^* are the variations of σ_m and σ_i, respectively, by means of annealing.

Speculating the mechanism of fracture on T_b with eq. (2), $\sigma_i + \sigma_i^*$ in eq. (2) will be almost equal to zero, because T_g of PEP which has diffused into the semicrystalline region of PP by annealing will approach the temperature of β-relaxation of PP. The amorphous component, rejected from the crystalline region by means of annealing, acts to disperse the impact energy corresponding to σ_m^*, as supported by the data (Fig. 6). Therefore, the annealing effect of T_b in each of PP and PP–PEP blends may be characterized only by the variation of matrix, that is, σ_m^* in eq. (2).

TIS measured at 23°C, the testing temperature, is affected by three main relaxations; β-relaxation of PP, principal relaxation of PEP, and local relaxation of PEP. Therefore, the value of $\sigma_i + \sigma_i^*$ is not zero. Due to the annealing effect of TIS [eq. (2)], σ_m^* is a negative value [Figure 6(c)] and σ_i^* will normally be a positive value on the basis of the formation of a transitional layer of PP and PEP. When $\sigma_i^* + \sigma_m^*$ is positive in the annealed system, TIS will be improved. However, [Fig. 6(d)], the energy (σ_i^*) dispersed at the PP–PEP transitional layer formed by annealing should be affected by the variation of the molecular weight of PP and PEP. In a blend of the low molecular weight PP and the high molecular weight PEP, σ_i^*, which represents the annealing effect at the PP–PEP interface, may be negative. Even though σ_i^* is positive, TIS of a blend will evidently decrease by means of annealing when $\sigma_i^* + \sigma_m^*$ is negative. The dependence of σ_i^* on the molecular weight of PP and PEP is due to the recrystallization rate and the rate of formation of the PP–PEP transitional layer. However, in this work it is not conclusively determined.

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