Investigation of the relaxation spectrum of multi-component systems by Pulsed NMR

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1. Introduction

Pressure sensitive adhesive (PSA) tapes are used in many fields, from the industrial, in such products as electronics, insulations, and packaging, etc. to the consumer.. The properties of PSA tape depend on the mechanical properties of the adhesives. For example, tackiness is a representative property of PSA tape, and dynamic viscoelasticity (DMA) is often evaluated to detect the mechanical properties of the adhesives. Dahlquist has discovered the relationship between the tackiness and the modulus of elasticity of the adhesives[1]. However, the tackiness should also correlate with the flowability of the adhesives within a short timescale. Therefore, tackifiers are often blended with elastomers, such as polyacrylate-type or polystyrene-type block copolymer, to improve the flowability. In order to design the flowability, it is important to know the molecular mobility of the materials in the adhesives.

Although the loss tangent (tangent delta) obtained by DMA is used as a measure for designing the composition of the adhesives, pulsed NMR is also a powerful tool to measure the molecular mobility of the components[2-4]. Free induction decay (FID) signals of macroscopic magnetization ($M(t)$) are obtained by the pulsed NMR. The initial value of the signal is proportional to the proton quantity in the materials. When the material consists of multi components, the whole signal is the sum of the signals from each component. Here, since the FID signal from each component can be detected separately, spin-spin relaxation time (T_2) of each component and the composition in the multi-component material can be calculated. For example, styrene - isoprene - styrene tri-block copolymer (SIS) consists of the polyisoprene as the soft segments and polystyrene as the hard segments. And the same polymer segments make their domains (phases) in the material. In the SIS, the polystyrene phases have shorter T_2 than the polyisoprene phases. Similar discussion can be made on the polymer blends quantitatively. Sasaki and others succeeded in the phase structural analysis of the tackifier blended PSA systems using the T_2 obtained by the pulsed NMR[5].

Meanwhile, it should be noted that the FID signals themselves include more information that relates to the molecular structure, the degree of crystallization, and the entanglement of the polymer chains. Although the FID signals have not been utilized enough until now[4], recent dramatic improvement of personal computers and evolution of algorithms for numerical treatment enable the direct numerical differentiation of the FID signals. I have just succeeded in makinga program that gives relaxation spectra of the FID signals[6]. The existing analysis method represented the molecular mobility of each component with one T_2. However, the distribution of the relaxation time of the multi-component materials depends

on the species of polymers and the additives, and their interaction in nature. Therefore, more information on the molecular mobility of each component and the interaction among the components would be given precisely from the whole relaxation spectra. This paper shows the relaxation spectra of SIS / tackifier PSA systems. Below, I will report the analysis method and the information on the molecular mobility obtained from the spectra analyses. The relaxation spectra from low resolution ^{1}H-Pulsed NMR enables the full use of the information from FID signals, and therefore the spectra will be a powerful tool for designing PSAs.

2. Analysis methods

2.1 Analysis of macroscopic magnetization $M(t)$

Figure 1 shows the FID signal of macroscopic magnetization ($M(t)$) by pulsed NMR (solid echo method) on the specimen of SIS-14 with 100phr (parts by weight) tackifier TZ-4. Figure 2 expressed the same data of Figure 1 as the relation between relaxation time and the FID signal of M (t), where the horizontal axis was shown as logarithm of the relaxation time. There are multi-relaxation points in the reverse-S-curve. A sharp relaxation exists about 10 microseconds, and a broad relaxation exists from 100 to 800 microseconds in Figure 2. In general, the obtained M (t) is divided into three components, namely, a "hard phase", a "soft phase", and the "interface" as the intermediate region. In Figure 2, an inflexion point around 10 microseconds corresponds to the hard phase, and another inflexion from 100 microseconds to 800 microseconds corresponds to the soft segment with the interface. Then, the relaxation time of each component is denoted in the next equation (1).

Fig.1 Time dependence of the Macroscopic magnetization M(t)

Fig.2 Time dependence of the Macroscopic magnetization M(t) (logarithmic time)

$$M(t) = a_1 \exp\left[-\left(\frac{t}{\tau_1}\right)^{m_1}\right] + a_2 \exp\left[-\left(\frac{t}{\tau_2}\right)^{m_2}\right] + a_3 \exp\left[-\left(\frac{t}{\tau_3}\right)^{m_3}\right]$$

(1)

Here, τ_i expresses the relaxation time and m_i expresses the weibull index. And, a_i is the intensity factor of each component. Stepwise regression analysis was applied to determine these values. First of all, a_1
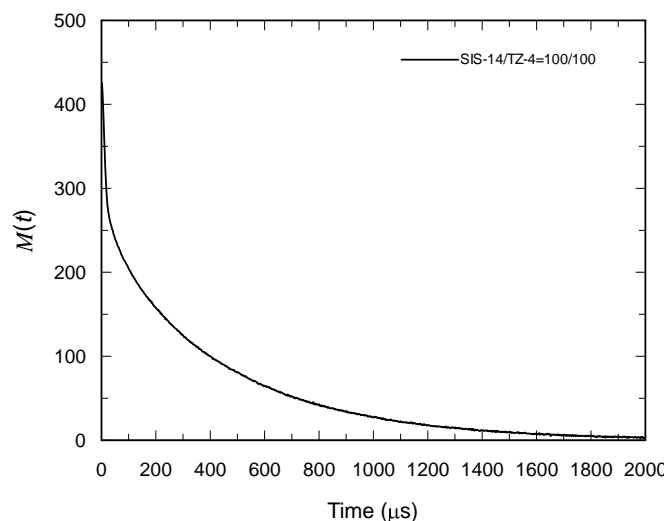
and τ_1 on the soft segment were calculated from the longest region of relaxation time of equation (1). Next, a_2 and τ_2 were calculated from the residue. Also, the composition f_i of the multi-component material was determined by the equation (2) using the a_i. The sequential analyses were conducted by repeating the same procedure.

$$f_i = a_i / \sum a_i \tag{2}$$

2.2 Relaxation spectrum of $M(t)$

However, Figure 2 indicates that the actual relaxation time is distributed continuously in nature from the long relaxation time to the short relaxation time. Namely, the "hard phase", the "soft phase", and the "interface" should connect with each other, and the distribution of the relaxation time changes continuously. If a FID signal of $M(t)$ is recognized as a superposition of exponential functions on the relaxation time, then the next equation (3) can be made.

$$M(t) = \int_{\infty}^{\infty} H(\tau) \left(e^{-t/\tau} \right) d\ln\tau \quad . \tag{3}$$

The equation (3) under the normalization condition defines the relaxation time distribution function $H(\tau)$. Here, $H(\tau)$ means the relaxation spectrum. FID signal of $M(t)$ measures the decay of the magnetized spin of the protons in the time course, and the relaxation-spectrum $H(\tau)$ is distribution function in nature. In order to treat $H(\tau)$ as a standardized distribution function without dimension, the time scale of the measurement should be expanded from 0 to infinity. Fortunately, however, when the normalization by the maximum value of the macroscopic magnetization $M(t)$ is applied, the distribution function can be standardized. In this paper, the first order differentiation by the next equation (4) was used to make the relaxation spectrum from the FID signal of $M(t)$ of pulsed NMR. Namely, the relaxation spectra were obtained using the numerical differentiation by the logarithm of the time on the FID signal.

$$H(t) = \frac{d}{d\ln t} M(t) \tag{4}$$

3．Experimental methods

3.1 Pulsed NMR measurement

[1]H spin-spin relaxation time (T_2) was measured by the solid echo method using a JEOL JNM-MU25 spectrometer. The width of pulse was 2.0μs. The pulse interval was 8.0μs. The integration time was 32. The ambient temperature was 35°C. The FID signals of the $M(t)$ of the samples were detected, and the spectra of the relaxation time were determined from the numerical differentiation of the $M(t)$.

3.2 Analytical program

The analytical program for determining the relaxation spectra was written using IgorPro 6.1. The IgorPro 6.1 is known not only as the software for graphic and data analysis, but also forprogramming software such as FORTRAN. It requires precise the type declaration of the variables and the matrix. Also, it resembles PASCAL language in terms of using many commands for numerical analyses and graphics. However, since the data- scattering of pulsed NMR is somewhat large, if the direct numerical differentiation using the equation (4) was applied to the raw $M(t)$ data, the differential coefficient would disperse from infinitesimal to infinity especially in long relaxation region. This means the relaxation spectrum could not be determined. Therefore, Savitzky-Golay smoothing, a kind of the least squares polynomial smoothing method in the IgorPro[7], was applied to the raw $M(t)$ data first. Next, the numerical differentiation by the logarithm of the time on the smoothed $M(t)$ data was conducted to get the relaxation spectra.

Table 1 Sample (Polymer)

Sample No.	Styrene Content (%)	Coupling Ratio (%)	Molecular Weight Mw	SI Diblock Content (%)	Polymer Structure
SIS-14	14.2	71.8	200,000	28.2	Linear
SIS-22	22	100	234,000	0	Linear
SIS-30	30	100	213,000	0	Linear
PS-1	100	-	250,000	-	-

Table 2 Sample (Tackifier)

Sample No.	Tackifier Type	Softening Point(℃)	Molecular Weight Mw	Mn
TZ-1	C5	70	2080	1030
TZ-2	C5	96	2150	1110
TZ-3	C5	96	2690	1240
TZ-4	C5	96	2240	1170
TZ-5	C5	100	4090	1380
TZ-6	C5	101	2800	1340
TZ-7	C5	101	2610	1230
TZ-8	C5	110		
TA-1	Hydrogenerated	70		
TA-2	Hydrogenerated	90		
TA-3	Hydrogenerated	100		
TA-4	Hydrogenerated	115		
TA-5	Hydrogenerated	125		
TA-6	Hydrogenerated	140		
TY-1	Terpene Resin	80		
TY-2	Terpene Resin	100		
TY-3	Terpene Resin	115		
TY-4	Terpene Resin	130		

3.3 Materials

Table 1 and Table 2 show the list of the materials used in the test. The SIS polymer (SIS-14: 14% styrene content), the polystyrene PS, and the tackifier TZ-5 (C5 resin) or TA-3 (hydrogenation resin) were used as it was for pulsed NMR measurement. Meanwhile, for PSAs consisting of SIS blends with TZ-5 or TA-3, the toluene solution of the blends were coated in 120 μm-thick on the silicone-treated PET films, and dried at 120°C in 3 minutes.
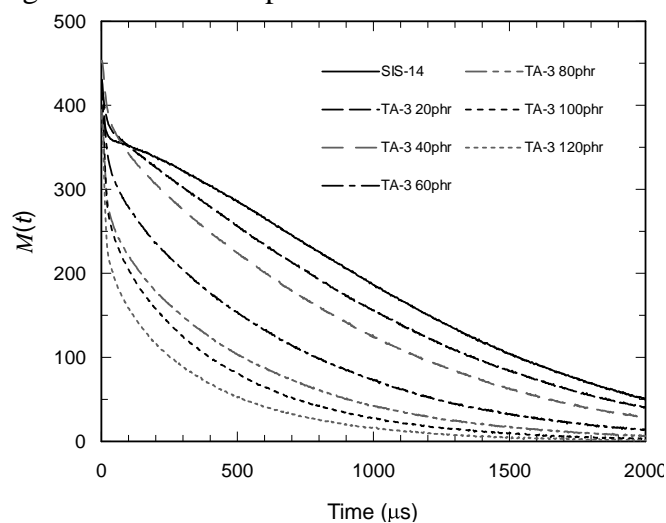

Fig. 3 Time dependence of the $M(t)$ of tackifier blended SIS block copolymers

4. Results and discussion

4.1 SIS / tackifier blends

4.1.1 FID of $M(t)$

Figure 3 shows the FID curves of $M(t)$ obtained from the pulsed NMR on SIS-14 / TA-3 blends. And Figure 4 shows the same data with the logarithm of the time as the horizontal axis. Pure SIS-14 has a small inflexion point roughly at 15 microseconds, and there is a sharp large inflexion point roughly at 1,000 microseconds. These inflexion points correspond to the peaks of the distribution curves of the relaxation time.

Meanwhile, as for the SIS-14 / TA-3=100 / 120 blend, the relaxation at 15 microseconds became large. Also, the sharp relaxation at 1000 microseconds of SIS-14 was changed to the broad distribution of the relaxation in which the peak was roughly at 200 microseconds.

4.1.2 Relaxation spectrum

Figure 5 shows the relaxation spectrum (the distribution curves of the T_2 relaxation time) according to the equation (4). The vertical axis shows the extent of the relaxation, and the horizontal axis shows the relaxation time. In the figure, the peak of $H(\tau)$ in the shorter relaxation time corresponds to polystyrene and tackifier, and the peak of L (t) in the longer relaxation time corresponds to polyisoprene. The decreasing tendency of $M(t)$ resulted in the formation of convex curves (peaks) of the $H(\tau)$. And the intermediate region corresponds to the part that has been recognized as the "interface". Here, the $H(\tau)$ curves gave more information than the existing T_2 relaxation times assigned to three components, namely "hard phase", "soft phase", and "interface". The T_2 relaxation time of the polyisoprene phase was distributed to relatively
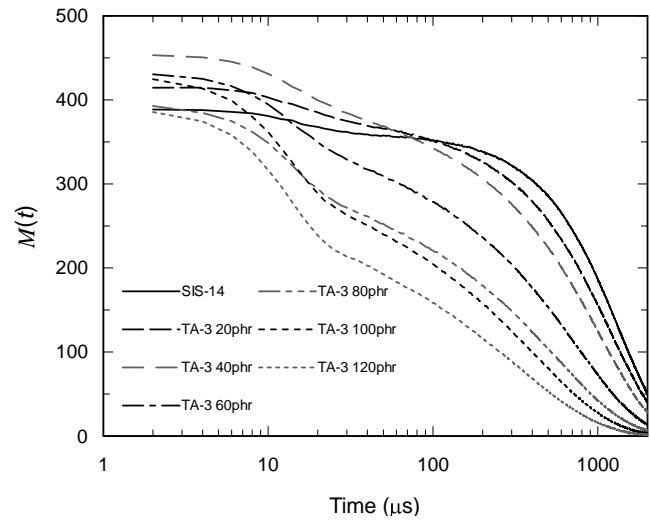

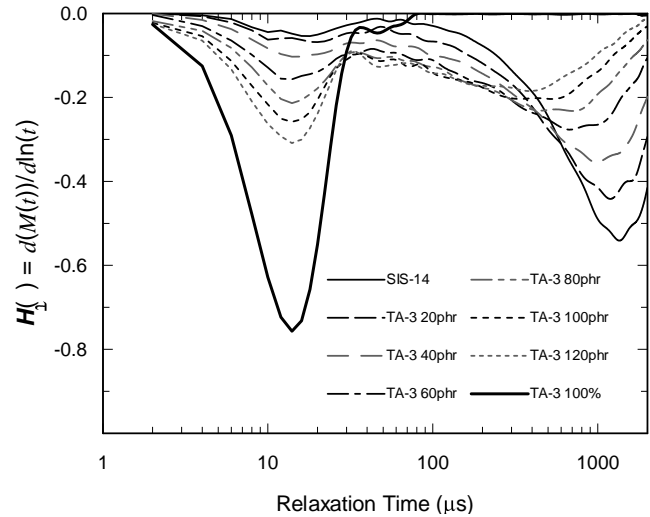Fig. 4 Time dependence of the M(t) of tackifier blended SIS block copolymers (log-time)

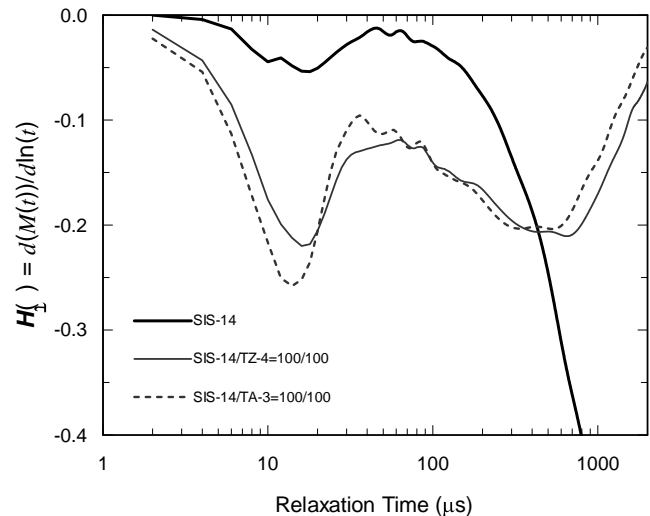Fig. 5 Relaxation Spectrum of SIS-14/TA-3 System

Fig. 6 Effect of Tackifiers on Relaxation Spectrum

short timescale. This has been explained as a constraining effect on the molecular mobility of the polyisoprene by the chemical bond with polystyrene, and the distributed part in the short timescale has been assigned as the "interface". In the figure, 100% tackifier indicated the large relaxation peak roughly at 10 microseconds as shown in the bold line. This indicates good agreement with the T2 relaxation times of the tackifier (12 microseconds), which has been calculated by the existing pulsed NMR measurement.

It should be noted that the "interface" regions on the relaxation time of the several SIS blends with tackifier were greatly different from the pure SIS. Figure 6 shows the relaxation spectra of SIS-14 / TA-3 = 100/100 and SIS-14 / TZ-4 = 100/100. The Figure 6 with the magnified vertical axis clarified that:

(a) SIS-14 / TA-3 has larger peak of the hard segment than SIS-14 / TZ-4.

(b) The peak of relaxation of the soft segment in the SIS-14 / TA-3 exists in shorter relaxation time than the SIS-14 / TZ-4.

(c) The SIS-14 / TZ-4 have more distribution of the relaxation time roughly at 40 microseconds, where is the foot of the peak of the tackifier, than the SIS-14 / TA-3.

These experimental data lead to the next postulations: The SIS-14 / TA-3 have more domains of the tackifier than SIS-14 / TZ-4. The domains of tackifier constrain the molecular mobility of the polyisoprene at long timescale. Conversely, the solubility of TZ-4 in the polyisoprene of SIS-14 is more than TA-3. As a result, tfewerdomains of TZ-4 were made than of TA-3. (If many domains of TZ-4 dispersed in the blends, large peak of the hard segment would be made.) Then, the dissolved tackifier TZ-4 constrained the molecular mobility of polyisoprene corresponding to 40 microseconds ("interface" region). However, no constrain effect was detected on the molecular mobility in long timescale of the polyisoprene segment (soft segment) of SIS.

4.2 SIS

Figure 7 shows the relaxation spectra of SIS polymers and polystyrene. The dotted line is the relaxation spectrum of polystyrene. The relaxation peak having the maximum roughly at 18 microseconds is originated from the polystyrene as the hard segment. The distribution increased with increasing the polystyrene content in the SIS, and the distribution from the polyisoprene decreased. Meanwhile, the intermediate region among them kept almost the same level of the distribution. The minimum of the distribution of relaxation

Fig. 7 Relaxation Spectrum of SIS and PS

existed roughly at 55 microseconds, where the border of the relaxation time of the polystyrene domain and that of the polyisoprene matrix are. In fact, Figure 7 shows the minimum of the distribution kept at a
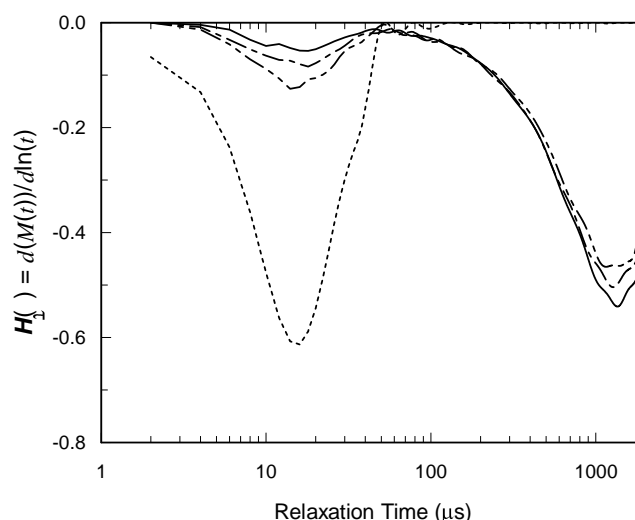
very low level. Even when the content of the polystyrene changed from 14% to 30%, the distribution level of the relaxation spectra from 50 microseconds to 300 microseconds did not change. One may think that the increased polystyrene content (30 %) would constrain the molecular mobility of the polyisoprene segment strongly, which would increase the distribution of the relaxation from "interface". However, the fact was different from the speculation. This may indicate that the mobility of polyisoprene segment having the molecular weight of 150,000 is not influenced by the both-end capping by the polystyrene segments, at least during a short relaxation time such as 55 microseconds. The comparison of Figure 7 on the SIS systems and Figure 5 on the SIS / TA-3 tackifier systems gives the next findings;

(a) Even when the content of the polystyrene changed from 14 % to 30 %, the distribution level of the relaxation spectra from 50 microseconds to 300 microseconds did not change in the SIS systems.

(b) Meanwhile, the 40phr (29 %) addition of the tackifier increased the distribution level of the relaxation from 50 microseconds to 300 microseconds.

(c) Both increase in polystyrene content and the addition of the tackifier decreased the distribution of the relaxation in the long timescale of more than 300 microseconds.

Although only the neighbor part bonded to polystyrene in the polyisoprene segment was constrained slightly by the polystyrene, the constraint effect was very small. Meanwhile, the increase in polystyrene content in SIS surely decreased the distribution of the relaxation of the polyisoprene in the long timescale such as 1000 microseconds, which indicates the molecular mobility was constrained by the polystyrene. Namely, "The neighbor part bonded to the polystyrene in the polyisoprene segment was not constrained by polystyrene, and the far part from the polystyrene in the polyisoprene segment was constrained by the polystyrene. Tackifiers having no chemical bond to the polyisoprene constrain the molecular mobility of the polyisoprene strongly." These are indicated from the experimental data, but are   beyond our existing theory. One plausible assumption to explain the experimental data is "the constraint effect of the polystyrene on molecular movement of the polyisoprene is simply   from the volume effect of polystyrene". The molecular mobility of the polyisoprene segment bonded to the polystyrene received the constraint effect from the polystyrene segment slightly, but the tackifier gave much more constraint effect to the polyisoprene segment than the polystyrene. This would be due to the molecular quantity of the tackifier dispersed in the PSAs.

4.3 Tackifier

Table 3 T_2 Relaxation Time of Tackifier Resins

Sample No.	TZ-1	TZ-2	TZ-3	TZ-4	TZ-5	TZ-6	TZ-7
T_2	15.5	14.1	14.1	14.1	13.9	14.0	14.0
W_2	1.5	1.88	1.85	1.87	1.91	1.87	1.88

Sample No.	TA-1	TA-2	TA-3	TA-4	TA-5	TA-6
T_2	12.8	12.0	11.8	11.7	11.7	11.6
W_2	1.99	2.19	2.23	2.22	2.26	2.23

Sample No.	TY-1	TY-2	TY-3	TY-4
T_2	16.2	14.2	14.1	14.2
W_2	1.03	1.96	1.99	1.96

Table 3 shows the T2 relaxation time of tackifiers and the weibull index. Also, Figure 8 shows the relation between the T_2 relaxation time and the softening temperature of the tackifiers. The T_2 relaxation time became shorter as the softening temperature of the tackifiers increased. However, the relation between the relaxation time and the softening temperature of TY tackifier (terpene type resin) was somewhat different from others. Namely, the TY-2, 3, 4 shows almost same relaxation time (14 microseconds). Only the TY-1 having the softening temperature of 80°C shows longer relaxation time (16 microseconds) than others. In general, the molecular mass of tackifiers has an effect on the softening temperature. Meanwhile, as far as the chemical structure of the repeat unit was same, relaxation times would not be influenced so much. However, only the experimental data of TY-1 was out of the general theory. Also, the weibull index of TY-1 was different from those of TY-2, 3, 4, which indicates the TY-1 has broader distribution of the relaxation time than others. Figure 9 shows the relaxation spectra of the TY tackifiers (terpene type resins). TY-2, 3, 4 indicate almost same distribution of the relaxation times. The spectrum of TY-1 suggests that the tackifier includes some additives having broad relaxation times roughly at 35 microseconds.

Fig. 8 T_2 Relaxation Time of Tackifier Resins

Fig. 9 Relaxation Spectrum of Terpene Resins

5. Conclusions

A method to give relaxation spectra has been established using numerical differentiation of macroscopic magnetization $M(t)$ by logarithm of the relaxation time that was obtained from the pulsed NMR measurement. The conventional pulsed NMR analyses have given the information on the phase structure and the adhesive properties of the PSAs. In precise, the method has just indicated the composition on the multi-component PSAs and the spin-spin relaxation time (T_2) of each component, such as the hard segment, the soft segment, and the interface. Although the measured macroscopic magnetization $M(t)$ was data with plenty of information, the data has not been fully analyzed by the conventional method. By the improvement in performance of personal computers and the development of the numerical processing algorithm, a program to obtain the relaxation spectra by direct numerical differentiation of
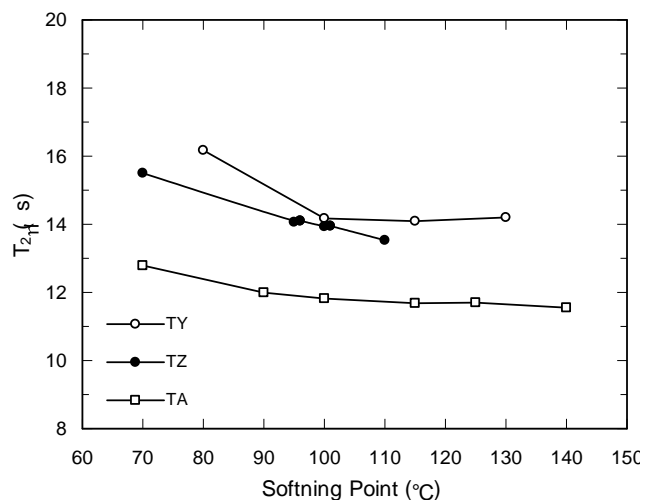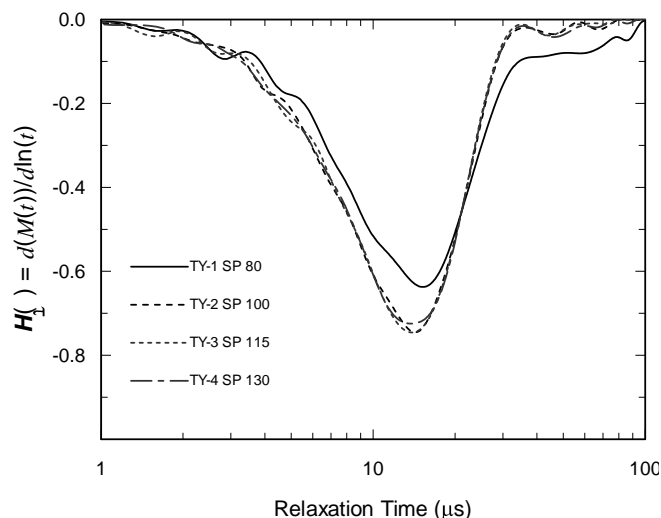
the macroscopic magnetization $M(t)$ was created. The relaxation spectra have much amount of information on molecular mobility of polymers, compared with conventional T_2 relaxation time. The relaxation spectra of pressure sensitive adhesives consisting of SIS and tackifier were obtained using the new analysis method. The increased tackifier content shifted the distribution of the T_2 relaxation time at long timescale (of the soft-segment in SIS) to the shorter timescale. Also, the addition of tackifier extended the distribution of the relaxation with decreasing the peak height. The distribution of the relaxation spectra was influenced by the types of tackifiers. The elucidation of the interaction of a polymer and a tackifier became clear from the relaxation spectra. The analysis using the relaxation spectra is a very powerful tool to lead the molecular design and the formulation of pressure-sensitive-adhesives.

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