Effects of the Compatibility of a Polyacrylic Block Copolymer/Tackifier Blend on the Phase Structure and Tack of a Pressure-Sensitive Adhesive

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ABSTRACT: Adhesion and viscoelastic properties and morphology of a polyacrylic block copolymer/tackifier blend were investigated. Special rosin ester resins with different weight average molecular weights of 650, 710, 890, and 2160 were used as the tackifier and blended with a polyacrylic block copolymer consisting of poly(methyl methacrylate) and poly(n-butyl acrylate) blocks at tackifier content levels of 10, 30, and 50 wt %. The compatibility decreased with an increase in molecular weight. From TEM observation, the number of formed agglomerates of the tackifier with sizes on the order of several tens of nanometers increased with increasing tackifier content and molecular weight of the tackifier in the range from 650 to 890. For the tackifier with a molecular weight of 2160, micrometer-sized agglomerates were observed. The storage modulus at low temperature and the glass transition temperature of adhesive measured by a dynamic mechanical analysis increased dependent on the number of formed nanometer sized agglomerates. Tack was measured using a rolling cylinder tack tester over wide temperature and rolling rate ranges, and master curves were prepared in accordance with the time-temperature superposition law. Tack and peel strength were optimum at a blend combination of intermediate compatibility, i.e., the molecular weight of 890. These optimum properties were correlated to maximal values of the storage modulus at room temperature and the glass transition temperature. Therefore, it was found that these features of blend properties are strongly affected by the nanometer sized agglomerates of tackifier. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2883–2893, 2012

Key words: adhesion; adhesives; block copolymers; blends; morphology

INTRODUCTION

Commonly, pressure-sensitive adhesive tapes contain a tackifier and a base polymer such as natural rubber, synthetic rubber, or a block copolymer. The tackifier develops the mobility of the base polymer during the taping process by acting as a diluent and also improves the peel strength during the peeling process. Many researchers[1–9] as well as ourselves[10–14] have investigated the mechanism of tackiness development through the addition of a tackifier.

In our previous study,[12] the effect of the compatibility of the tackifier on phase structure and adhesion properties was investigated. For this purpose, a polyacrylic block copolymer consisting of poly (methyl methacrylate) (PMMA) and poly(n-butyl acrylate) (PBA) blocks and three types of tackifiers with different chemical structures and compatibilities with the polyacrylic block copolymer were used. From transmission electron microscopic observations (TEM), agglomerates of the tackifier were observed and their size was found to increase from several tens of nanometers to several tens of micrometers depending on the compatibility of tackifier and basepolymer. Improved adhesion properties were obtained in the phase structure when the agglomerates were on the order of several tens of nanometers. A similar result was obtained in polystyrene block copolymer/tackifier blends.[10,11,13] The above results, however, are affected by the influence of the chemical structure of the tackifier on the adhesion properties.

The first aim of this study was to clarify the influence of phase structure on the adhesion properties using tackifiers with similar chemical structures. To achieve this goal, special rosin ester resins with different weight average molecular weights were blended with a polyacrylic block copolymer. The phase structure, namely the size of the tackifier agglomerates, was varied by changing the molecular weight of the tackifier to diminish any influence of the chemical structure of the tackifier.

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	M_n	M_w	M_w/M_n	Softing point/°C	T_g/°C
RE-650	600	650	1.1	70–80	36
RE-710	670	710	1.1	95–105	60
RE-890	750	890	1.2	108–120	70
RE-2160	100	2160	2.2	120–130	84

The second aim of this study was to clarify the factors that contribute to development of adhesion properties. The adhesion strength of pressure-sensitive adhesives increases in response to two factors: the development of interfacial adhesion and the mechanical properties of the adhesive. Tse[15] and Yang[16] explained the properties of pressure-sensitive adhesive (T) as follows:

$$T = W_a \cdot B \cdot D \qquad (1)$$

where W_a is the work of adhesion between the adhesive and the adherend, namely the aforementioned interfacial adhesion. B and D are related to the viscoelastic properties of the adhesive; B depends on the plateau modulus of the adhesive, and D increases with increasing of loss modulus. Creton et al. considered B and D to be "cohesive."[17] They observed the deformation behavior of an adhesive layer during a probe tack test with a very low probe velocity of 1 μm s^{-1} using a high-speed camera and discussed about the contribution of D to tack.[18]

In this study, tack was measured using a rolling cylinder tack tester over wide temperature and rolling rate ranges. The master curves for tack were prepared in accordance with the time-temperature superposition law[19–23] to clarify the deformation rate on tack. Pressure-sensitive adhesives are typical viscoelastic materials. The relationship between the viscoelastic and tensile properties and the adhesion properties, such as the rolling rate at which tack begins to appear and tack value, were therefore evaluated.

EXPERIMENTAL

Materials

A mixture of a PMMA-*block*-PBA-*block*-PMMA triblock copolymer with a weight average molecular weight (M_w) of 75,000 and a PMMA segment content of 23 wt % (MAMTRI, LA2140e, Kuraray, Tokyo, Japan) and a PMMA-*block*-PBA diblock copolymer with a M_w of 71,000 and a PMMA segment content of 6.3 wt % (MADI, LA1114, Kuraray, Tokyo, Japan) (1/1, w/w) was used as the base polymer. The mixture is hereafter denoted as "MAM" and its PMMA content is 15 wt %.

Four types of commercially available tackifiers, special rosin ester resins (Super ester A-75, A-100, A-115, and A-125, Arakawa Chemical Industries, Osaka, Japan) were used as received. Their number (M_n) and weight-average molecular weights (M_w), polydispersities, softening points and glass transition temperatures (T_g) are listed in Table I. These values were shown by the manufacture maker. In this study, the resins are denoted as RE-650, RE-710, RE-890, and RE-2160. The numbers in the abbreviations indicate the weight-average molecular weight. Chemical structures of the compounds used in the tackifiers are shown in Figure 1. The tackifiers are mixtures of these structures, and their molecular weights are dependent on the mixing ratio of the compounds. Reagent grade toluene was used as a solvent.

Compatibility test

The compatibility of each tackifier with MAM was estimated qualitatively using the following simple tests as described in the previous study.[12] First, the phase separation of MAM and the tackifier in toluene solution was examined. Individual solutions of MAM in toluene (40 wt %) and tackifier in toluene (40 wt %) were prepared. These two solutions were then mixed in a test tube and stirred with an agitator for 1 h. After the test tube was allowed to stand for 1 week at 25°C, the mixture in the tube was observed visually. Solutions with tackifier content of 10, 30, and 50 wt % based on total solid content were evaluated.

Next, 40 wt % toluene solutions of MAM/tackifier were cast on a poly(ethylene terephthalate) (PET, thickness: 38 μm) sheet. After evaporating the toluene at room temperature, the transparency of the films was observed visually. For these experiments, tackifier content ranged from 10 to 60 wt %.
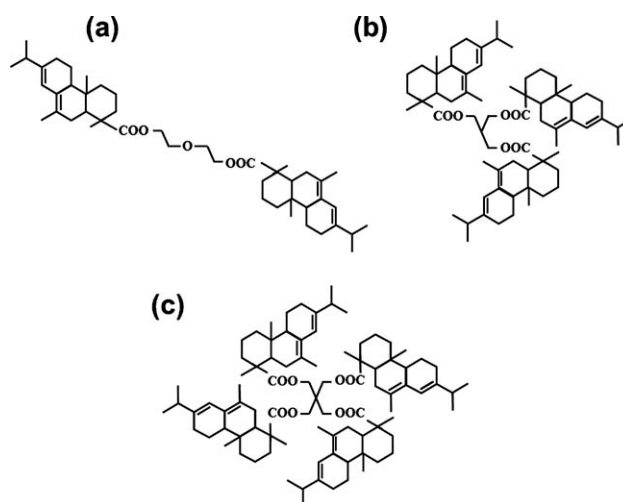
Figure 1 Structure of tackifier used.

Sample preparation

Solutions of 50 wt % MAM/tackifier in toluene were prepared. The tackifier content in the solid ranged from 0 to 60 wt %. The solutions were cast on a polyethylene terephthalate (PET, thickness: 38 μm) sheet. After the toluene evaporated at room temperature, the cast film was heated at 100°C for 10 min *in vacuo*. The resulting thickness of the pressure-sensitive adhesive layer was measured using a thickness indicator (Dial thickness gauge H-MT, Ozaki, Tokyo, Japan) and typically was determined to be about 60 μm. A silicone release agent-coated PET sheet was used for the tack test, whereas an uncoated PET sheet was used for the peel test.

To prepare thick sheet specimens, the toluene solutions were cast on release paper and the toluene was evaporated at room temperature for 1 week. Thick sheet specimens with a thickness of about 2 mm were obtained.

TEM observation

TEM images were obtained with a TEM (H7100FA, Hitachi, Tokyo, Japan) using an acceleration voltage of 100 kV. The pressure-sensitive adhesive was sliced into thin sections of about 80 nm thickness using a low-temperature ultramicrotome (Ultracut S/FCS, Leica Microsystems, Wetzlar, Germany) after freezing in liquid nitrogen. The thin sections were stained with vapors of an aqueous 0.5% RuO_4 solution for 3 min or by dipping in 10–15% phosphorous tungstate aqueous (PTA) solution.[24]

Dynamic mechanical analysis

An about 2 mm thickness sheet (described above) was cut in rectangles (9×40 mm^2) and peeled off. The temperature dependence of its dynamic viscoelastic properties were studied using a dynamic mechanical analyzer (DMS-6000, SII NanoTechnology, Chiba, Japan) in the tensile mode at 10 Hz frequency with a heating rate of 2°C min^{-1} and 8 μm applied strain. The measurements were conducted over the temperature range −80–200°C. The frequency dependence of its dynamic viscoelastic properties were measured at constant temperature and variable frequency. The measured temperature and frequency were in the range from −80 to 80°C and from 0.1 to 100 Hz, respectively. The obtained results were shifted and superposed, and the master curve was made in accordance with the time-temperature superposition law.[19–23] The reference temperature was 25°C.

Tensile test

The sample films cast on a PET sheet coated with a silicone release agent were cut in squares (50×50 mm^2) and peeled off. The films with a thickness of about 60 μm were rolled and the cylindrical shaped specimens were prepared. Stress–strain curves were recorded using a tensile testing machine (AG-5KNIS, Shimadzu, Kyoto, Japan) with a chuck distance of 10 mm and a tensile rate of 300 mm min^{-1}.

Peel strength

The PET sheet with the cast pressure-sensitive adhesive film prepared in the sample preparation section was cut into strips of 25 mm width, and the strips placed onto a stainless steel plate (SUS304BA, Nippon Tact, Tokyo, Japan) that was used as the adherend. The strip on the stainless steel plate was pressed using a 2 kg iron-roller with a rubber sheet on the surface to develop good contact between the adhesive and the steel plate. Test specimens were subjected to five press cycles, with a press cycled defined as the movement of the iron-roller backward and forward once. For further development of interfacial adhesion, the test specimens were heated at 100°C for 2 h. The time between specimen preparation and the peel adhesion test was about 20 min.

The 180° peel adhesion test was carried out at a peel rate of 300 mm min^{-1} at room temperature using a tensile testing machine in accordance with JIS Z 0237 (Japanese Industrial Standards) as previously described.[10–14]

Rolling cylinder tack test

Tack was measured using a rolling cylinder tack tester (TSC-2000, Mitsuwa Scientific, Osaka, Japan) as reported previously.[13] The schematic view of the apparatus is shown in Figure 2. The 30-mm width pressure-sensitive adhesive layer on the PET sheet coated with a silicone release agent was taped on a bakelite plate, and the adhesive layer transferred onto the plate. The coated plate was then inserted into the adhesive holder. The stainless steel SUS304 cylinder of 20 mm in width and 10 mm in diameter was brought into contact with the adhesive and the adhesive holder moved at a constant rate. The
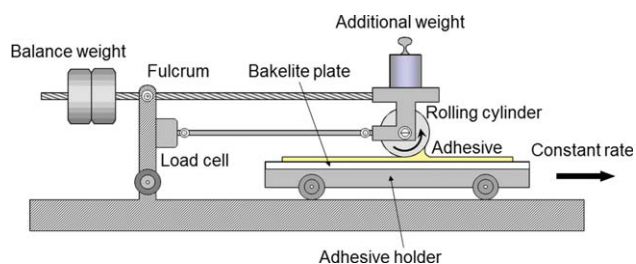
Figure 2 Rolling cylinder tack tester. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
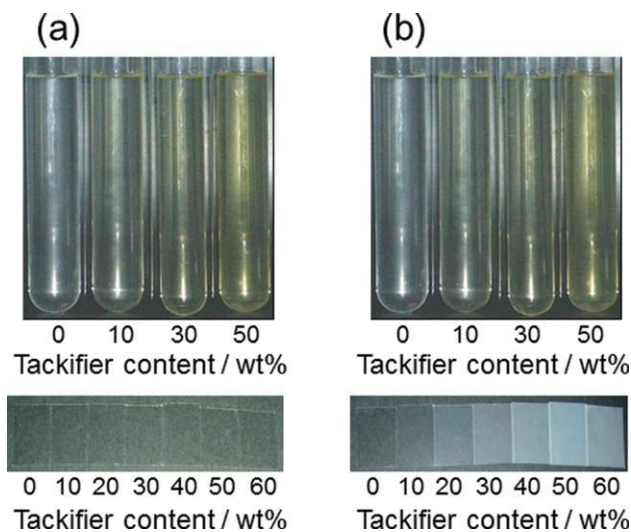
Figure 3 Mixtures of MAM/tackifier/toluene solutions (top) with tackifier contents of 0–50 wt % and transparency of prepared films from the mixtures (bottom) with tackifier contents of 0–60 wt % for tackifiers RE-710 (a) and RE-2160 (b). The test tubes were allowed to stand for 1 week after mixing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

additional weight was 100 g. The load generated by the rolling of the cylinder was measured as tack value. The rate and temperature values ranged from 0.03 to 300 mm s^{-1} and from 25 to 80°C, respectively. Master curves were prepared in accordance with the time–temperature superposition law.[19–23]

RESULTS AND DISCUSSION

The compatibility of a base polymer and tackifiers were confirmed by the simple compatibility test both in the toluene solution and the cast film states in the same way as the previous study.[12] The results of the compatibility tests can be seen in Figure 3. The top photographs show the toluene solutions of the mixtures of MAM and tackifier in the test tubes for RE-710 (a) and RE-2160 (b), respectively. The test tubes were allowed to stand for 1 week after mixing was discontinued. No interface was observed in any of the test tubes and the mixtures were transparent. The same results were obtained for the MAM/RE-650 and MAM/RE-890 mixtures. These results indicate that MAM and the tackifiers have good compatibility in the solution state independent of the molecular weight of both the tackifier and the tackifier content.

The bottom photographs in Figure 3 show the transparency of the prepared films. The films were transparent for the MAM/RE-710 blend at all tackifier content levels (0–60 wt %, a). The same results were obtained for the MAM/RE-650 and MAM/RE-890 blends. The films were turbid for the MAM/RE-2160 blend (b), however, and the turbidity became more

significant with increasing tackifier content. This result indicates that the MAM/RE-2160 blend is incompatible in the solid state, even though it is compatible in the presence of toluene. The other three tackifiers, on the other hand, exhibited good compatibility with MAM for the conditions of the compatibility tests employed in this study.

Detailed compatibility was confirmed via TEM observation. TEM images of MAM (a) and MAMTRI (b) stained with PTA solution are shown in Figure 4. The PTA solution stains the PMMA portions in the MAM and not the PBA.[24] Therefore, the sea-island structure with spherical PMMA domains possessing a mean size of about 20 nm dispersed in the PBA continuous phase was observed for MAM (a). The similar morphology was also observed in MAMTRI (b). However, the portion with which PMMA domains were connected increased slightly as compared with MAM (a). The clear morphology was never observed for MADI. The PMMA contents of MAMTRI, MAM, and MADI were 21, 14, and 6 vol %, respectively. Matsen and Bates[25] demonstrated that there is the relation between the morphology of polystyrene block copolymer and the PS content. According to the phase diagram obtained by them, MAMTRI and MAM should form a cylindrical structure and a sea-island structure, respectively. And MADI should form a compatible system. The tendency of the relation between the morphology and PMMA content was in good accord with their phase diagram, although the kind of polymer differed.

TEM images of MAM/RE-710 (a–c), MAM/RE-890 (d–f), and MAM/RE-2160 (g–i) blends stained with RuO$_4$ and prepared at tackifier content levels of 10 (a, d, g), 30 (b, e, h), and 50 wt % (c, f, i) are shown in Figure 5. It is difficult to observe in the TEM image that the PMMA and PBA phases show different darkness levels due to the RuO$_4$ staining. RuO$_4$ stains the tackifier preferentially, therefore the white and the gray parts are the PMMA domains and the PBA continuous phase with dissolved tackifier, respectively. From the images it can be seen that the tackifier preferentially exists in the PBA
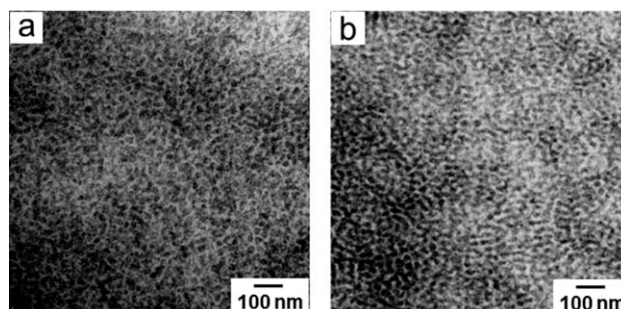
Figure 4 TEM images of thin sections of MAM (a) and MAMTRI (b). TEM samples were stained with PTA.
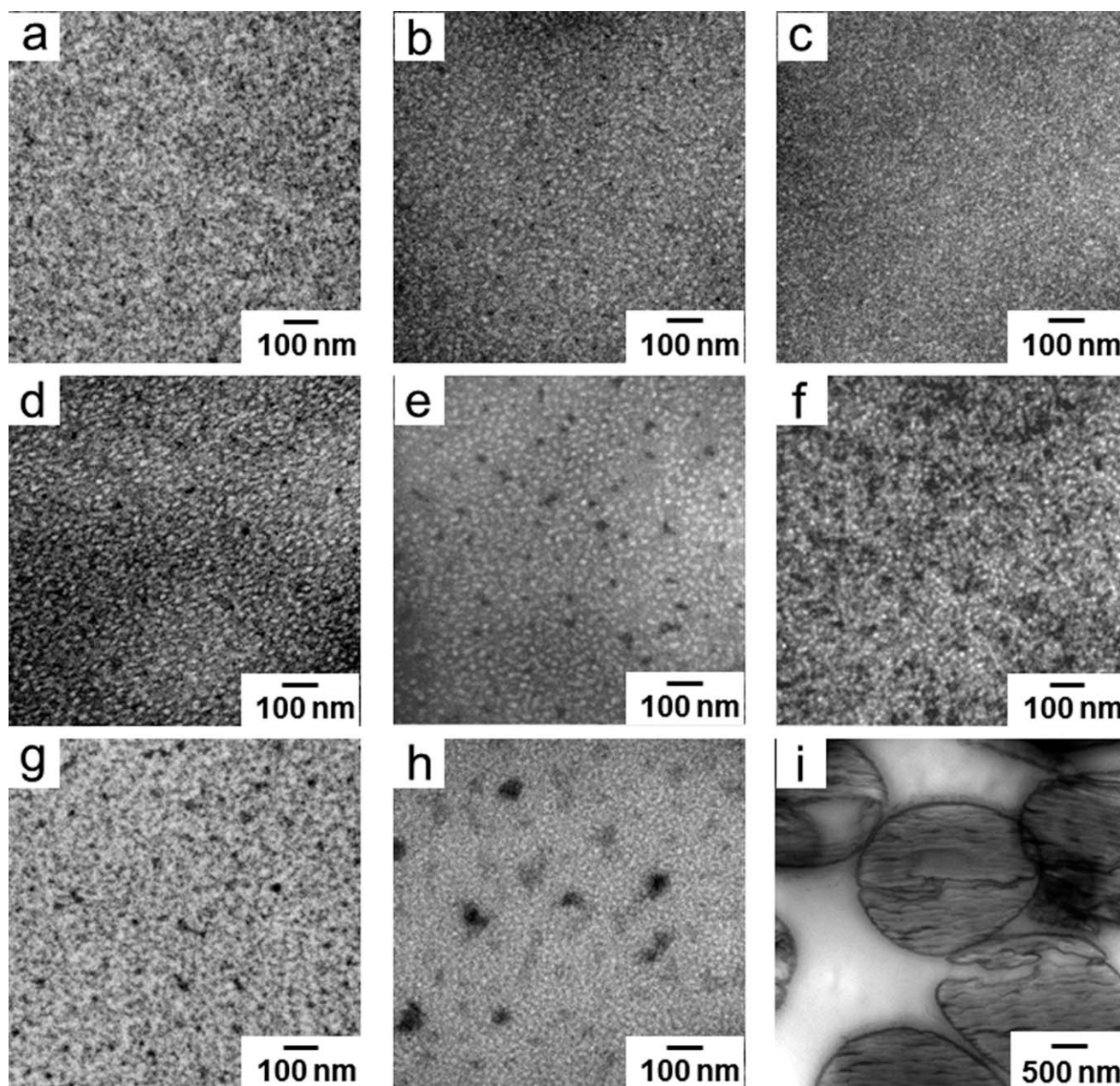
Figure 5 TEM images of thin sections of MAM with tackifier RE-710 (a–c), RE-890 (d–f), and RE-2160 (g–i). Tackifier contents are 10 (a, d, g), 30 (b, e, h), and 50 wt % (c, f, i). TEM samples were stained with RuO$_4$.

continuous phase rather than in the PMMA domains. In the MAM/RE-890 blend (d–f), black spots on the order of several tens of nanometers in size were observed. These spots represent agglomerates of tackifier. The size and number of the agglomerates increased with an increase in tackifier content. Secondary agglomeration was observed at 50 wt % (f). In the MAM/RE-710 blend (a–c), the number and size of the agglomerates was much less than that in the MAM/RE-890 blend (d–f). A similar observation was obtained in the MAM/RE-650 blend (no photo in this article). On the other hand, the agglomerate size increased in the MAM/RE-2160 blend (g–i) and reached several micrometers at 50 wt % (i). In general, the number and size of the agglomerates increased with increasing molecular weight and tackifier content. It was therefore confirmed that the compatibility of MAM and the tackifier decreased in conjunction with an increase in molecular weight of the tackifier.

The temperature dependence of the storage modulus (E') (a) and loss tangent (tan δ) (b) for MAM (●) and the MAM/RE-890 blends with tackifier content levels of 10 (○), 30 (Δ) and 50 wt % (□) are shown in Figure 6. Notably, E' decreased drastically at about −45°C for MAM; this temperature is the T_g of
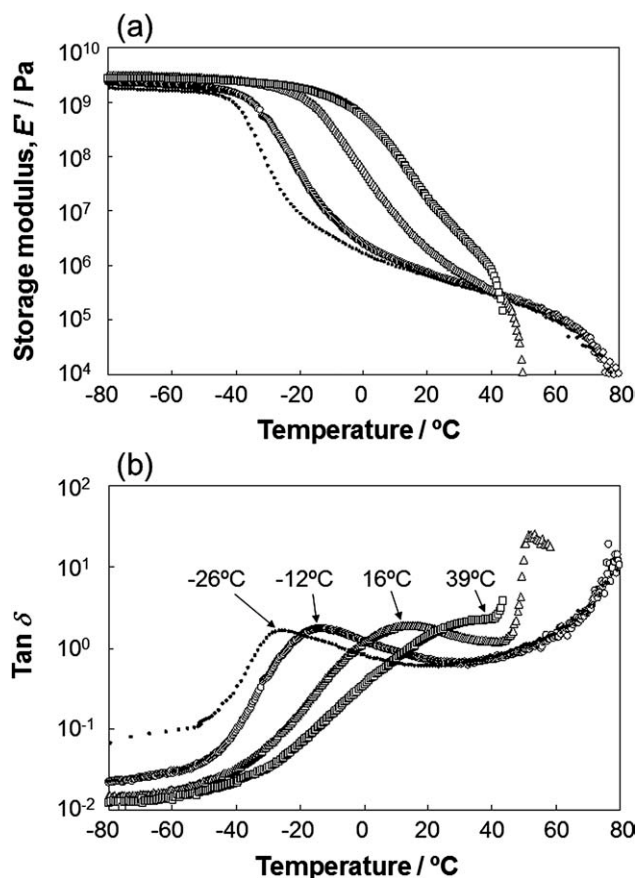
Figure 6 Temperature dependencies of storage modulus (E') (a) and loss tangent (tan δ) (b) for MAM/tackifier RE-890 system with tackifier contents of 0 (●), 10 (○), 30 (Δ), and 50 wt % (□) measured by a dynamic mechanical analysis at 10 Hz.

the PBA matrix. The addition of the tackifier, however, resulted in an increase in the T_g, and the increase was greatest at the highest tackifier content level. For all of the tackifier content levels, E' was higher than that of MAM at temperatures below about 50°C, at which point they decreased drastically for the films with a tackifier content of 30 and 50 wt %. The tackifier hardens the PBA (increases both the E' and T_g) below T_g of PBA but softens it above T_g of PBA.

Looking at the plots of tan δ (b), the sharp peaks corresponding to the T_g of PBA are clearly observed. The values for the T_g increased with an increase of the RE-890 content in the same as those observed in the temperature dependence of E' (a).

The E' values at 25°C (a) and the peak temperatures of the tan δ (b) for all of the MAM/tackifier blends shown in Figure 6 are plotted in Figure 7. The values of E' at 25°C (a) are lower than that for MAM for the RE-650 blend of 10 and 30 wt %, the RE-710 blend of 10 wt % and the RE-2160 blend of 10 wt %. This fact shows that the tackifier dissolved in the base polymer reduced the E' by acting as a

plasticizer. Because there were very few amount of agglomerates in these adhesives from Figure 5. For all of the films, the E' value increased with increasing molecular weight and content, although the effect for RE-2160 was lower than that for RE-890.

The peak temperature of tan δ also rose with the addition of tackifier and increased with increasing molecular weight. The largest effect was observed for the RE-890 blend, while the least effect was noted for RE-2160. It seems that the increase of E' and T_g at low temperature is related to the amount of formed several tens nm-sized agglomerates of tackifier as observed in Figure 5.

To confirm this point, the measured peak temperature of tan δ values were compared with the T_gs calculated by the rule of mixture (Fox equation[26]) using the T_g values of tackifier. The closed symbols show the calculated T_g values for MAM with tackifier RE-650 (●), RE-710 (▲), RE-890 (■), and RE-2160 (◆). All
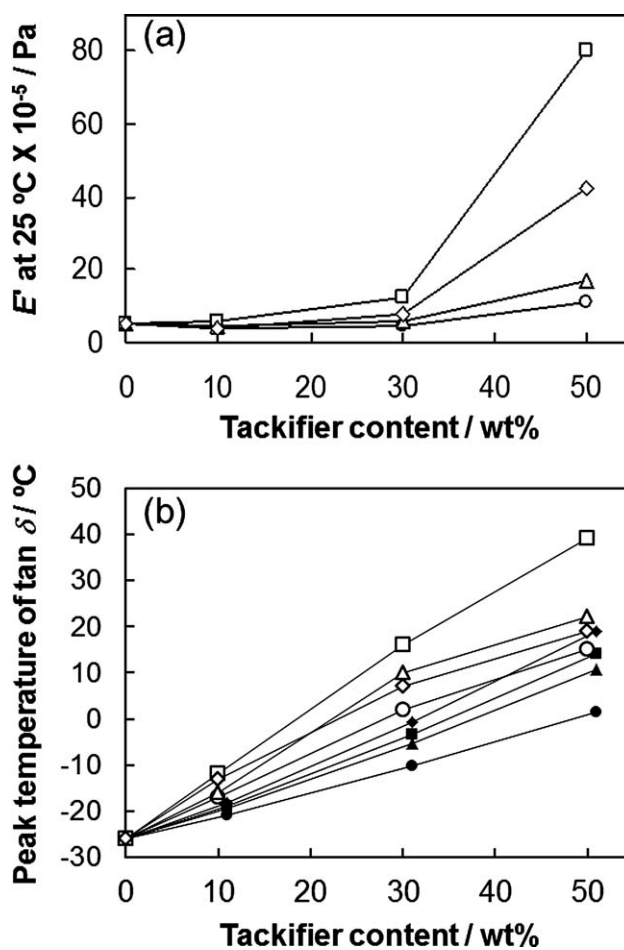
Figure 7 Storage modulus (E') at 25°C (a) and peak temperature of tan δ (b) for MAM with tackifier RE-650 (○), RE-710 (Δ), RE-890 (□), and RE-2160 (◇) measured by a dynamic mechanical analysis at 10 Hz. The closed symbols show the T_g values calculated in accordance with the rule of mixture (Fox equation) using the T_g values of tackifier for MAM with tackifier RE-650 (●), RE-710 (▲), RE-890 (■), and RE-2160 (◆).
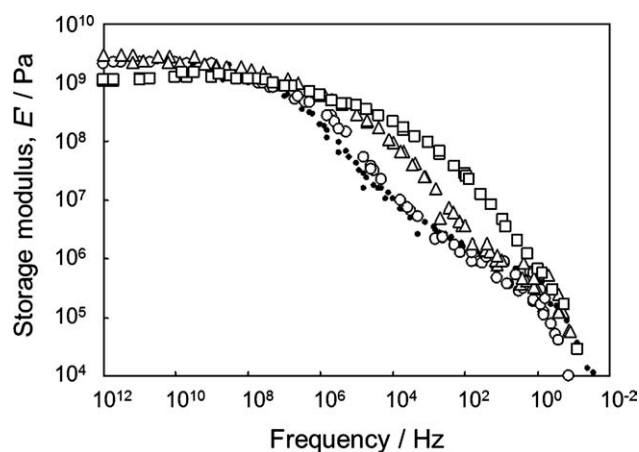
Figure 8 Frequency dependencies of storage modulus (E') for MAM/tackifier RE-890 system with tackifier contents of 0 (●), 10 (○), 30 (△), and 50 wt % (□) measured by a dynamic mechanical analysis. Reference temperature is 25°C.

actual measured values were higher than the calculated values. Moreover, the calculated value was large in order of MAM with RE-2160 > RE-890 > RE-710 > RE-650, and differed from the order of the actual

measured value. These results are supporting the aforementioned view that the increase of E' and T_g at low temperature is dependent on the morphology instead of composition.

In our previous study,[12] the micronmeter-sized silica particle-filled MAM was investigated. As a result, although the silica particles increased E', they did not raise T_g. The agglomerates of tackifier act as filler, and increase E'. Furthermore, when the agglomerates are nano-size with large interfacial area like nano-composite and have a large interaction between agglomerates and matrix polymer, the T_g thought to be rose.

The frequency dependence of E' for MAM (●) and MAM/RE-890 blends with tackifier content levels of 10 (○), 30 (△), and 50 wt % (□) can be seen in Figure 8. Not surprisingly, the frequency dependence of E' is similar to the temperature dependence of E' (Fig. 6). For viscoelastic polymers, a high frequency is observed at low temperature, while a low frequency is observed at high temperature.

Stress–strain curves for the MAM/tackifier blends are displayed in Figure 9. Several changes were noted with an increase in tackifier content. In the
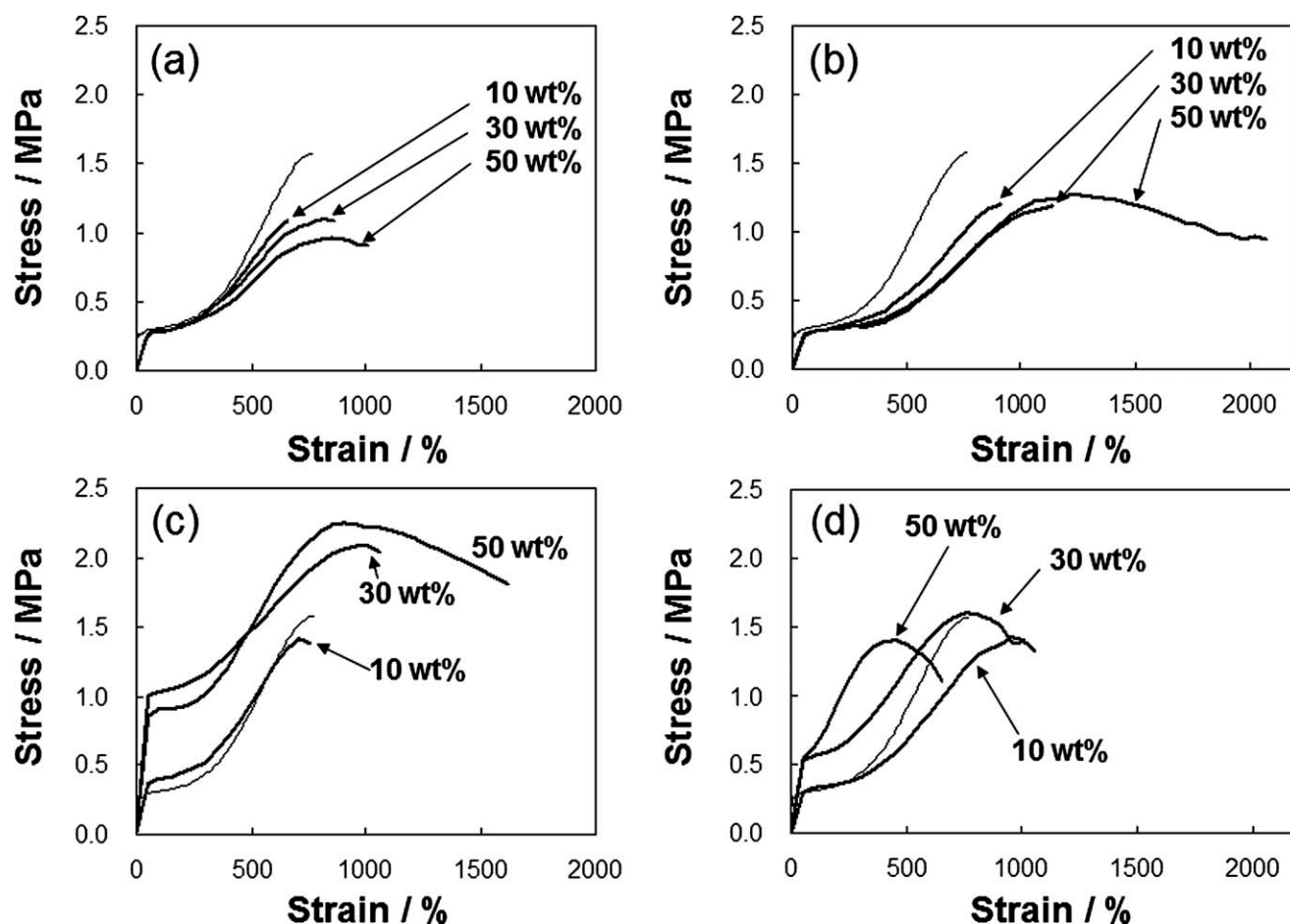
Figure 9 Stress–strain curves of MAM with tackifier RE-650 (a), RE-710 (b), RE-890 (c), and RE-2160 (d) measured by a tensile test with displacement rate of 300 mm min^{-1}.
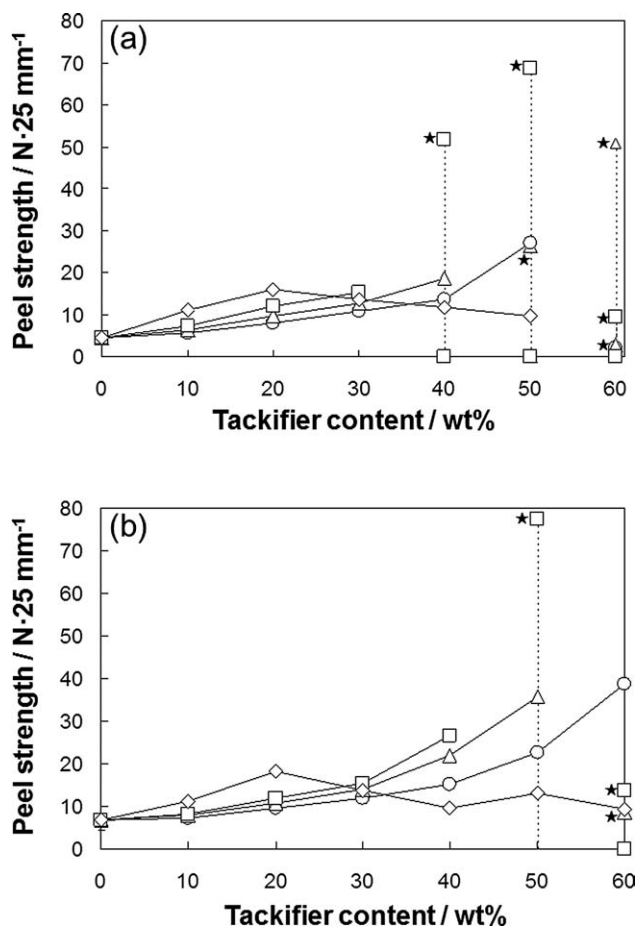
Figure 10 The 180° peel strength of MAM with tackifier RE-650 (○), RE-710 (Δ), RE-890 (□), and RE-2160 (◇). The test specimen was five times pressed with 2-kg iron-roller (a) and heated (100°C, 2 h) after five times pressing before peel test (b). Fracture modes are stick-slip failure (★) and interfacial failure (no mark). Tape width is 25 mm. Peel rate is 300 mm min⁻¹.

MAM/RE-650 blend (a), only the stress decreased. In the MAM/RE-710 blend (b), the stress also decreased while the strain increased. This film with the tackifier content of 50 wt % showed the maximum strain. In the MAM/RE-890 blend (c), both the stress and strain increased for tackifier content levels of 30 and 50 wt %. In the MAM/RE-2160 blend (d), the strain at maximum stress decreased. It seems that the maximum stress is related to the amount of formed several tens nm-sized agglomerates of tackifier.

The 180° peel strength of the MAM/tackifier blends for RE-650 (○), RE-710 (Δ), RE-890 (□), and RE-2160 (◇) can be seen in Figure 10. Failure modes are indicated as interfacial failure (no mark) and stick-slip failure (★). For specimens that were pressed five times using the 2-kg iron-roller (a), the peel strength increased gradually with an increase in tackifier content for RE-650 (○), RE-710 (Δ), and RE-890 (□). Peel strength also became slightly higher

with an increase in the molecular weight of the tackifier at content levels below 30 wt %. For the RE-2160, peel strength increased with an increase of tackifier content, but decreased for content levels above 30 wt %. Interestingly, the failure mode changed from interfacial failure to stick-slip failure at higher tackifier content, and the tackifier content level at which the shift in failure mode occurred decreased to a lower level with an increase in the molecular weight. These results seem to be caused by the phase separation of the tackifier. A tackifier dissolved in the base polymer develops interfacial wettability by acting as a plasticizer. As the amount of tackifier separated from the polymer increases, there is less tackifier in the base polymer to provide that interfacial wettability.

For the samples that were heated after being pressed five times (b), the behavior was nearly the same as those that were not heated (a), but the overall peel strength was elevated and the tackifier content at which the failure mode changed from interfacial failure to stick-slip failure was shifted to a higher content level. These results were due to the development of interfacial adhesion through heating of the samples. The influence of the molecular weight of the tackifier on the tackiness could not be determined by the peel strength, however, because sufficient interfacial adhesion was developed with pressing alone.

Tack was therefore next evaluated. Pressure-sensitive tack is described as the property of an adhesive that enables it to form a bond of measurable strength upon brief contact with another surface under light pressure.[27] In this study, the rolling rate dependency of tack results measured at various temperatures were shifted and superposed, and the master curves were prepared in accordance with the time–temperature superposition law.[19–23] The reference temperature was 25°C.

The rolling rate dependency of the master curves for tack values measured for MAM blended with RE-650 (a), RE-710 (b), RE-890 (c), and RE-2160 (d) are shown in Figure 11. In these graphs, the failure modes are indicated as interfacial failure, (◇, ○, Δ, □) and cohesive failure (■). In the MAM/RE-650 blend (a), the tack of MAM (◇) increased with an increase in the rolling rate. Addition of a tackifier led to an increase in the tack as well as a shift to a lower rolling rate at which tack began to appear, with these changes becoming more marked at higher tackifier content. In addition, tack increased with cohesive failure and reached a maximum value at a tackifier content of 50 wt %. After that, tack remained constant with interfacial failure and disappeared at higher rolling rates because the viscoelastic properties of the adhesive changed from viscous to rubbery to glassy with an increase in the
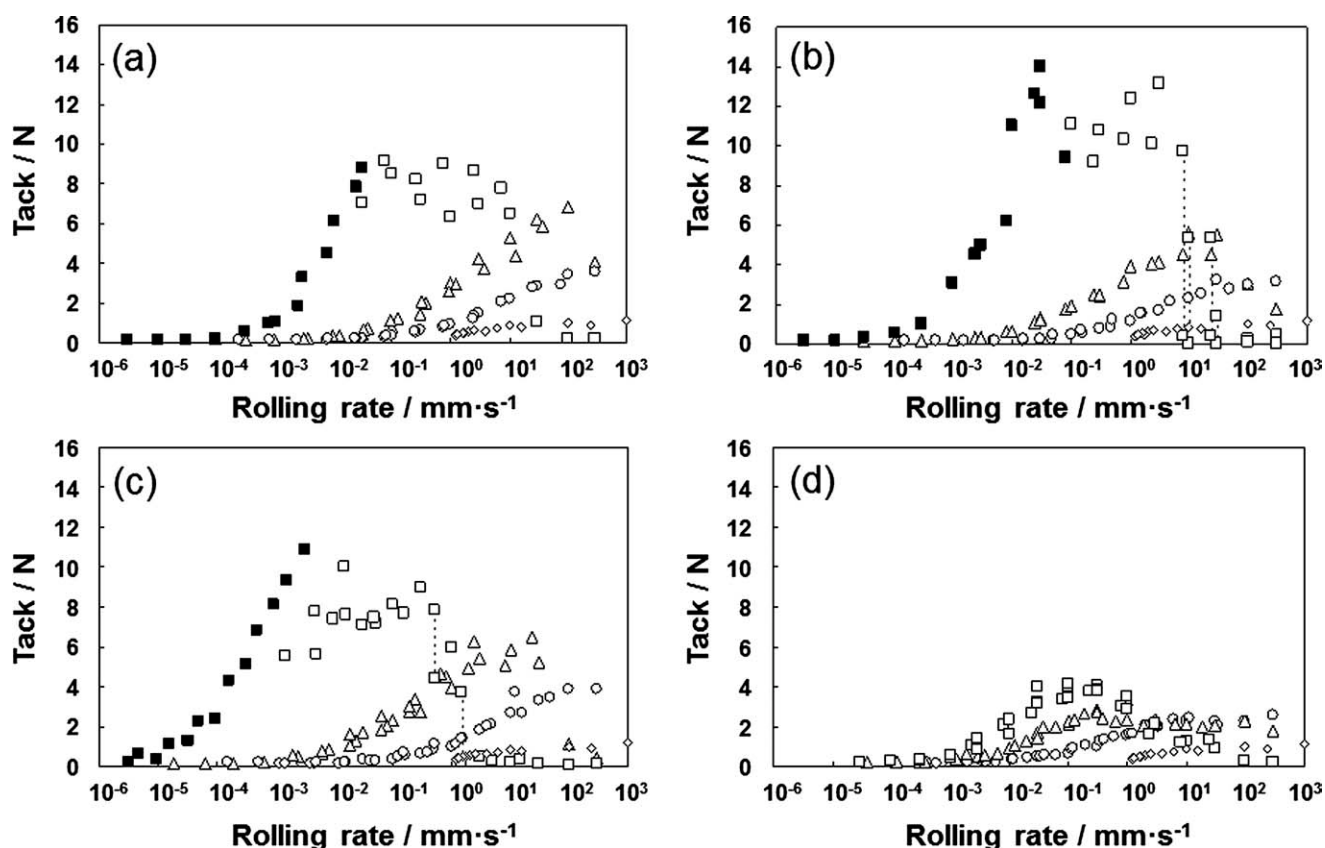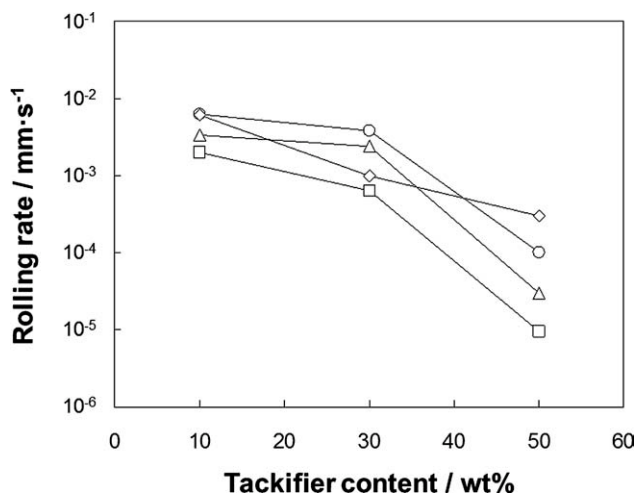
Figure 11 Tack versus rolling rate for MAM with tackifier RE-650 (a), RE-710 (b), RE-890 (c), and RE-2160 (d) with tackifier contents of 0 ($\diamond$), 10 ($\bigcirc$), 30 ($\triangle$), and 50 wt % ($\square$) measured by a rolling cylinder tack tester. Failure modes are interfacial failure ($\diamond$, $\bigcirc$, $\triangle$, $\square$) and cohesive failure ($\blacksquare$). The master curves were made in accordance with the time-temperature superposition law. Reference temperature is 25°C. Cylinder width is 20 mm.

rolling rate. In the MAM/RE-710 (b) and the MAM/RE-890 (c) blends, this behavior was more marked and the rolling rate at which tack began to appear shifted to lower rates with an increase in molecular weight of the tackifier. Furthermore, the rolling rate at which tack disappeared at the tackifier content of 50 wt % also shifted to lower rates with increasing molecular weight of the tackifier. The MAM/RE-2160 blend (d), however, exhibited lower tack, and the rolling rate at which the tack began to appear shifted to a higher rate. The highest tack at a tackifier content level of 50 wt % was observed for the MAM/RE-710 blend (b). That is, the lowest rolling rate at which tack began to appear and the maximum tack were observed in the different tackifier systems.

The effect of tackifier content on the rolling rate at which tack begins to appear is shown in Figure 12. The rolling rate shifted to a lower rate with an increase in the tackifier content and molecular weight of the tackifier for RE-650 ($\bigcirc$), RE-710 ($\triangle$), and RE-890 ($\square$). The effect was, however, reduced for RE-2160 ($\diamond$). The observed behavior was similar to those for E' at 25°C and T_g shown in Figure 7.

The compatibility of the tackifier and the base polymer seems to affect the E', the T_g and the rolling rate at which tack begins to appear as follows. The dissolved tackifier molecules in the base polymer act

Figure 12 Rolling rate that tack began to be measured versus tackifier content for MAM with tackifier RE-650 ($\bigcirc$), RE-710 ($\triangle$), RE-890 ($\square$), and RE-2160 ($\diamond$).
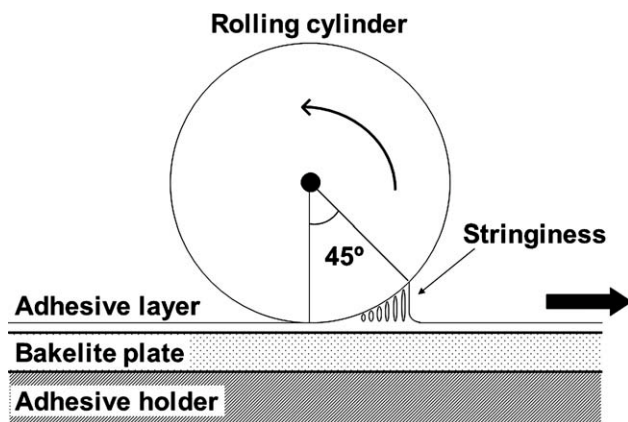
Figure 13 Schematic view of the stringiness occurred during rolling cylinder tack test.

as a plasticizer and develop molecular mobility, namely interfacial adhesion, and thus the value of E' decreases. The agglomerates of the tackifier, however, act as a filler and thus increase the value of E'. The number of agglomerates on the order of several tens of nanometers in size increased with an increase in the molecular weight of the RE-650, RE-710, and RE-890 tackifiers. As the agglomerates increased, the amount of dissolved tackifier in the base polymer decreased accordingly. The compatibility was lowest in the RE-2160 blend, with the agglomerates reaching micrometer size at 50 wt % tackifier. Because of the smaller total surface area of these agglomerates, their effect on E' and T_g decreased.

As mentioned above, the highest tack at a tackifier content of 50 wt % was observed in the MAM/RE-710 blend (b) in Figure 9. In the rolling cylinder tack test, stringiness of the adhesive was expected to occur as shown in Figure 13, but this behavior could not be observed directly with the apparatus used in this study. The diameter of the cylinder is ten mm and the thickness of the adhesive layer is about 60 μm (Fig. 2). If the stringiness occurs in the center angle range of 45° as shown in Figure 13, an elongation of 2400% at the front edge of the stringiness would be required. The greatest elongation was observed for the RE-710 blend at a tackifier content of 50 wt % as shown in Figure 9(b). Therefore, this system showed the highest tack, as can be seen in Figure 11(b). The second greatest elongation was observed for the RE-890 blend at a tackifier content of 50 wt %, but this system showed a higher initial elastic modulus [Fig. 9(c)], which seems to lower the interfacial adhesion. If interfacial adhesion is sufficient, a higher elongation of the adhesive would be expected to aid in development of the tack value. It was found that the stress-strain curves of adhesives are an important tool for estimating tack. This fact shows the loss modulus (D) affects on tack as explained by Tse[15] and Yang[16] in eq. (1). The contri-

bution of loss modulus to the adhesion properties will be discussed in our next study by observing the deformation behavior of adhesive at tack test.

CONCLUSIONS

The effects of the compatibility of MAM/tackifier blends on the phase structure of the tackifier and the adhesion properties of the blends were investigated. Special rosin ester resins with different weight-average molecular weights of 650, 710, 890, and 2160 were used as the tackifiers. Tack was measured with a rolling cylinder tack tester over wide temperature and rolling rate ranges, and master curves were prepared in accordance with the time-temperature superposition law. The following results were obtained.

1. The compatibility of MAM/tackifier blends decreased with an increase in the molecular weight of the tackifier. Further, the number of formed agglomerates of the tackifier with sizes on the order of several tens of nanometers increased with increasing tackifier content and molecular weight of the tackifier in the range from 650 to 890. For the tackifier with a molecular weight of 2160, micrometer-sized agglomerates were observed at a tackifier content of 50 wt %.
2. The T_g and the E' at low temperature increased by with the addition of a tackifier, and these effects became more remarkable pronounced with an increase in the molecular weight of the tackifier and the tackifier content in the molecular weight range from 650 to 890. These effects, however, were lower in the case of the tackifier with a molecular weight of 2160.
3. The rolling rate at which the tack begins to appear shifted to a lower rate with an increase in the molecular weight of the tackifier and was lowest for the tackifier with a molecular weight of 890. Again, this effect was lower in the case of the tackifier with a molecular weight of 2160.
4. It was estimated that the dissolved tackifier molecules in the base polymer develop molecular mobility, namely interfacial adhesion, and the agglomerates of the tackifier with a size on the order of several tens of nanometers increase the E' and T_g. In the case of the tackifier with a molecular weight of 2160, the increase in the values of E' and T_g is less because of the larger size, and thus the smaller total surface area of the agglomerates.
5. The greater elongation of an adhesive improves the maximum value of its tack.

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