# The Properties of Reactive Hot Melt Polyurethane Adhesives Modified with Novel Thermoplastic Polyurethanes

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**ABSTRACT:** A reactive hot melt adhesive (RHMA) consisting of thermoplastic polyurethane (TPU) was modified with sodium montmorillonite (Na-MMT) intercalated with poly(ethylene glycol) (PEG), and their effects on the adhesion, rheological, and mechanical properties of the RHMA were examined. The Na-MMT intercalated with PEG (Na-MMT/PEG) effectively enhanced the initial bond strength development of the RHMA, although the amounts of Na-MMT/PEG in the RHMA were less than 0.2%. The increase of the complex viscosity and pseudo-solid like behavior observed at low shear rate indicates that there are intimate interactions between the RHMA molecules and Na-MMT/PEG. The improved modulus and tensile strength of the cured RHMA film in the presence of Na-MMT/PEG demonstrates that Na-MMT/PEG effectively reinforced the RHMA. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1169–1175, 2009

**Key words:** adhesives; viscoelastic properties; polyurethanes; sodium montmorillonite; poly(ethylene glycol)

## INTRODUCTION

Reactive hot melt adhesives (RHMAs), which are solvent free, one-part solids at room temperature, have superior properties compared with conventional hot melt adhesives in terms of heat stability and solvent resistance. The majority of RHMAs are moisture curing polyurethane (PU) adhesives whose main component is an isocyanate-terminated PU prepolymer that can be cured after application by reaction with ambient moisture. RHMAs are generally applied in a molten form, solidified by cooling, and subsequently, are cured by chemical cross-linking with the initial bond strength developing during solidification upon cooling from the molten state. The subsequent curing reaction improves the final bond strength and endows the adhesive with its final characteristics.[1–8]

Because PU prepolymers were designed to have a low melt viscosity for facile handling and applica-tion, they generally have a molecular weight of only a few thousand daltons. Therefore, they exhibit poor initial bond strength immediately following application after cooling, compared to conventional non-RHMAs. To overcome this drawback, polymers with a high glass transition temperature or with high crystallinity, either of which can accelerate solidification after application upon cooling, were generally incorporated in moisture-cure reactive hot melt PU adhesives. High molecular weight thermoplastics such as polyacrylate,[9–11] PU,[12] styrenic copolymer,[13,14] and polyester[15,16] are typical examples of polymers used.

Nanocomposites, which consist of silicate layers that are ~ 1-nm thick and finely dispersed in a polymer matrix, have attracted increasing interest from both science and industry because they exhibit significantly enhanced mechanical strength, heat resistance, UV resistance, and reduced gas permeability compared to conventional composites.[17–22] These beneficial effects are produced by greatly increased interfacial contact and interactions between the matrix polymer and layered silicates which have a high aspect ratio.

The segmental motions of polymer chains are restricted in such nanocomposites due to the confinement of polymer chains between the silicate layers, and silicate surface-polymer interactions. Thus, we anticipated that finely dispersed silicate layers would accelerate the solidification of an RHMA

during cooling to produce early and enhanced development of the initial bond strength. Also, we found in our previous studies that organoclay or sodium montmorillonite (Na-MMT) intercalated with poly(ethylene glycol) (PEG) improved the initial bond strength of RHMAs.[23,24]

Na-MMT intercalated with PEG has a high stability and thus, the intercalated PEG cannot easily be replaced by other segments or organic compounds that have a high affinity for Na-MMT such as dimethyl sulfoxide.[25,26] Further, the intercalated PEG has terminal hydroxyl groups to react with isocyanate. Therefore, Na-MMT intercalated with PEG (Na-MMT/PEG) can be considered as an inorganic–organic hybrid compound with a stable intercalated structure and reactive hydroxyl groups.

In this study, we synthesized thermoplastic polyurethanes (TPUs) that incorporated Na-MMT/PEG as a new and novel modifier. This modifier was utilized to enhance the initial bond strength of RHMA due to the anticipated synergistic effects of TPU and Na-MMT/PEG for accelerating initial solidification to induce early development of the initial bond strength. The mechanical, rheological, and adhesion properties of the modified RHMAs are reported in this article.

## EXPERIMENTAL

### Materials

Two kinds of poly(tetramethylene glycol) (PTMG), PTMG-1000 (molecular weight of 1,000 g/mol), and PTMG-2000 (molecular weight of 2,000 g/mol), were obtained from BASF Korea. Poly(butylene adipate) diol (PBA, molecular weight of 2,000 g/mol) was obtained from Union Chemical. The crystalline polyester diols Dynacoll 7360 (molecular weight of 3,500 g/mol, melting point of 55°C) and Dynacoll 7381 (molecular weight of 3,500 g/mol, melting point of 55°C) were obtained from Degussa. Liquid methylene diphenyl diisocyanate (MDI) containing 50% *para, para′*-MDI and 50% *ortho, para′*-MDI were obtained from BASF Korea. The catalyst 2,2′-dimorpholino diethyl ether (DMDEE, Huntsman) was used as received. Na-MMT was purchased from Southern Clay Products and was dried at 60°C in a vacuum for 2 days before use. PEGs with molecular weights of 400 g/mol (PEG-400), 1,000 g/mol (PEG-1000), and 2,000 g/mol (PEG-2000) were purchased from Wako Pure Chemical Industries Ltd. (Japan). Acetonitrile (Aldrich) and methanol (Aldrich) were used as received.

### Preparation of TPU and RHMA

Na-MMT/PEG was prepared using a 1 : 1 (by volume) acetonitrile/methanol solvent system.[25,26]

### TABLE I
### Properties of TPUs

| Sample | Molecular weight | | Melt viscosity (Pa × s) | | DSC |
|---|---|---|---|---|---|
| | $M_n$ | $M_w$ | 45°C | 55°C | $T_m$(°C) |
| TPU-0 | 25,450 | 51,339 | 123,100 | 78,700 | 44.3 |
| TPU-MP4 | 18,100 | 39,492 | 427,800 | 27,800 | 44.8 |
| TPU-MP10 | 16,356 | 35,577 | 258,500 | 25,270 | 44.9 |
| TPU-MP20 | 16,603 | 35,163 | 135,000 | 19,490 | 44.5 |

Briefly, 3 g of PEG was dissolved in 100 mL of the solvent mixture, which was stirred with 7 g of Na-MMT for 1 day at room temperature. The intercalated compound was separated with a centrifuge and repeatedly washed successively with acetonitrile and methanol to remove any nonintercalated physisorbed PEG. The newly prepared compound was dried at 25°C for 2 days in a vacuum before use.

A 1 L round-bottomed, four-necked flask equipped with a mechanical stirrer, a thermometer, a nitrogen gas inlet, and a condenser with a drying tube which was used as the reaction vessel for the preparation of TPU. The reaction temperature was controlled with an oil bath. The reference TPU which contained no Na-MMT (TPU-0) was prepared as follows. PBA (89.59 g, 44.80 mmol) was added into the reactor, melted, and maintained at 90°C. Subsequently, liquid MDI (10.41 g, 41.64 mmol) at 60°C was fed into the reactor and reacted with PBA for 3–6 minutes at 90°C to obtain a TPU. TPUs synthesized with an additional four parts (4.00 g) of Na-MMT/PEG per 100 parts of TPU were prepared using the same procedure as described above, except that Na-MMT/PEG was fed into the reactor together with PBA. The sample designation codes shown in Table I provide information about the molecular weights of the intercalated PEG. Here, TPU-MP4, TPU-MP10, and TPU-MP20 are the TPUs modified with 4 phr of Na-MMT intercalated with PEG-400 (Na-MMT/PEG-400), Na-MMT intercalated with PEG-1000 (Na-MMT/PEG-1000), and Na-MMT intercalated with PEG-2000 (Na-MMT/PEG-2000), respectively.

A 1 L round-bottomed, four-necked flask equipped with a mechanical stirrer, a thermometer, a nitrogen gas inlet, and a condenser with a drying tube was used as the reaction vessel for the preparation of RHMA. The reaction temperature was controlled with an oil bath. The RHMA-0 listed in Table II was prepared as follows. PTMG-2000 (33.36 g, 16.68 mmol), PTMG-1000 (22.24 g, 22.24 mmol), Dynacoll 7360 (11.91 g, 3.40 mmol), Dynacoll 7381 (11.91 g, 3.40 mmol), and TPU-0 (5 g) were added to the reactor and agitated for drying under vacuum for 2 h after heating to 100–110°C. After drying, DMDEE (0.025 g) and liquid MDI (20.56 g, 82.24 mmol) were added

**TABLE II**
**Mechanical Properties of RHMAs**

| Sample | $E'$(MPa) | | Tensile properties | | |
|---|---|---|---|---|---|
| | $-100°C$ | $50°C$ | 5% secant modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) |
| RHMA-0 | 2,805 | 11.3 | 4.8 ± 0.1 | 27.5 ± 3.2 | 502 ± 6 |
| RHMA-MP4 | 3,598 | 29.9 | 6.2 ± 0.1 | 30.1 ± 4.8 | 467 ± 12 |
| RHMA-MP10 | 3,764 | 15.7 | 5.2 ± 0.1 | 29.1 ± 1.8 | 448 ± 18 |
| RHMA-MP20 | 2,223 | 7.2 | 4.4 ± 0.1 | 27.9 ± 0.7 | 495 ± 4 |

sequentially into the reactor, and the reaction between the hydroxyl group of polyol and the isocyanate group of liquid MDI was carried out for about 4 h under a nitrogen atmosphere to obtain the RHMA containing the PU prepolymer with terminal isocyanate groups. The isocyanate group content in the prepolymer was controlled by the feed recipe to be 3.0% by weight. After the reaction was completed, the RHMA was further degassed in the reactor for 1 h at 100–110°C. The other RHMAs were prepared using the same procedure as described above, except that other kinds of TPUs were fed into the reactor instead of TPU-0. The sample designation codes listed in Table II give information about the type of TPU used in the preparation of RHMA. For example, RHMA-MP4 is RHMA modified with 5 phr of TPU-MP4. The RHMA (control) shown in Table III is the reference RHMA prepared with the same procedure as described above, but without TPU.

**Measurements**

The film for dynamic mechanical properties and tensile test were obtained by curing the RHMA at 30°C in a 50% relative humidity environment for 2 days.

The number average molecular weight ($M_n$) and weight average molecular weight ($M_w$) of the TPUs shown in Table I were measured at 43°C using gel permeation chromatography (GPC, Waters M510). TPUs were dissolved in tetrahydrofuran and the solution was filtered with a 0.45 μm membrane filter before measurement.

The steady shear viscosity of the TPUs shown in Table I was measured by a capillary rheometer (Shimazu, CFT-500C).

$T_m$ of the TPUs shown in Table I was measured by a Differentail scanning calorimetry (DSC, TA, Q10). The sample weight was ~ 10 mg and the heating rate employed was 10°C/min.

X-ray diffraction (XRD) patterns were obtained with an x-ray diffractometer (Rigaku, RAD-3C, Japan) using Cu $K_\alpha$ radiation ($\lambda$ = 1.54 Å) as the x-ray source. The diffraction angle was scanned from 1.5°at a rate of 1.2°/min.

Dynamic mechanical properties of cured RHMA film were determined using a dynamic mechanical analyzer (DMA, TA, 8300) with a bending mode at a heating rate of 5°C/min and 3 Hz.

Tensile tests were performed with a tensile tester (Instron 3365) according to ASTM D882. The dumbbell-shaped microtensile specimen of cured RHMA film had the following dimensions: 100 mm length, 10 mm width, and 0.2 mm thickness. The specimen was elongated at a rate of 200 mm/min.

Dynamic rheological properties of RHMA before curing were measured with a cone and plate rheometer (Physica, MCR 301) at 120°C and a 15% strain level, which was the upper limit where the linear viscoelastic behavior was maintained. The cone angle and the diameter of the plate were 1.0°and 50 mm, respectively.

An acrylonitrile-butadiene-styrene copolymer sheet was coated with RHMA melted at 120°C to a thickness of 0.2 mm and PU foam (thickness of 2 mm, width of 10 mm, length of 80 mm) was brought in contact and pressed with a 5 kg roller and allowed to stand at 30°C in a 50% relative humidity environment. The bond strengths after 2, 5, 10, 20 min, and 2 days were measured by a 180° peel test with a tensile tester (Instron 3365) at the peel rate of about 100 mm/min.

**TABLE III**
**Adhesion Properties of RHMAs**

| Sample | Bond strength (N/m) after various times | | | | |
|---|---|---|---|---|---|
| | 2 min | 5 min | 10 min | 20 min | 2 day |
| RHMA (control) | 181 | 255 | 265 | 300 | Fracture |
| RHMA-0 | 250 | 920 | 2,400 | 2,400 | Fracture |
| RHMA-MP4 | 500 | 1,050 | 2,400 | 2,550 | Fracture |
| RHMA-MP10 | 750 | 1,100 | 2,400 | 2,450 | Fracture |
| RHMA-MP20 | 250 | 1,160 | 3,150 | 3,200 | Fracture |

## RESULTS AND DISCUSSION

### Properties of TPUs

The molecular weights of TPUs measured by GPC were shown in Table I, where one can see that the molecular weights of TPUs modified by Na-MMT/PEG are less than pristine TPU. This suggests that the polymerization of TPU was hindered by Na-MMT/PEG. The steady state viscosity measured at 40°C, a temperature near $T_m$ was increased by the modification by Na-MMT/PEG, as anticipated, because the melt viscosity is generally increased when there are intimate interactions between nano-filler and matrix polymer in the nanocomposite. However this enhancement of viscosity was reduced when the molecular weight of PEG was increased, probably due to the plasticizing effect of high molecular weight PEG. Whereas, the melt viscosity of TPU measured at 55°C was decreased compared to that of TPU-0 when modified with Na-MMT/PEG, more evidently as the molecular weight of PEG was increased. The plasticizing effect of PEG seems to be a cause, however, to explain this abnormal result exactly, further study will be necessary.

### X-ray diffraction

The XRD patterns of the Na-MMT, Na-MMT/PEGs, TPUs, and RHMAs are shown in Figure 1. Na-MMT [Fig. 1(a)] has a peak at around $2\theta = 7.0°$, whereas the Na-MMT/PEG samples made with PEG-2000 [Fig. 1(b)] or PEG-1000 (not shown in Fig. 1) have peaks at $2\theta = 4.9°$, and Na-MMT/PEG made with PEG-400 [Fig. 1(c)] has a broad peak in the range of $2\theta$
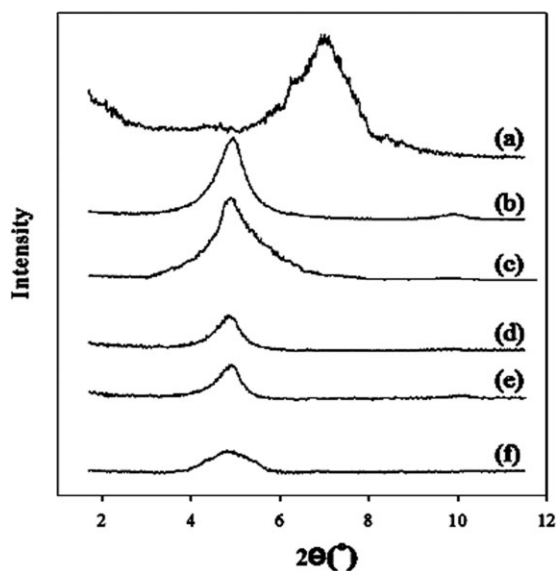


**Figure 1** XRD patterns of (a) Na-MMT, (b) Na-MMT/PEG-2000, (c) Na-MMT/PEG-400, (d) TPU-MP4, (e) TPU-MP20, and (f) RHMA modified with 9 phr of TPU-MP20.

$= 4.9–6.5°$. These results indicate that the basal plane spacing $d_{001}$, which was calculated by Bragg's law where $d_{001} = \lambda/2\sin\theta$, increased from 12.8 to 18.0 Å by the intercalation of PEG-2000 or PEG-1000. Taking into account that the thickness of the silicate layer itself was $\sim 9.5$ Å,[25,27] the results of Figure 1 show that the interlayer distance, which is the height of the gap between the layers of silicate, is 8.5 Å when PEG-2000 or PEG-1000 is intercalated, and that the interlayer distance is broadly distributed in the range of 4.1 Å–8.5 Å when PEG-400 was intercalated. Similar results have been previously obtained by other researchers and had been explained as follows.[25–28] In the case of a 4 Å interlayer distance, it was reported that the dominant morphology was a single layer of PEG intercalated at up to 0.15 g-PEG/g-Na-MMT by a planar zigzag conformation. However, when the interlayer distance was approximately two-fold at 8 Å, it was reported that PEG molecules could be intercalated up to 0.30 g-PEG/g-Na-MMT and two kinds of models, either a helical conformation or a double layer planar zigzag arrangement, had been suggested to explain the intercalated structure.

The weight loss by pyrolysis in a furnace at 600°C showed that the amounts of PEG in the gallery were 0.25 g/g-Na-MMT when PEG-400 was used and 0.28 g/g-Na-MMT when either PEG-2000 or PEG-1000 was used. These results are consistent with previous reports.[26,29]

We observed that the XRD patterns of all the TPUs modified with Na-MMT/PEG had a peak at around $2\theta = 4.9°$, irrespective of the PEG molecular weight, as shown in Figure 1. This result shows that Na-MMT/PEG has good stability such that the intercalated PEG segment cannot be easily replaced by a different segment or solvent having high affinity toward Na-MMT[25] and that all of the PEG segments adopt the same conformation when the chain length is extended by the reaction with isocyanate, independent of the original molecular weight.[24]

We did not observe any distinct XRD peak due to Na-MMT when RHMAs were modified with 5 phr of the TPUs. Because this seems to be due to the low content of Na-MMT in the RHMAs, we made additional RHMA samples containing 9 phr of TPU-MP20 for XRD analysis. Figure 1(f) shows that the XRD peak of this RHMA appears at the same position as that of TPU-MP20. The result that Figure 1(b,e, and f) have the XRD peak due to Na-MMT at the same position shows that the stable structure of Na-MMT/PEG-2000 was retained in both the TPU and RHMA.

### Mechanical properties

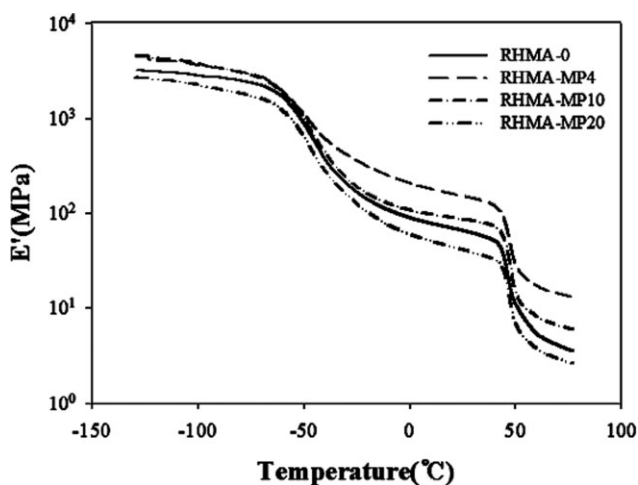The tensile storage modulus, $E'$, of the cured RHMA measured by DMA is shown in Figure 2, where it

**Figure 2** Tensile storage modulus of RHMAs.



**Figure 3** Complex viscosity versus frequency of RHMAs.

can be noted that a broad glass-rubber transition occurs at a temperature around $-50°C$ and another sharp transition due to melting exists at a temperature near $50°C$. The quantitative $E'$ values are summarized in Table II. It can be seen in Table II and Figure 2 that the $E'$ of RHMA-MP4 is increased compared to that of RHMA-0, which shows that Na-MMT/PEG-400 reinforces the RHMA effectively even though its content in the RHMA is only 0.18%. However, the reinforcing effect of Na-MMT/PEG is decreased in RHMA-MP10 compared with RHMA-MP4 and this decrease is more evident in RHMA-MP20, which shows that the reinforcing effect is reduced as the molecular weight of PEG is increased. Because the PEG segment can soften the RHMA, these results indicate that the softening effect by PEG becomes more evident when the molecular weight of PEG was high, although the reasons for this can not be explained clearly.

From Table II, both the tensile modulus and tensile strength were improved by an effective reinforcing effect when Na-MMT/PEG segments exist in RHMA. Also, these enhancements are reduced when the molecular weight of the PEG used was 2000, as with the results of DMA. The elongation at break values shown in Table II generally decreases when Na-MMT/PEG exists in the RHMA compared to that of RHMA-0, which shows that defects, from which the fracture can initiate at high deformation, may exist and that chain rearrangement during deformation was hindered by the presence of Na-MMT.

## Rheological properties

Figure 3 shows a log–log plot of the complex viscosity, $\eta^*$, versus angular frequency, $\omega$, at $120°C$. RHMA-0 exhibits a Newtonian fluid behavior, having a nearly constant $\eta^*$ at oscillation frequencies ($\omega$)
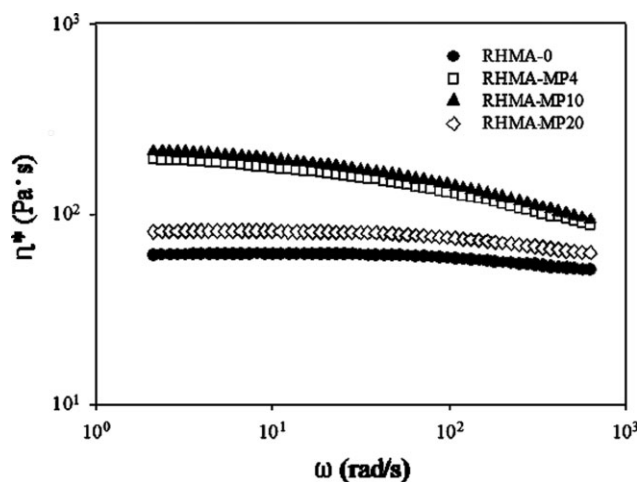
less than 100 rad/s. This behavior shows that the molecular weights of the majority of RHMA constituents were not high enough to cause shear thinning behavior, which can be observed in polymers that have polydispersity in their molecular weight. Figure 3 shows that $\eta^*$ increased and non-Newtonian fluid behavior, i.e., the increase of $\eta^*$ at low shear rate, was induced when Na-MMT/PEG was present in the RHMA.

This peculiar behavior at low shear rate was also observed in the log–log plot of the storage shear modulus, $G'$, versus $\omega$, as shown in Figure 4. Specifically, the $G'$ values of RHMA-0 increased monotonically at low frequencies with a slope of $\sim 1.8$. However, a transition of the slope to a flattened behavior, i.e. nonterminal behavior, was observed at low frequencies in the presence of Na-MMT/PEG, as the increase of $G'$ was more evident at low shear rate. That is, the slope was 1.1 and 1.0 for RHMA-MP4 and RHMA-MP10, respectively. This diminished
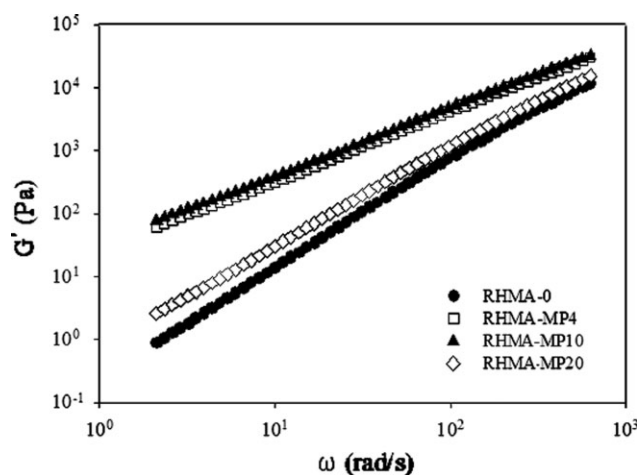


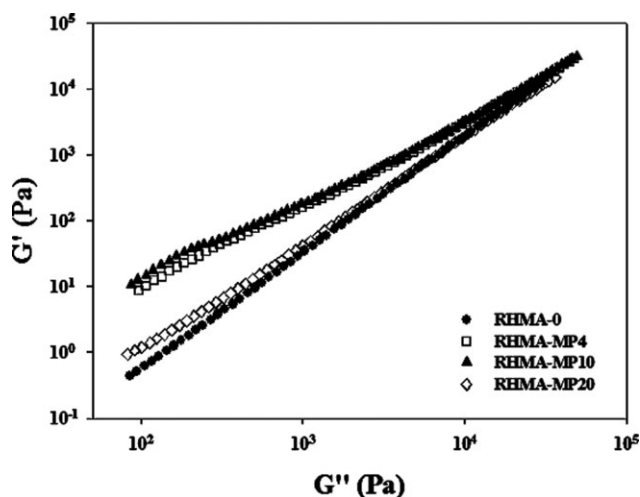**Figure 4** Storage shear modulus versus frequency of RHMAs.

**Figure 5** Storage shear modulus versus loss shear modulus of RHMAs.

frequency dependence of $G'$ at low shear rates suggests the possibility of pseudo-solid like behavior that may be attributed to incomplete relaxation. Incomplete relaxation of dispersed Na-MMT can be caused by physical congestion of highly anisotropic dispersed silicate layers, which prevents free rotation in compliance with external dynamic shear. This incomplete relaxation and interaction between the silicate layers can create a three-dimensional meso-scopic silicate layer structure, resulting in silicate layers which are unable to independently relax, which in turn cause the observed pseudo-solid like behavior.[17,30,31] The increase of $\eta^*$ and the diminished frequency dependence of $G'$ at low frequency may also be attributed to the slower relaxation of matrix molecules due to strong interactions between silicate layers and RHMA molecules.[32,33]

In Figures 3 and 4, the increase of $\eta^*$ and the pseudo-solid like behavior is evident when PEG-400 or PEG-1000 was used. However, these effects are reduced when PEG-2000 was used. That is, the log–log plot of $G'$ versus $\omega$ has the slope of 1.6. The interaction between Na-MMT/PEG and RHMA matrix molecules will be reduced when high molecular weight PEG, which has fewer reactive hydroxyl groups and consequently, can generate a lower amount of chemical bonds, was used. This mechanism appears to be the cause of the above results. The softening effect of PEG-2000, as in the explanation of mechanical properties, can also cause the above results.

The modified cole–cole plot, a log–log plot of $G'$ against $G''$ shown in Figure 5, also demonstrates that the elasticity is increased by the strong interaction between Na-MMT and RHMA molecules, however there is softening effect when PEG-2000 was used.

## Adhesion properties

Table III shows that the initial bond strengths of RHMA modified by TPU-0 are much higher than those of RHMA (control). In addition, this enhancement is further improved when the TPU was modified by Na-MMT/PEG. This demonstrates that TPU can enhance the initial solidification of RHMA after application, with this effect more evident when the TPU was modified with Na-MMT/PEG. The effect of the molecular weight of PEG on the initial bond strength development shown in Table III displays somewhat complicated behavior. However, it can be seen that the bond strengths are generally increased, with some exceptions, as the molecular weight of PEG was increased, despite the softening effects observed in RHMA-MP20. Because the reinforcing effect of Na-MMT, the softening effect of PEG, the crystallization behavior of TPU and Dynacoll's, and the diffusion rate of humidity can all affect initial bond strength development, it was not easy to explain the above results probably due to the complicated contributions of these factors.

## CONCLUSIONS

Our experimental results showed that the improvement of initial bond strength of RHMA by TPU was further enhanced when the TPU was modified with 4 phr of Na-MMT/PEG, even though the content of the Na-MMT/PEG in the RHMA was less than 0.2%.

XRD patterns showed that Na-MMT/PEG was sufficiently stable such that the PEG segments intercalated in the gallery of Na-MMT could not be easily displaced by other segments during the preparation of TPU or RHMA.

The rheological properties, including the increase of $\eta^*$ and the pseudo-solid like behavior at low shear rate caused by the Na-MMT/PEG, demonstrated that intimate interactions exist between the RHMA matrix molecules and Na-MMT/PEG.

The mechanical properties of cured RHMA films, such as improved modulus and tensile strength, indicate that Na-MMT/PEG effectively reinforced the RHMA, especially when the molecular weight of PEG was 400.

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