

ABSTRACT

Is it feasible to use reactive hot-melt (RHM) adhesives based on an isocyanate-terminated prepolymer from polyether polyols? We tested the performance of RHM adhesives of polyurethane prepolymers prepared with MDI (methylenediphenyl diisocyanate) prepolymers and polyether polyols. Initial viscosity, initial bond strength, tack free time, and melt stability were determined. The results show that polyurethane RHM adhesives produced from polyether polyols perform as well as those obtained from polyester polyols.

Application: Commercial reactive hot melts are solids at room temperature. Costs would be lower if the user could handle the hot melt as a liquid, as long as the adhesive performed as well.

HOT-MELT ADHESIVES ARE WIDELY used in manufacturing processes that require quick, strong bonding. These adhesives are solids at room temperature, but they liquefy when heated to the temperatures at which they are applied. When applied, hot melts bond and cool rapidly. This ability to solidify immediately gives hot melts their quick grab properties. In an assembly line, the bonded assembly can be handled in the next step of the process without the bond being broken (1).

Reactive hot-melt (RHM) adhesives based on polyurethane are used in industrial processes that require superior initial bond strength and supreme thermoset properties. The commercial use of these adhesives is increasing for applications ranging from woodworking to automobile assembly. These adhesives are usually pure MDI (methylenediphenyl diisocyanate) prepolymers of adipate-based polyester polyols. One disadvantage of these raw materials is that

Performance control of reactive hot melt adhesives based on polyether

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they are solids at room temperature, which means that the handling costs are greater than the costs would be for liquid materials (2).

Over the years, formulators have searched for less expensive RHM adhesives in which the polyol component consists entirely of polyether polyols. Polyether polyols can be handled easily because they are usually liquids. Most of these efforts have met with limited success, because most polyether polyol-based RHM adhesives lacked sufficient initial bond strength and melt stability.

Our purpose here is not to provide specific guidelines for formulating polyether polyol-based RHM adhesives. Instead, our objective is to show that RHM adhesives can be produced in which the polyol component consists entirely of polyether polyols, with performance comparable to that of adhesives based on polyester polyols.

EXPERIMENTAL PROCEDURES

To qualify as a candidate for the purposes of this study, a polyether-based RHM formulation had to have the following properties:

- Solid or semi-solid at room temperature
- Viscosity of 5000–20,000 cp at the application temperature
- Initial bond strength (180° peel test) of 3–7 pli after 2 min, 3–9 pli after 15 min (3, 4), and 3–9 pli after 24 h
- Normalized viscosity growth of <10% per hour

Normalized viscosity growth, or percent rise, is calculated from the data for viscosity, η , versus time, t . These data are acquired for a prepolymer sample held at the application temperature (typically 120°C) for 4 h.

$$\% \text{ Rise} = [(\Delta\eta/\Delta t) \div \eta_0] \times 100 \quad (1)$$

where $(\Delta\eta/\Delta t)$ is the slope of η vs. t and η_0 is the initial viscosity.

Prepolymer preparation

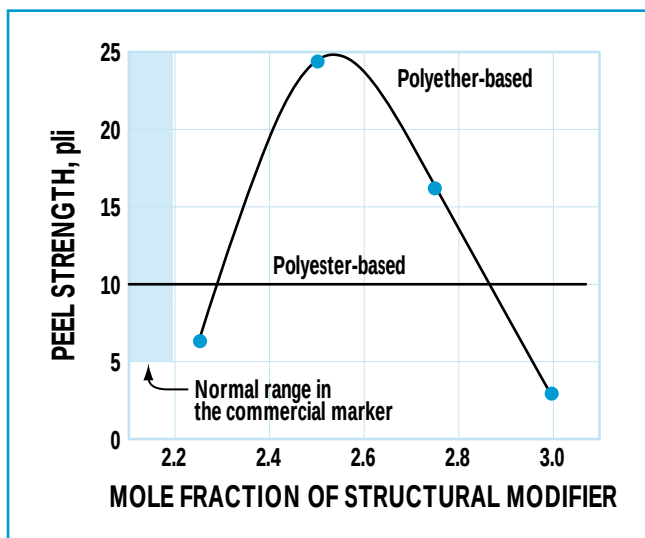
Prepolymers were prepared using no catalyst, targeting 2% and 3% free NCO, and maintaining the ratio of NCO to OH below 1.9:1 (3, 4). Residual water in the polyols was reduced via vacuum stripping to less than 0.07% by weight. In some cases, the index was adjusted to offset the contribution of the residual water remaining after vacuum stripping.

As the control, we used a prepolymer made from adipate polyester polyol (mol. wt. = 3700) and MDI. To prepare all of the prepolymers, we used MDI containing 50% of *o,p'*-isomer, which is liquid at room temperature. Two polyether polyol-based prepolymers were identified as potential candidates. These prepolymers are based on ordinary polyether polyol diols, and they differ only in structure. For simplicity, we will call them System A and System B.

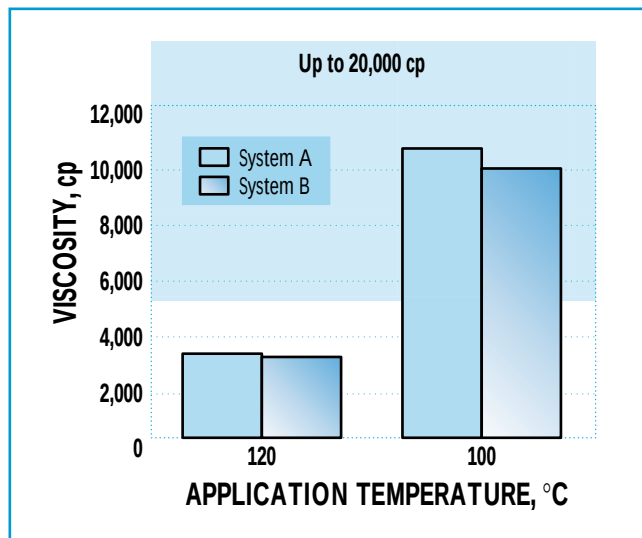
Performance tests

Viscosity, initial bond strength (or "green" strength), tack free time, and melt stability were measured on all the prepolymers.

Green strength was measured on an Instron 1125. Samples for these 180° peel tests were prepared by



1. Effect of molecular composition on initial bond strength



3. Viscosity measurement

drawing down thin films (about 20 mils) of the prepolymer at 100° and 120°C onto metal strips and adhering cotton cloth to the metal using a 4.5-lb roller. Peel measurements were taken at 2 min, 15 min, and 24 h.

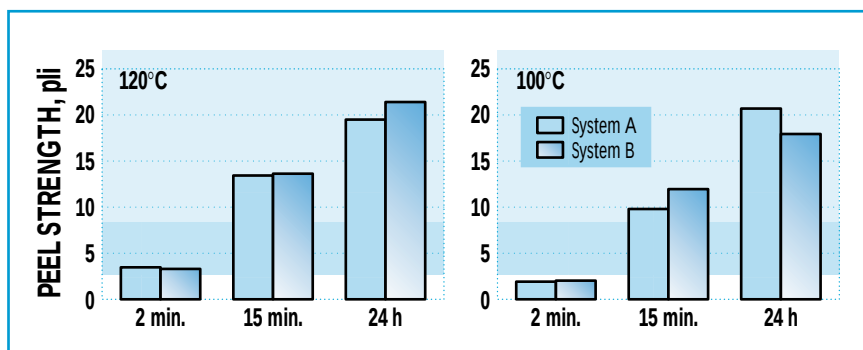
Initial viscosity and melt stability were measured on a Brookfield thermostet. Melt stability analyses were conducted under conditions of low rotational shear (cup and bob geometry, Brookfield Spindle No. 27). The spindle speed was adjusted to maintain the torque between 10% and 90% to ensure data accuracy. Viscosities were measured over 4–6 h at 100°C and 120°C under continuous nitrogen purge.

Open time, which is similar to tack free time, was measured by drawing down a thin film (about 10 mils) of the prepolymer onto a pre-roughened steel panel substrate at room temperature and performing a finger tack test. Nitrile rubber gloves were worn during the test. The film was touched at about 3-s intervals, each time in a different location, until it reached an effective tack-free state.

RESULTS AND DISCUSSION

Green strength

The first step in proving the feasibility of polyether polyol-based RHM formulations is demonstrating that



2. Peel strength data at 100°C and 120°C. Shaded areas indicate the acceptable ranges. Failure mode = cohesive.

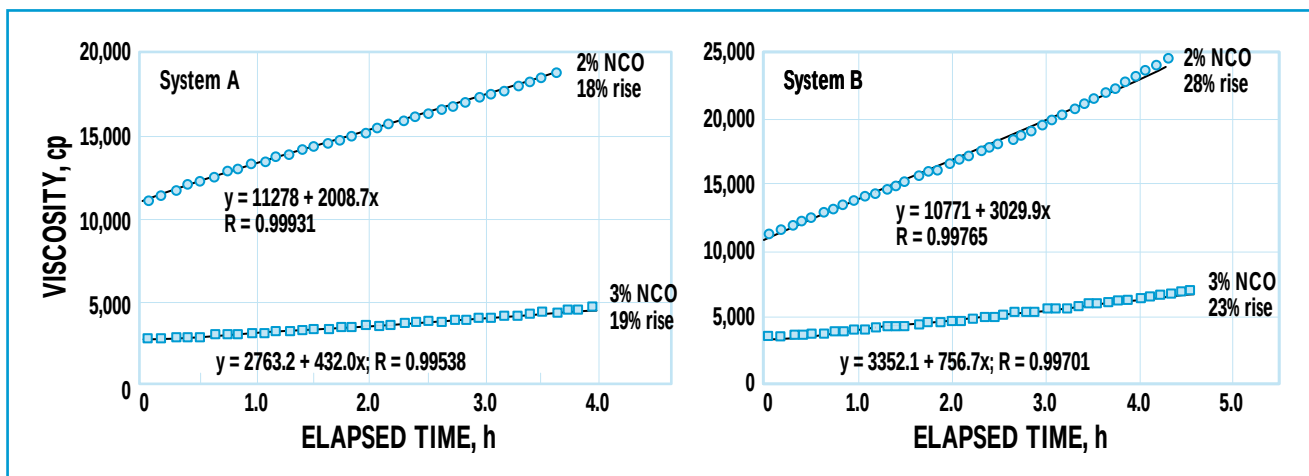
green strengths are comparable to those obtained with systems based on polyester polyols. System A was used to demonstrate how green strength is affected by the polymer's molecular composition.

Figure 1 shows green strength as a function of the polymer's molecular composition. The shaded bar along the y axis indicates the range normally encountered in the commercial market. The solid line parallel to x axis is the typical value obtained with the adipate polyester polyol-based prepolymer. As the mole fraction of the structural modifier increases, the peel strength goes through a maximum, which indicates an effect that is structurally induced.

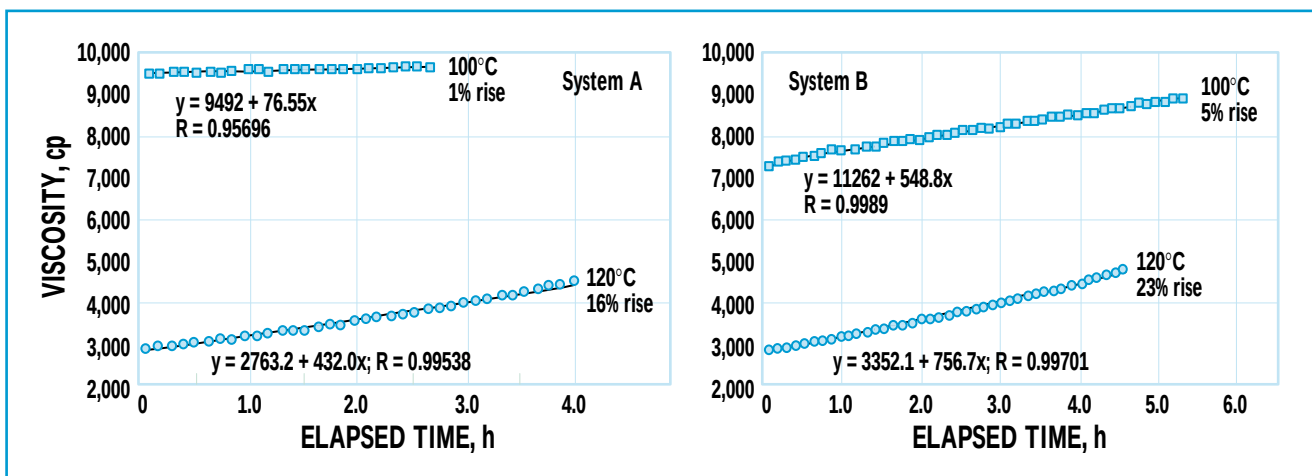
These data show that acceptable

green strengths can be attained from RHM prepolymers containing polyether polyols as the only polyol component. These initial bond strengths are similar to the green strengths of RHM prepolymers based on polyester polyols. Moreover, the green strength can be controlled by adjusting the level of structural modifiers.

The peel strengths for Systems A and B over 24 h are compared in Fig. 2. As the bars show, RHM prepolymers based on polyether polyols can be used to obtain performance comparable to RHM prepolymers based on polyester polyols. The shaded areas behind the bars indicate the acceptable ranges. Furthermore, it is possible to apply the polyether polyol-based RHM systems at lower temperatures (100°C rather than



4. Melt stability at 120°C for System A and for System B



5. Melt stability for the 3% NCO only at 100°C for System A and for System B, with the curves at 120°C from Fig. 4 for the sake of comparison

120°C in the figure) without significant loss in peel strength performance. Cohesive failure, the preferred failure mode, was obtained for both samples at both application temperatures.

Viscosity

Initial viscosity is important in the process of forming a bond. The adhesive must be able to flow and wet the surface at the application tempera-

ture without being so thin as to flow out of the bond line. Initial viscosities from 5000 to 20,000 cp are acceptable for RHM adhesives. This range is indicated by the shaded area in Fig. 3.

As the figure shows, the initial viscosities of both System A and System B are slightly lower than the acceptable range at 120°C. The viscosity at 120°C could be increased by adding inexpensive thickening agents, or fillers.

At 100°C, the initial viscosities of both systems lie well within the acceptable range. Consequently, the initial viscosity of a polyether polyol-based system can be easily adjusted by changing the application temperature or by adding thickeners, or both.

Melt stability

Another important performance criterion for RHM adhesives is the increase in viscosity at the application temperature. Such a thickening of the adhesive can cause problems for the user. Production can be interrupted because of plugging in the transfer lines or the applicator. The cleaning process can be costly in terms of parts replacement and downtime.

In general, RHM adhesives must have a viscosity growth rate of less than 10% per hour to be acceptable. The graphs in Fig. 4 show the viscosity growth at 2% and 3% NCO for Systems A and B at 120°C. Prepolymers with higher final isocyanate

KEYWORDS

Adhesives, bonding strength, diisocyanates, hot melts, melt properties, polyethers, polyurethanes, setting time, tack, viscosity.

content (3% NCO) exhibit lower rates of viscosity growth than do those prepolymers with lower final NCO content. In fact, the increase in viscosity at 3% NCO is lower by a factor of about four after 4 h. Nevertheless, the normalized viscosity growth rates for both Systems A and B are unacceptably high in regard to customer requirements.

Interestingly, the final viscosity of the 3% NCO prepolymer is significantly less than that of the 2% NCO prepolymer. Furthermore, the final viscosity of the 3% NCO prepolymer is not significantly different from its initial viscosity, whereas the viscosity of the 2% NCO prepolymer has almost doubled. Thus, it is important to consider the viscosity growth rate when assessing the RHM prepolymer's melt stability.

When the same study was conducted at 100°C, the prepolymers made with a higher NCO had significantly lower viscosity growth, as the graphs in **Fig. 5** illustrate. These values for percent rise, 1% for System A and 5% for System B, are well within specifications. Furthermore, the initial viscosities of Systems A and B at 100°C lie well within the acceptable limits specified by users, making these systems attractive for RHM adhesives.

Tack free time

Although tack free time does not correlate directly with open time, the relative order of tack free time for these systems is expected to be the same as the order for open time. The open time test assesses the length of time during which a sufficient bond can be made. Although it is a qualitative test, it can differentiate between RHM adhesives that set rapidly and those that set slowly. What constitutes a desirable open time depends on how the adhesive is to be used. In other words, how much time can be allowed after the adhesive is applied before the part has to be fixed in place?

Tack-free time is the moment at

which the adhesive is no longer sticky. Therefore, it represents the interval during which the adhesive is tacky.

Figure 6 shows the tack free times for Systems A and B at 100° and 120°C. System A exhibits shorter tack free time and is less sensitive to temperature than is System B. This outcome shows that the tack free time can be adjusted by changing the molecular composition of the polyether polyol-based RHM prepolymers. As indicated in **Fig. 6**, the intervals to tack-free adhesive for both Systems A and B are shorter at the lower application temperature. Although the times to reach tack-free adhesive are shorter than the acceptable range indicated by the shaded area, the adhesive formulator can use waxes and tackifiers to make adjustments.

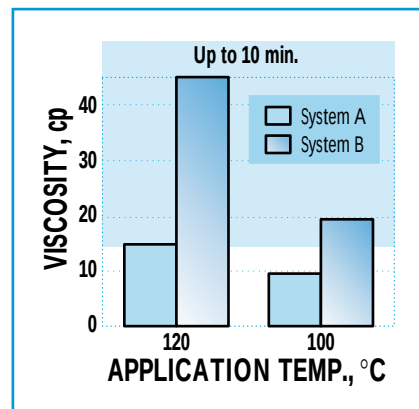
CONCLUSIONS

By manipulating the polymer structure, it is possible to produce excellent polyurethane RHM adhesives systems based on polyether polyols. These systems have green strengths, viscosities, and melt stability properties comparable to those of systems based on polyester polyols.

Melt stability is affected by the final NCO content of the prepolymer and the temperature of application. A higher index allows for lower application temperatures, which is preferable because of concerns over industrial hygiene.

For the purposes of this study, the tack free times were lower than what normally is expected, but this work was carried out on prepolymers without any further formulation additives. The adhesive manufacturer can manipulate this variable to some extent by using tackifiers. TJ

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6. Tack free time

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