

High-performance hot-melt adhesives from ethylene copolymers via grafting

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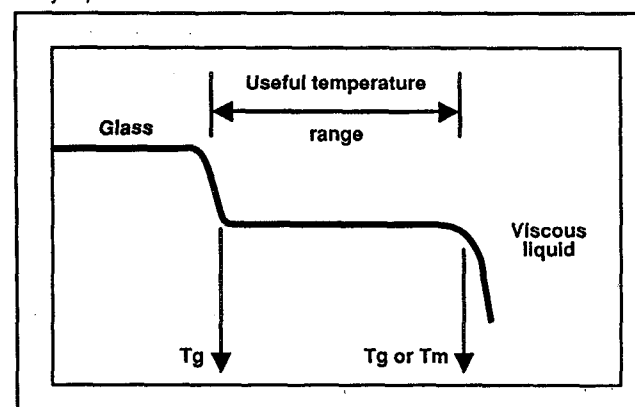
A novel grafting technology was used to produce a versatile adhesive system which allows tailoring of such properties as viscosity, high-temperature performance, low-temperature performance, and tensile strength.

Ethylene copolymers (mainly ethylene-vinyl acetate) are widely used as the polymeric component of hot-melt adhesives for packaging, book binding, etc. However, ethylene copolymers have relatively poor heat resistance due to their low crystalline melting point and cannot be used for demanding applications such as product assembly, automotive bonding, construction, etc.

Ethylene copolymers are directly synthesized in high-pressure equipment, and the comonomer is randomly distributed along the polymer chain. For copolymers containing large amounts of softening comonomer, the polyethylene segments are short and melting point and percent crystallinity are depressed, reducing heat resistance. Even the highest melting point (and heat resistance) obtainable when no comonomer is present (less than 120°C for low-density polyethylene) is not very good for a structural adhesive. Also, low-density polyethylene is a low-surface-energy material and does not bond well to polar substrates; consequently, it is not used as an adhesive.

Demands on adhesives are increasing in terms of an operating window, with a desired operating temperature as broad as possible. Figure 1 demonstrates the useful operating range for a thermoplastic adhesive as measured by thermomechanical analysis. The transition at the left represents the glass transition temperature (T_g) below which the material is too brittle to be useful as an adhesive. The transition on the right represents either a crystalline melting point (T_m) or a high T_g , above which the material becomes a viscous liquid and no longer has holding power. The region between these two transitions represents the useful temperature window. Graft or block copolymers are ideal as adhesives because their two-phase structure provides such a broad operating range. They can be designed to microphase separately into a tough, "rubbery" low- T_g phase and into a hard reinforcing phase which can be either a glass or a crystalline material.

1. Useful temperature range for adhesives (thermomechanical analysis)



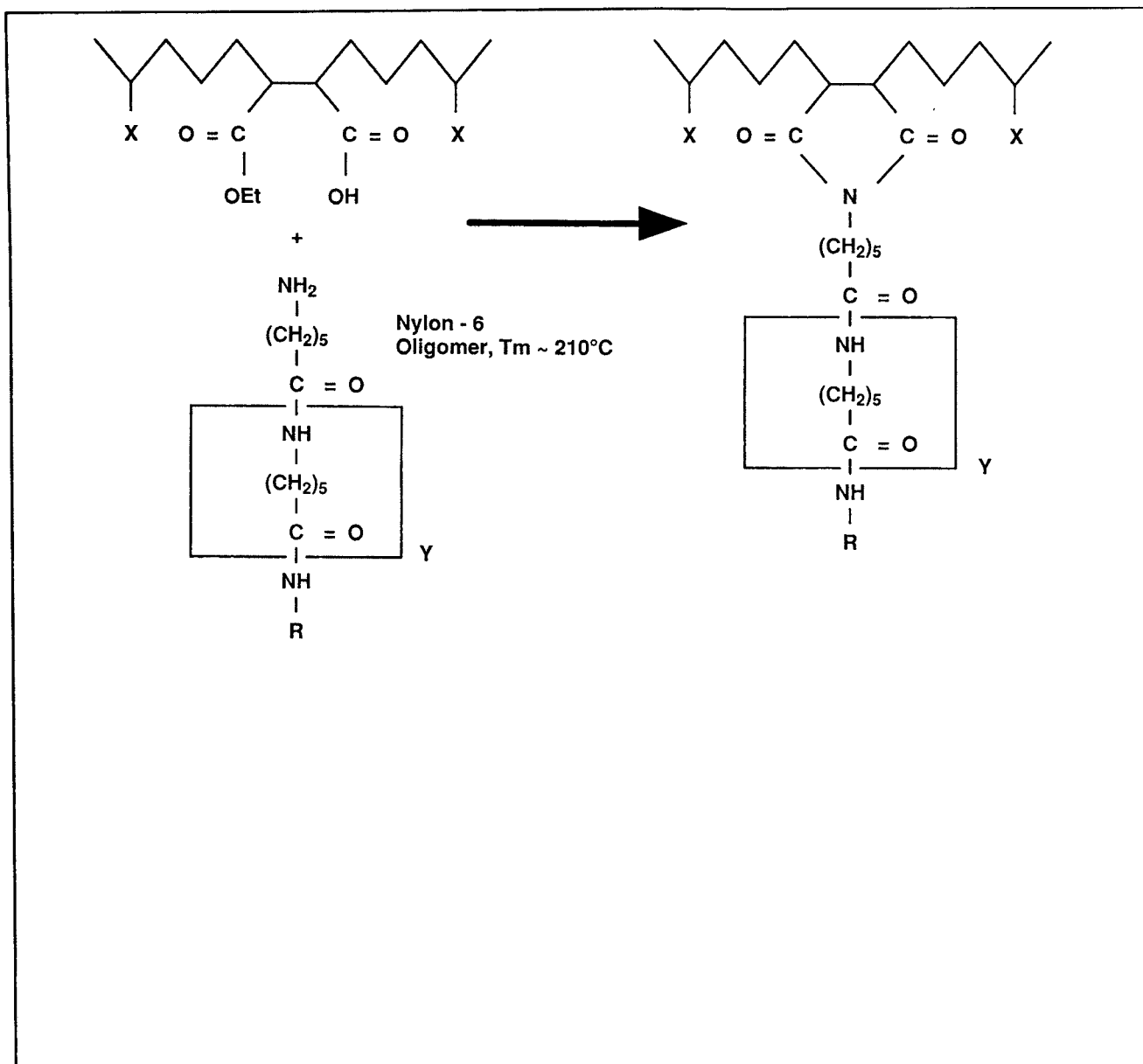
Discussion

Grafting is a "secondary process" which can be considered for stretching the potential of ethylene based polymers for future high-performance adhesives. The novel approach of grafting an amine ended oligomer to an ethylene copolymer backbone containing an anhydride precursor as the graft site could be utilized in this regard. The basic chemistry of this grafting reaction is shown in Fig. 2. If more than one primary amine group per oligomer molecule is present, crosslinking will occur. Ethyl hydrogen maleate (MAME), which reacts with amines similar to an anhydride, is utilized as the graft site. An imide bond is formed with elimination of water and ethanol. An ethylene terpolymer with a relatively large amount of a low- T_g toughening comonomer incorporated in the polymer backbone was used to maximize low-temperature toughness. An amine ended nylon-6 oligomer was utilized as the hard phase.

It turns out that excellent high-temperature performance is obtained only when nylon is the continuous phase for this system. Physical crosslinks provided by a nylon dispersed phase, when the ethylene copolymer phase is continuous, leads to only a marginal improvement in heat

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2. Grafting reaction (X = toughening comonomer, grafting site = ethyl hydrogen maleate)

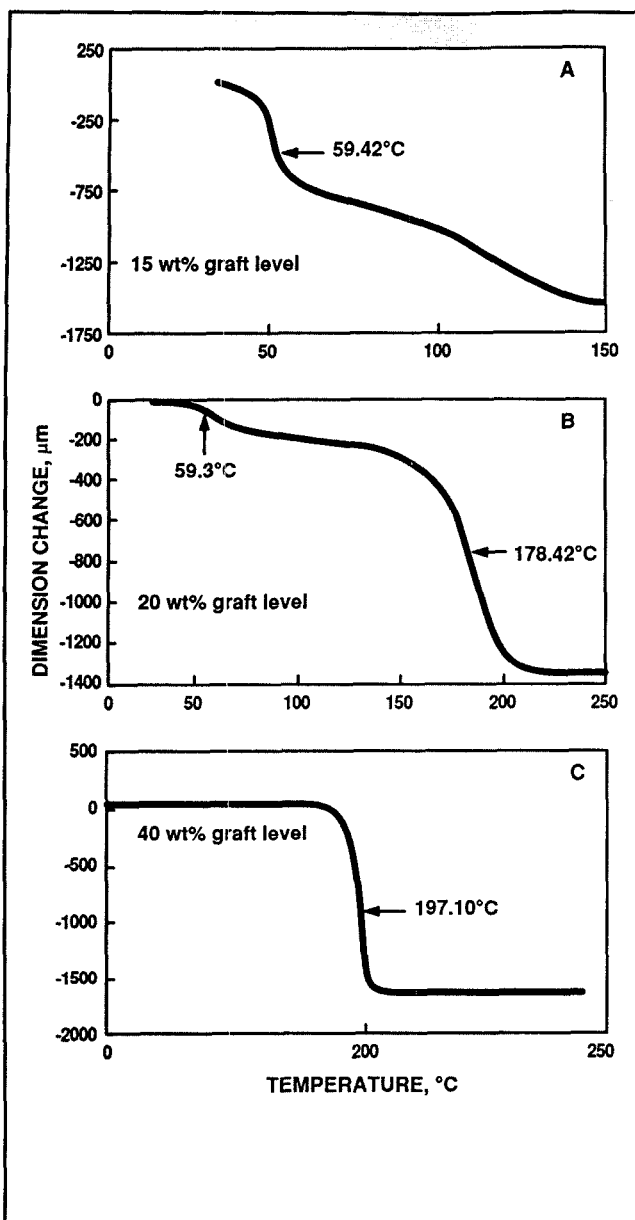


resistance over neat ethylene copolymer. Quite unexpectedly, nylon becomes the continuous phase at relatively low concentrations. **Figure 3A** shows a thermomechanical scan of grafted terpolymer with a graft level of 15 wt%. Thermomechanical analysis correlates well with adhesive end-use performance. Probe penetration starts at approximately 60°C, which is not far above the ethylene copolymer phase melting point, indicating that it is the continuous phase. **Figure 3B** shows a 20-wt% graft level. Two transitions are seen, one near the melting point of each phase, indicating the possibility of continuous morphology. **Figure 3C** depicts a 40-wt% graft level where nylon is fully continuous and heat resistance is maximized.

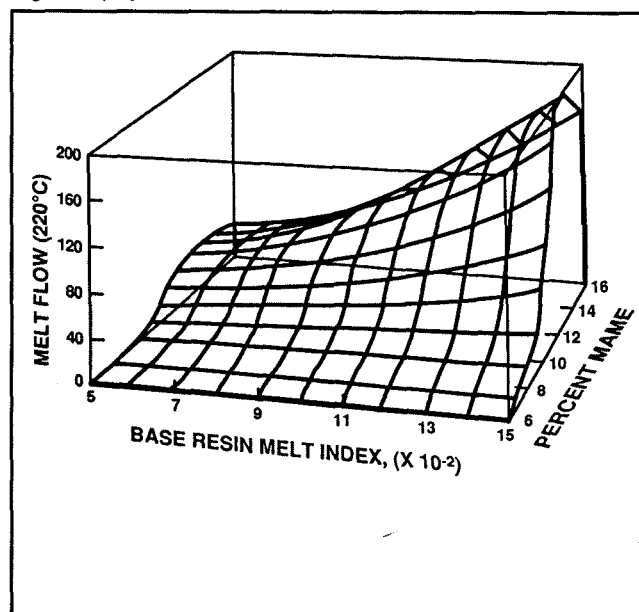
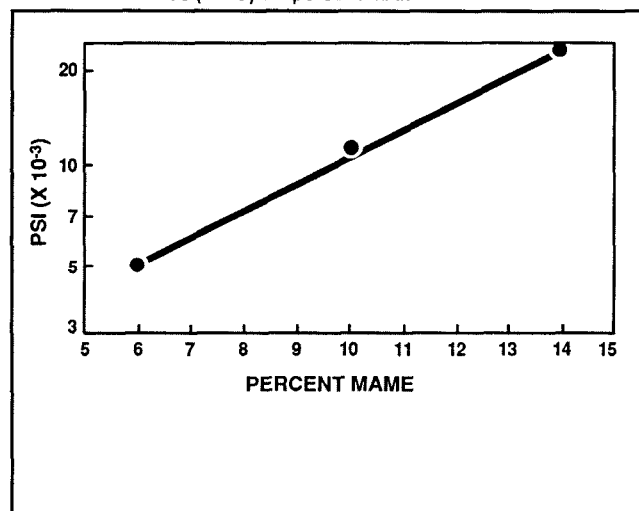
For application as a hot-melt adhesive, the viscosity must be minimized while maintaining the best possible properties at both high and low temperatures. Adhesive viscosity should be as low as possible so it can be easily

pumped through a nozzle and to achieve good substrate wetting (less than 100M cp and preferably less than 20M cp at the application temperature). Ethyl hydrogen maleate concentration, terpolymer melt index, graft level, nylon oligomer molecular weight, and formulation with plasticizers have been studied to determine their effect on viscosity, as well as high- and low-temperature properties. Analysis of the data led to surprising results. The amount of excess ethyl hydrogen maleate in the backbone polymer had a dramatic effect on viscosity (as measured by melt flow at 220°C) of the grafted system (**Fig. 4**). In fact, it was this effect that allowed development of adhesive systems with sufficiently low viscosity. By excess ethyl hydrogen maleate, I mean the amount in excess of stoichiometric. For the graft level studied here, 6 wt% was required for a stoichiometric balance with the amine ended nylon oligomer. As seen, the ethylene copolymer melt index

3. Thermal mechanical analysis



4. Effect of base resin melt index and percent MAME on melt flow of graft terpolymer

5. Tensile modulus (25 $^{\circ}\text{C}$) vs. percent MAME

has a large effect on the grafted adhesive viscosity only when a large excess of ethyl hydrogen maleate is present. Another surprising result is the effect of excess ethyl hydrogen maleate on modulus (Fig. 5). The modulus essentially doubles for every 4-wt% increase in ethyl hydrogen maleate. Graft terpolymers produced with very little or no excess ethyl hydrogen maleate in the backbone are very high in viscosity and not useful as adhesives; however, their moduli are in the thermoplastic elastomer range, and they are very resilient. These grafted terpolymers are currently being evaluated as thermoplastic elastomers. An added benefit is their transparency. The effect of excess ethyl hydrogen maleate on viscosity and modulus is not understood at this time.

The effect of graft level on the grafted adhesive viscosity is shown in Fig. 6. Graft levels of most interest lie between 20 wt% and 40 wt%. Remember, below approximately 20

wt%, nylon becomes the disperse phase and good heat resistance is lost. At graft levels about 40 wt%, low-temperature toughness is significantly reduced. A number average molecular weight of approximately 1500 provides the greatest tensile strength.

Formulation work with plasticizers led to the discovery of a plasticizer package with the appropriate solubility parameter balance to plasticize only the ethylene terpolymer phase (minimizing any adverse effect on high-temperature properties). Surprisingly, only one plasticizer combination was found that, at a 10–12% concentration level, would not adversely affect adhesion. This plasticizer package significantly reduced viscosity and improved low-temperature properties, as evidenced by the reduction in Tg. Lap shear performance at 100 $^{\circ}\text{C}$ was still reasonably good despite the marked reduction in tensile strength.

Viscosity stability for hot-melt adhesives (referred to as

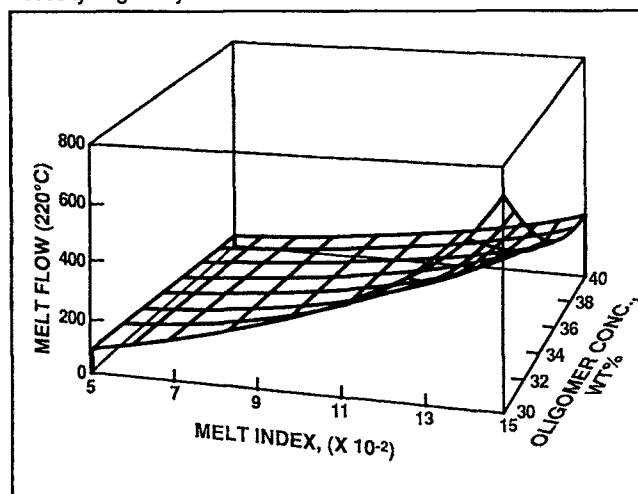
pot life) is important for obvious reasons. A formulated, grafted adhesive gives excellent stability. Surprisingly, plasticizer used at low concentration levels in combination with the stabilizer package significantly improves viscosity stability.

Open time for adhesives is defined as the time available to make a useful bond to a second substrate after applying the adhesive to the first substrate. Freezing point (not melting point) generally correlates with open time. All the nylon grafted adhesives have short open times since the nylon phase has rather high freezing and melting points and consequently provides good heat resistance. However, varying the graft level gives some control over freezing point, and thus open time, without significantly affecting the melting point (correlates with heat resistance). Freezing point varies significantly from a graft level of 15 wt% to a level of 40 wt%, while the melting point varies only slightly.

Conclusion

In summary, a novel grafting technology was utilized to produce a versatile adhesive system. There are many degrees of freedom which allow tailoring of viscosity, open time, high-temperature performance, low-temperature performance, tensile strength, etc. The adhesive system is 60–80% ethylene copolymer; consequently it exhibits excellent moisture resistance (no change in lap shear performance after being exposed to boiling water for 2

6. Effect of base resin melt index and oligomer concentration on viscosity of graft system



h) relative to nylon. However, since nylon is the continuous phase, resistance to many organic solvents and oils is quite good. □

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