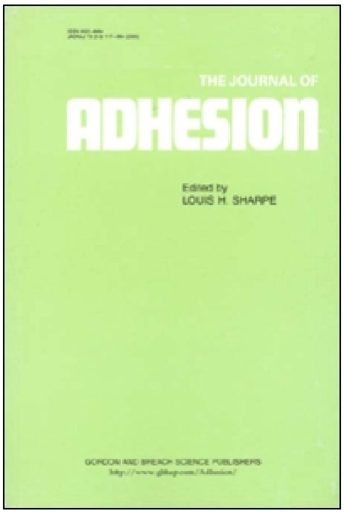
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Cross-Linking of Hot-Melt-Processible Acrylic Pressure-Sensitive Adhesives using Acid/Base Interaction

Albert Everaerts[a]; Ken Zieminski[a]; Lang Nguyen[a]; Jeff Malmer[a]
[a] 3M Company, St. Paul, Minnesota, USA

To cite this Article Everaerts, Albert , Zieminski, Ken , Nguyen, Lang and Malmer, Jeff(2006) 'Cross-Linking of Hot-Melt-Processible Acrylic Pressure-Sensitive Adhesives using Acid/Base Interaction', The Journal of Adhesion, 82: 4, 375 — 387
To link to this Article: DOI: 10.1080/00218460600683860
URL: http://dx.doi.org/10.1080/00218460600683860

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Journal of Adhesion, 82:375–387, 2006

ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460600683860

Cross-Linking of Hot-Melt-Processible Acrylic Pressure-Sensitive Adhesives using Acid/Base Interaction

Albert Everaerts
Ken Zieminski
Lang Nguyen
Jeff Malmer
3M Company, St. Paul, Minnesota, USA

Hot-melt pressure-sensitive adhesives (PSAs) advantageously reduce or eliminate the use of organic solvents. To provide for easy processing and good coating quality, hot-melt PSAs typically are relatively low in molecular weight, but this can compromise cohesive strength. Physical cross-linking and ionic cross-linking provide thermoreversible methods to increase cohesive strength. This study focuses on the use of acid/base interaction between two polymers as a possible route toward hot melt coatable acrylate PSAs. Adhesive performance and rheological data suggest that a good balance of properties can be obtained while maintaining melt processibility. The rheological data also clearly demonstrate that the strength of the acid/base interaction and the structure of the base have a significant effect on the final properties of the adhesive.

Keywords: Acid; Base; Cross-linking; Hot melt; Pressure-sensitive adhesive; Rheology

INTRODUCTION

Hot-melt pressure-sensitive adhesives (PSAs) advantageously reduce or eliminate the use of organic solvents during synthesis and coating. Among hot-melt PSA chemistries, tackified block copolymers and more recently (meth)acrylates are the most prominent. To provide for easy processing and good coating quality, these materials typically are relatively low in molecular weight. The inherent physical cross-linking

Received 15 November 2005, in final form 2 March 2006.

Presented in part at the 28th Annual Meeting of the Adhesion Society, Inc., Mobile, Alabama, USA, 13–16, February, 2005.

Address correspondence to Albert I. Everaerts, 3M—CRML, Building 201-3N-04, Maplewood, MN 55144, USA. E-mail: aieveraerts@mmm.com

of block copolymers results in a good balance of cohesive strength and processibility. However, although the thermoreversible nature of the physical cross-linking allows for hot-melt processing, the higher service temperature of the PSA is typically also limited by the glass transition of the hard block. Rubber block copolymers (commonly based on a combination of polystyrene hard blocks with soft blocks, such as polyisoprene, polybutadiene, or ethylene–butylene copolymers) have been common for many years. In contrast, acrylic block copolymers have only recently become available on a very limited commercial scale. To make these block copolymers, highly specialized controlled free-radical polymerizations have to be used. To take advantage of the acrylic PSA properties such as inherent tack, optical clarity, and weatherability, a need still exists to make these polymers hot-melt processible without having to resort to these more complex polymerization methods. Unfortunately, as with other classes of adhesives, the low molecular weight of the polymer required for easy processing also results in limited cohesive strength and the need for a final processing step to cure or cross-link the polymer after the coating process. Ionic cross-linking, electron beam or ultra violet (UV) initiated cross-linking have all been employed for various applications [1–4]. Each type of cross-linking has its own set of advantages and disadvantages.

One way to effectively improve cohesive strength of an adhesive is by ionic cross-linking. Ionic cross-linking offers the following benefits:

- No need for special curing equipment.
- No interference from pigments or fillers.
- Thickness of the adhesive is not limiting the curing efficiency or process speed.
- Cross-linking may be thermally reversible, or in some cases it may also be used to thermoset a formulation.

Ionic cross-linking may be achieved by introducing metal ions into an acid-containing adhesive or by generating acid/base interaction between polymer chains. This article focuses on the use of acid/base interaction, its effect on PSA performance, and the rheological characteristics that result from this interaction.

METHODOLOGY

The objective of this research project was to develop an ionic cross-linking method for use in a variety of hot-melt adhesive formulations while also allowing for easy adjustment of the strength and density of the network. Although this work is focused on acid/base cross-linking of an acrylic PSA, the cross-linking mechanism can be extended to other types of chemistries and adhesives provided acidic or basic functional groups are present in the adhesive components.

To facilitate evaluation of formulations on a laboratory scale, the components were mixed in solvent, knife coated, oven dried, and tested. Peel performance, shear holding power, and rheological behavior were employed to study the effectiveness of the cross-linkers in the various compositions. The rheology was used to predict hot-melt processibility, which was later confirmed in an actual hot-melt coating experiment.

Polymer Synthesis and Characterization

Both the acrylic PSA polymer and the basic, acrylic cross-linking polymers were prepared using standard solution polymerization techniques in ethylacetate or methylethyl ketone using azo-isobutyronitrile (AIBN) thermal initiator and commercially available monomers. The monomers used include isooctylacrylate (IOA), acrylic acid (AA), and N,N-dimethylaminoethyl methacrylate (DMAEMA). The polymers were characterized using inherent viscosity (IV) measurements in ethylacetate solvent at a concentration of 0.2 g/dl with a Cannon-Fenske viscometer mounted in a water bath held at 27°C.

The solution polymers used in this study are summarized in Table 1.

Other basic cross-linking materials that were used include a 700-molecular-weight polyethyleneimine (PEI) available from Sigma-Aldrich (Milwaukee, WI, USA) and dicyandiamide (DICY) available from Alpha-Aesar (Ward Hill, MA, USA). The generic structure of these two materials is shown in Figure 1.

To adjust the rheology of the adhesive, ECR180 (an experimental aromatic tackifier derived from a C9 monomer stream made by Exxon, Baton Rouge, LA, USA) and Santicizer® 141 (a phosphate ester available from Ferro, Walton Hills, OH, USA) were used.

Sample Preparation

Because of the strong acid/base interaction between the 90/10 IOA/AA and the basic cross-linkers, it was often very difficult to coat

TABLE 1 Acrylic Polymer Compositions and Inherent Viscosities

Composition	IV (dl/g)
90/10 IOA/AA	0.7
40/60 IOA/DMAEMA	0.43
89.1/1.2/9.7 IOA/DMAEMA/AA	0.65
40/58/2 IOA/DMAEMA/AA	0.45

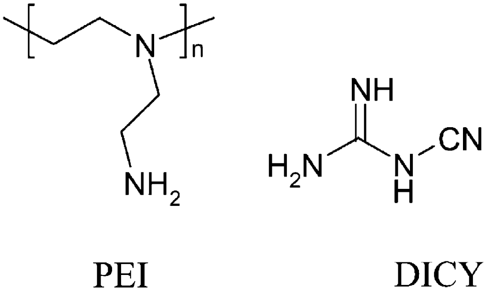


FIGURE 1 Polyethyleneimine (PEI) and dicyandiamide (DICY).

the materials directly from solvent, and indeed melt mixing and coating is preferred. However, for lab-scale experimentation, it is sometimes desirable to mix the materials in solvent and coat them as hand spreads. To avoid premature gelation of the mixture in solvent, we neutralized the 90/10 IOA/AA polymer first with the help of triethylamine. This allowed us to mix the materials with the basic cross-linker and coat them on the desired backing or release liner for testing. Alternatively, one can also neutralize the basic cross-linker first with formic acid and add the acidic polymer component next. It is important to dry the coating at a sufficiently high temperature to allow the neutralizing agent to be displaced and the polymer interaction to be established. DICY is not very soluble at room temperature, and it can be dispersed in the adhesive just prior to coating without the use of a neutralizing agent.

To calculate the individual charges of each component in the final adhesive samples, we used their dry weights. The 90/10 IOA/AA polymer was typically the starting material for adhesive blending and all other charges were calculated as parts by weight per hundred parts by weight of this polymer.

For rheological testing, samples were typically knife coated on a silicone release liner and layered to create the required thickness for testing. For adhesive property testing, the solutions were knife coated on a 37.5-micron-thick, primed polyester film to yield a dry adhesive thickness of about 25 microns.

Adhesive Property Testing

Although more detail may be found in the ASTM D-3330 standard, the peel test was typically carried out as follows: the tape is conditioned at 23°C and 50% relative humidity for one day. Next, the tape is rolled down with a 2-kg standard roller onto a clean glass substrate, allowed to dwell for 1 min, and clamped with the testing fixture of an I-Mass^{TM} peel tester. The peel force (in Newtons/decimeter) at 180° peel angle and 229 cm/min peel rate is reported.

Shear testing was performed following ASTM D-3654. A 1.27-cm-wide sample of the conditioned tape is rolled down with a 2-kg rubber-covered roller on a polished 302 stainless steel panel. The tape is trimmed to provide a 1.27-cm square overlap with the panel. The panel is fixed in a 2° tilted back position, so that there is no element of low angle peel in the test. A 1-kg weight is fixed to the free end of the tape and the time to failure (*i.e.*, complete detachment from the plate) is measured. Unless the shear holding was more than 10,000 min (at which point the test was discontinued), the failure modes were all cohesive.

To get a better idea about the effect of cross-linking on the tack of the adhesive, probe tack measurements were made on the adhesive samples following ASTM D-2975 using a Polyken Probe Tack tester. Tape samples were applied to a 20-g annulus, probe contact was maintained for 1 s, and the probe was pulled back at a speed of 1 cm/s to give the pull-off force in grams. The reported data is an average of five measurements.

The rheological characterization was performed on a Rheometrics/TA Instruments ARES rheometer (New Castle, DE, USA). Dynamic temperature step (3C, 30-s soak time) scans were performed using 8-mm parallel plates at a frequency of 1 Hz and run from 30°C down to –50°C and from 20°C to 200°C. Several of the samples were run repeatedly to verify the thermoreversibility of the cross-linkers, and within the time frame of the test conditions and precision of the rheometer there were no significant differences found between the DMA properties during repeated thermal cycles.

DISCUSSION OF RESULTS

For the purpose of this study, we solution-blended several basic materials with an acidic PSA component. Although hot-melt blending was our ultimate target, solution blending was much more convenient on a small scale, and the hot-melt processibility characteristics could easily be predicted from the rheological measurements. Actual hot-melt coating was independently carried out and found to confirm the predictions made. In all our experiments, we selected the acid-containing polymer as the major and pressure-sensitive component. Clearly, the PSA polymer component does not have to be the 90/10 IOA/AA material we used in our experiments, and indeed as long as the PSA polymer contains an acidic comonomer such as a carboxylic acid, a sulfonic acid, or similar, the material can be cross-linked with a basic material. Similarly, it is not necessary that the PSA component is acidic in nature, and indeed a basic PSA polymer can be used for cross-linking with an acidic polymer.

The basic cross-linkers used in this study are of three different types:

- Acrylic copolymers containing a strong, tertiary amine comonomer. We either used a 40/60 IOA/DMAEMA copolymer or a 40/58/2 IOA/DMAEMA/AA terpolymer where the basic monomer is in molar excess relative to the acrylic acid.
- A 700-molecular-weight PEI, a branched polymer derived from ethyleneimine containing primary, secondary, and tertiary amines.
- DICY, a nonpolymeric, primary amine functional material that is not soluble in the acrylic solution and remains heterogeneous until heated during oven drying, where it can intimately mix with the acrylic polymer.

To allow for additional comparison, we also included a standard solution-coated formulation where we cross-linked the adhesive during the drying step using CX-100 (a polyfunctional aziridine cross-linker available from DSM–Neoresins, Wilmington, MA, USA). Note that the basic cross-linkers are in essence nonvolatile (allowing for hot-melt processing) but by themselves not necessarily PSAs in nature. Each of these materials contains amine groups that are clearly basic in nature and can be titrated with an acid for easy determination of the basic molar content. As is demonstrated in the more detailed discussion, the actual nature of the amine group (primary, secondary, tertiary) in the cross-linker is an important variable that allows the adhesive formulator to chose between a thermoreversible type of cross-linking site and one that thermosets. The acid/base interaction between the two adhesive components is shown in Figure 2 (with the structure of the basic monomer DMAEMA included).

Table 2 summarizes the formulation, the PSA properties, and some of the rheological properties for the different samples that were used in this study.

Analysis of the results reveals that without any cross-linking the 90/10 IOA/AA solution polymer (sample A) shows aggressive tack, good peel strength against glass, but only low shear holding power and cohesive failure. By cross-linking the adhesive with the reactive aziridine, the tack decreases and the peel strength is reduced, but the cohesive strength improves significantly as demonstrated by the enhanced shear holding (reference sample). This behavior is typical for covalently

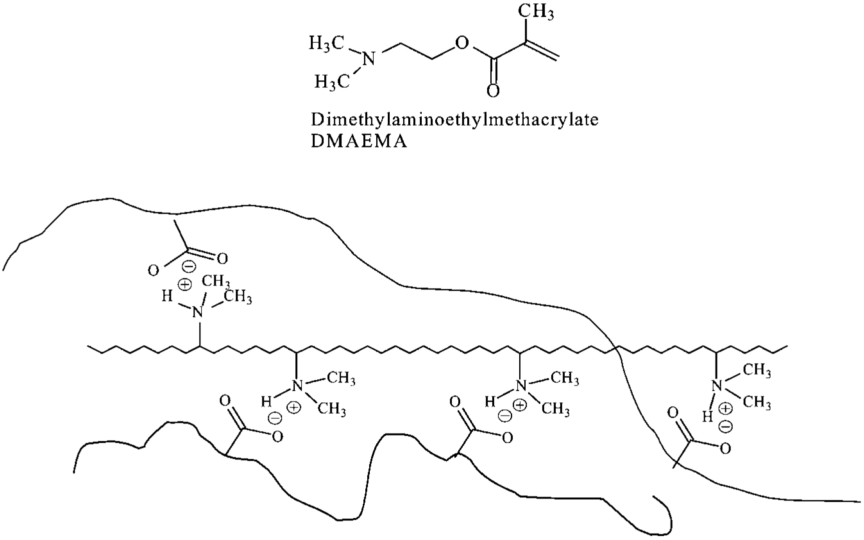


FIGURE 2 Acid/base interaction between the adhesive components. (Reprinted with permission from *Adhesion Science and Engineering 2, Surfaces, Chemistry and Applications, Pressure Sensitive Adhesives*, pp. 464–534. Copyright 2002 Elsevier.)

cross-linked solution adhesives. The 40/60 IOA/DMAEMA polymer (sample B) used as one of our cross-linking components is very soft and also offers poor adhesive properties. However, blending of two parts IOA/DMAEMA copolymer into 100 parts of the 90/10 IOA/AA adhesive provides a very significant gain in cohesive strength with this new composition (sample D), now showing shear holding in excess of 10,000 min. Unfortunately, this gain in cohesive strength also comes at the expense of tack, which at 398 g is significantly lower than what was measured for both the aziridine cross-linked and the uncross-linked adhesive. Similarly the peel has dropped from about 67 N/dm width to about 29 N/dm width. This significant change in properties is a clear demonstration of the very strong interaction between the acid in the PSA component and the base in the cross-linker.

To try to recover some of the peel performance, this same sample was further formulated with a combination of a tackifier and a plasticizer to maintain a similar T_g. The new sample, E, indeed showed a gain in tack and peel performance without giving up the cohesive strength, indicating that when properly chosen the presence of these additives does not detrimentally disrupt the acid/base interaction between the two polymers.

TABLE 2 Adhesive and Rheological Properties of the Different Compositions

Sample	Polymer component A	Cross-linker	Parts cross-linker	Additives	Parts of additive	Tack (g)	Peel (N/dm)	Shear (min)	Cross-over temperature (°C)
Reference	90/10 IOA/AA	CX-100	0.15			563	49.3	10,000 +	None
A	90/10 IOA/AA		0			712	66.9	65	129
B	40/60 IOA/ DMAEMA		0			NM	0.4	20	96
C	89/1.2/9.8 IOA/ DMAEMA/AA		0			603	53.2	39	111
D	90/10 IOA/AA	40/60 IOA/ DMAEMA	2			398	28.6	10,000 +	None
E	90/10 IOA/AA	40/60 IOA/ DMAEMA	2	ECR 180/ Santicizer 141	15/5	508	41.8	10,000 +	169
F	90/10 IOA/AA	40/58/2 IOA/ DMAEMA/AA	2			412	36.4	10,000 +	None
G	90/10 IOA/AA	PEI	2			NM	Not PSA		None
H	90/10 IOA/AA	DICY	2			NM	Not PSA		None

NM = Not measured.

When compared with sample C, samples D and E use equimolar amounts of each of the IOA, AA, and DMAEMA components. Yet, sample C shows much lower cohesive strength than either one of these samples. Sample C relies on intramolecular acid/base interaction, whereas the other samples are polymer blends allowing for intermolecular acid/base cross-linking. Because the terpolymer used in sample C has a similar IV to the 90/10 IOA/AA component in the blends, we conclude that the intermolecular cross-linking is more effective.

Finally, in sample F, we used the 40/58/2 IOA/DMAEMA/AA terpolymer as the cross-linking component. When compared with sample D, the adhesive performance is very similar, suggesting that presence of a small amount of acid in the cross-linker does not interfere with the intermolecular cross-linking process as long as an excess amount of base is maintained.

The rheological data not only support the observed adhesive performance, but they also indicate that the acid/base interaction acts as a reversible cross-linker for the adhesive. The storage modulus (G′) and tan(δ) ($= G''/G'$) *versus* temperature are shown in Figures 3 and 4, respectively, for the 90/10 IOA/AA (sample A) and 40/60 IOA/DMAEMA (sample B) polymers, along with the reference adhesive used in this study.

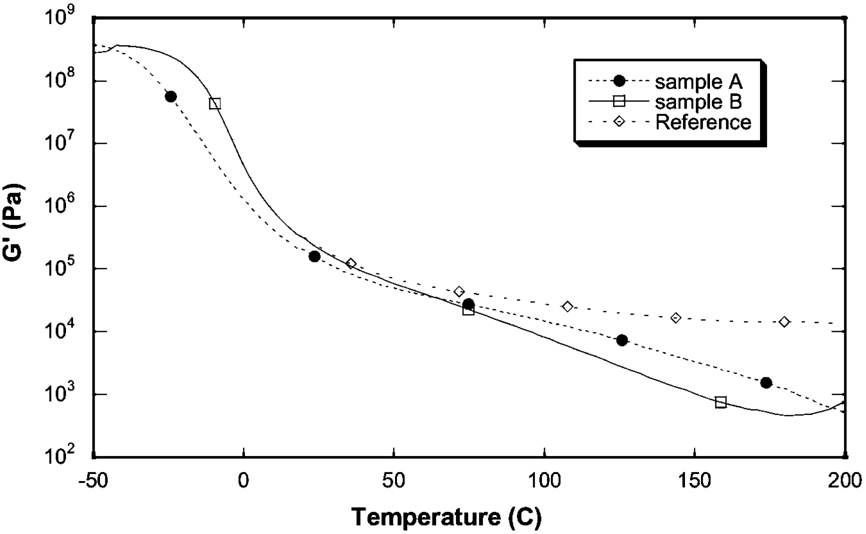


FIGURE 3 Storage modulus as a function of temperature for samples A and B and the reference.

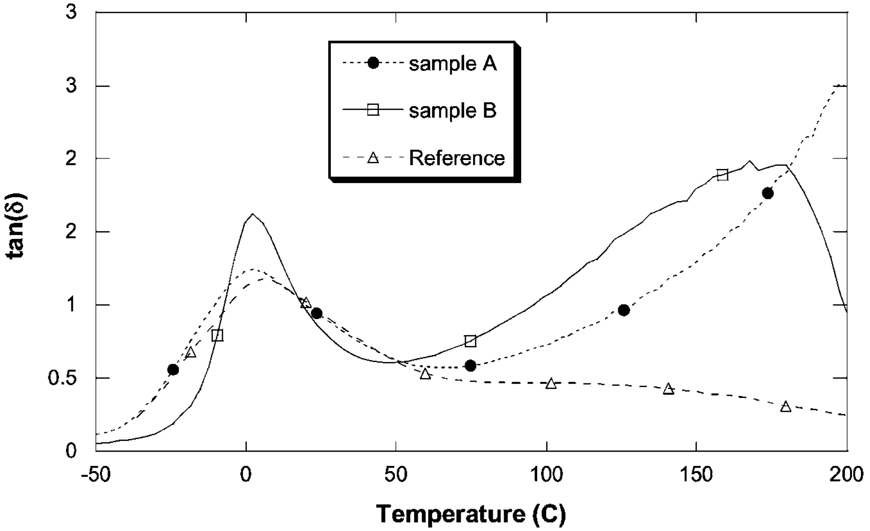


FIGURE 4 Tan(δ) as a function of temperature for samples A and B and the reference.

The ratio of loss modulus (G″) to storage modulus (G′), tan(δ), is used to assess the relative fluidity of the materials. For tan(δ) values greater than 1, the material can be considered more of a viscous fluid than an elastic solid. Figure 3 shows behavior typical of uncross-linked polymers; the modulus decays rapidly after passing through T_g. One criterion of processibility is the temperature at which the storage modulus G′ equals the loss modulus G″. This criterion only applies to temperatures above the glass transition temperature(s) of the polymer or polymers in a phase-separated compound. For the 90/10 IOA/AA polymer this crossover temperature was 129°C, where for the 40/60 IOA/DMAEMA it was 96°C. The crossover temperature also has implications with regard to the molecular architecture: for a given polymer composition, a higher crossover temperature implies a higher molecular weight or evidence that the material is cross-linked (*i.e.*, the material will not become a liquid at temperatures lower or times shorter than the crossover temperature/time). The reference adhesive shows behavior typical of cross-linked materials (relatively constant storage modulus at temperatures above T_g, along with lower tan(δ) values).

The results for samples C–F are shown in Figures 5 and 6.

Blending the 90/10 IOA/AA with the 40/60 IOA/DMAEMA (sample D) shows the effectiveness of the ionic cross-linking (the absence

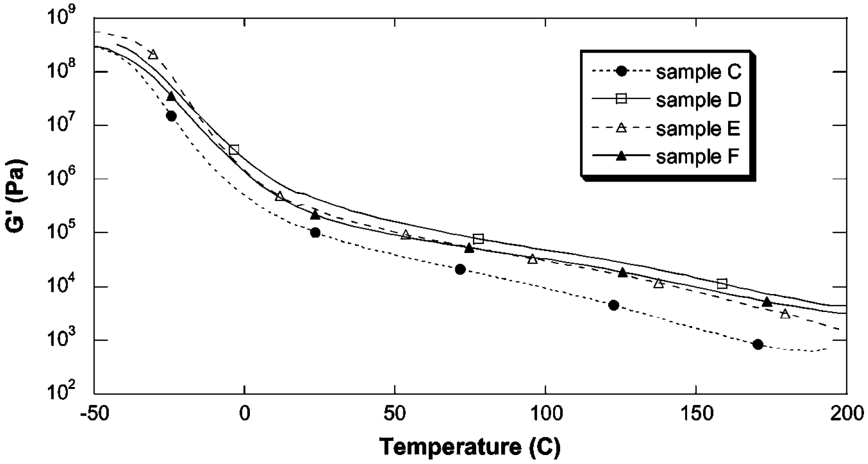


FIGURE 5 Storage modulus as a function of temperature for samples C, D, E, and F.

of a crossover temperature up to 200°C) with a slight increase in the rubbery plateau modulus *versus* the 90/10 IOA/AA by itself. Although not shown here, reducing the amount of the IOA/DMAEMA component in the blend brings the crossover temperature down. Very similarly, the processibility of the ionically cross-linked adhesive can be improved by proper formulation with tackifiers and plasticizers. In

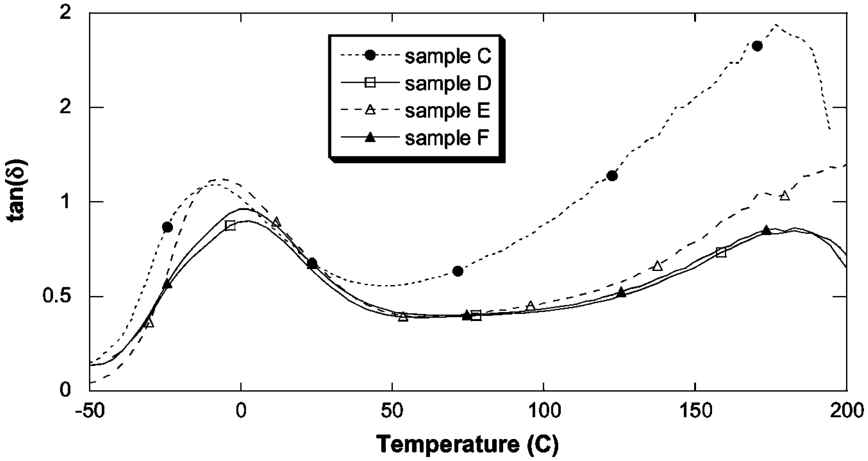


FIGURE 6 Tan(δ) as a function of temperature for samples C, D, E, and F.

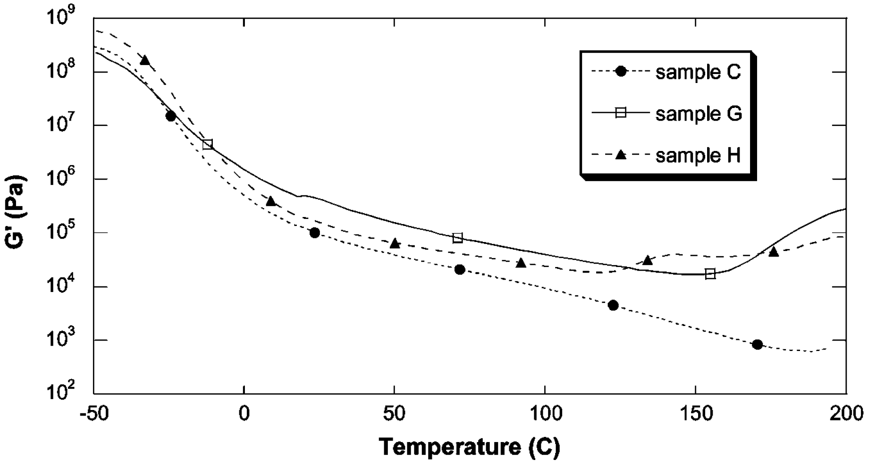


FIGURE 7 Storage modulus as a function of temperature for samples C, G, and H.

this sample, E, the crossover temperature is indeed brought down to 169°C. As already seen for the PSA properties, the addition of a small amount of acrylic acid to the basic copolymer does not appear to affect its effectiveness in the blend with the 90/10 IOA/AA copolymer (sample F). Finally, sample C, having equimolar amounts of the acid and base to the blends, shows a crossover temperature of only 111°C *versus*

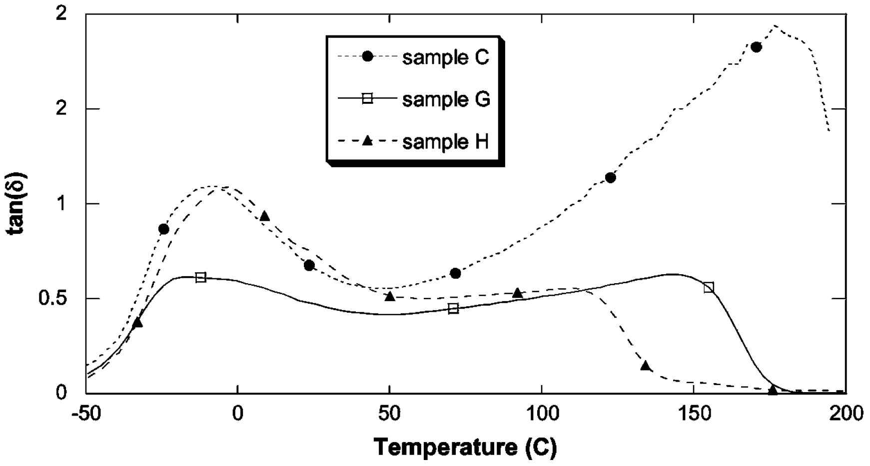


FIGURE 8 Tan(δ) as a function of temperature for samples C, G, and H.

a crossover in excess of 200°C for the blend, again indicating reduced effectiveness of the intramolecular cross-linking.

Samples G and H were not tested for peel or shear because when exposed to heat in the rheometer they clearly start to thermoset. Figures 7 and 8 indeed show the characteristic rise in modulus and divergence of G'/G'' as the samples are heated to elevated temperature. Because of the nucleophilic nature of the primary and secondary amine groups in the cross-linker, permanent cross-linking sites are generated in the form of covalent bonds.

CONCLUSION

It has been demonstrated that blending of a basic cross-linker with an acid functional PSA is an effective way to increase the cohesive strength of the material. Rheological evidence suggests that the onset of flow can be controlled in these materials by proper formulation of the blends. In contrast to block copolymers, the onset of flow is not controlled by the T_g of the polymer but by the strength of the acid/base interaction, making adhesive formulation with higher service temperatures possible. When primary or secondary amine functionality is present in the cross-linker, a thermosetting adhesive can be obtained when heated to elevated temperatures. When only tertiary amines are used in the cross-linker, a thermoreversible network is maintained. Typically, the acid/base interaction between functional monomer units is strong, and indeed the amount and type of interaction will need to be controlled to allow for hot-melt processing without degrading the polymer. Tackifiers and plasticizers can be used to adjust the rheology of the material without interfering with the cross-linking mechanism. This allows the adhesive formulator to achieve a better balance of peel, tack, and shear holding power for the final blend. Rheological data demonstrate the effectiveness of the acid/base interaction and provides evidence that these types of blends retain their hot-melt processibility.

REFERENCES

[1] Rehmer, G., Boettcher, A., and Portugall, M. US patent 5,264,533, November 23, 1993.

[2] Su, S., Ozari, Y., Vargas, R. R., and Lum, H. Jr., US patent 5,252,662, October 12, 1993.

[3] Auchter, G., Barwich, J., and Jager, H., *Adhesive Age* July, **37** (8), 20–25 (1994).

[4] Ramharack, R. and Chandran, R., US patent 5,536,759, July 16, 1996.