International Journal of
Adhesion &
Adhesives

ELSEVIER

Miniemulsion polymerization of acrylated methyl oleate for pressure sensitive adhesives

Shana Bunker[a], Christelle Staller[b], Norbert Willenbacher[b], Richard Wool[a],*

[a] *Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA*
[b] *BASF Akiengesellschaft, 67056 Ludwigshafen, Germany*

Abstract

The focus of this work was to improve the aqueous emulsion polymerization of a highly water-insoluble monomer derived from plant oil, acrylated methyl oleate. Conventional emulsion polymerization requires excessive amounts of surfactant and long reaction time. Miniemulsion polymerization improved the polymerization significantly. Only a fraction of the surfactant and reaction time that was necessary in the conventional emulsion polymerization is required. The resulting polymers have properties comparable to petroleum-based polymers commonly used in pressure sensitive adhesive applications.
© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: A. Pressure sensitive; Miniemulsion polymerization; Renewable; Plant oil; Methyl oleate; Fatty acid

1. Introduction

The demand for pressure sensitive adhesives (PSA) has been increasing over the last several years. PSAs are almost indispensable in everyday life as they are used for labels, tapes, films and other special adhesive applications. Currently, the majority of PSAs are made from petroleum-based acrylate monomers, such as 2-ethyl-hexyl acrylate, *n*-butyl acrylate, and isooctyl acrylate [1]. To alleviate this dependency on petroleum, it is desirable to investigate the synthesis of these adhesives from a renewable resource, such as plant oil. Plant oils are triglyceride esters of fatty acids which vary in chain length and functionality. Their chemical versatility and abundancy make them an ideal starting material [2]. The most common oils have a carbon–carbon double bond functionality. An example of a triglyceride molecule is shown in Fig. 1.

The double bonds of unsaturated fatty acids have traditionally been used for oxidative coupling reactions leading to "air drying" of some plant oils. This is the chemistry of the well-known alkyd resins used for paint and varnish binders. While there are many examples for the use of drying oils for surface coating applications, the unsaturation on the fatty acid is not sufficiently reactive to allow homo- or co-polymerizations of the molecule directly to give resins with any degree of structural strength or stiffness. However, both triglycerides as well as individual fatty acids can be chemically modified in order to participate in free radical polymerization reactions. The fatty acid molecule offers a number of reactive sites for functionalization. These include the double bond, the allylic carbons, the ester group, and the carbon alpha to the ester group, as shown in Fig. 1. Typical modifying reactants include maleic acid, maleic anhydride, methacrylic acid and acrylic acid [3]. Besides conventional bulk polymerization, these components can also be polymerized using emulsion polymerization, a common practice used in the PSA industry. Solution polymerization should work as well. However, the PSA industry has moved towards eliminating solvent based material for ecological and economical reasons. Therefore, this work focused on optimizing a water based emulsion system.

The polymer in a pressure sensitive adhesive is a viscoelastic material that is permanently as well as aggressively tacky and has enough cohesive strength and elasticity to be cleanly removed from a substrate surface
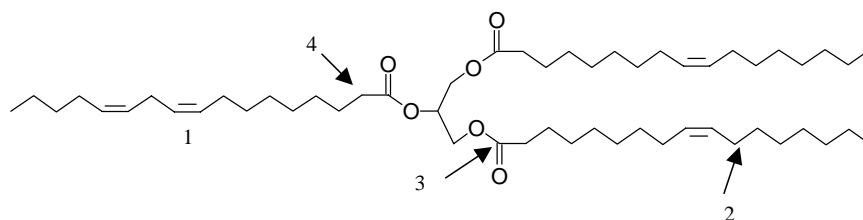
Fig. 1. Diagram of a triglyceride molecule. A triglyceride is composed of three fatty acids connected at a glycerol center. The different functionalities are shown with the corresponding numbers; (1) double bond, (2) allylic carbons, (3) ester group, and (4) alpha carbon.

[1]. These polymers are typically linear polymers with a slight degree of cross-linking. The degree of cross-linking is one of the key features controlling the balance between cohesive and adhesive strength of the polymer. Monomers derived from plant oils possess an inherent degree of unsaturation that varies from plant to plant. The variation of unsaturation among the various plant oils, and hence the fatty acids, can be used to advantage. Depending on the property desired in the final product, various oils, or mixtures thereof, may be used in synthesizing the monomers. Functional groups to increase adhesive strength can also be placed onto the unsaturation sites.

Previous work in this area focused on synthesizing a monomer from a fatty acid methyl ester that is capable of forming high molecular weight polymers using conventional (macro) emulsion polymerization [4]. This technique suffers from the high amount of surfactant needed, approximately 15 wt% and the slow reaction kinetics, which is due to the low solubility of the monomer in water, approximately 10^{-7} M [4]. Current work further improves the emulsion polymerization of this monomer by using miniemulsion polymerization techniques. Miniemulsion is an appropriate polymerization method for highly hydrophobic monomers because each droplet can be considered a mini-batch reaction for the polymerization [5]. This is different than conventional emulsion polymerization that has both monomer droplets and polymer particles. The conventional emulsion requires the transport of water-insoluble monomers from droplets to growing polymer particles, which can yield slower kinetics and therefore longer polymerization times [5,6]. The work presented here demonstrates an improved polymerization process compared to previously reported results [4]. Miniemulsion polymerization usually requires the addition of a co-surfactant, specifically either a long chain alkane (e.g. hexadecane) or alcohol (e.g. hexadecanol). Essentially, the co-surfactant helps to limit the diffusion of the oil phase from smaller to larger droplets by virtue of its low aqueous solubility. Diffusion out of the particle is proportional to the monomer concentration in the aqueous phase and therefore due to the low water solubility of the monomer used in this work, a co-

surfactant was not required. The reaction time, as well as required surfactant amount, is significantly decreased using miniemulsion polymerization. The emulsions formed using the technique presented in this paper were stable for several months.

In addition to the processing improvement, the physical properties of the resulting polymers are also improved. The mechanical and adhesive properties of polymers derived from conventional and miniemulsion polymerizations are compared. Mechanical properties of the renewable resource based dispersions are also compared to two petroleum-based dispersions. The first one is a market standard for filmic labels application, Acronal® A220 (www.basf.de/dispersions/) which is known for its high transparency, excellent water resistance and outstanding adhesion to polyolefinic substrates. The second is a model dispersion of 2-ethylhexyl acrylate (2-EHA)-co-methyl methacrylate (MMA). This system was selected because the 2-EHA is one of the acrylate monomer typically used for PSAs and has similar structure to the fatty acid methyl ester based monomer (branched long hydrophobic side chain).

2. Experimental

2.1. Materials

The main monomer used in this work, acrylated methyl oleate (AMO), was synthesized using methods previously reported [4]. A schematic of the monomer synthesis is shown in Fig. 2. The emulsifier sodium lauryl sulfate (SLS) (15 wt% aqueous solution) (Aldrich) and the initiator, 2,2′-Azobis (2-methybutyronitrile) (Vazo 67, Dupont) were used as received. Reagent grade methyl methacrylate (Aldrich), 1,4-butanediol diacrylate (Aldrich) and 2-ethylhexyl acrylate (Aldrich) were also used as received. Materials used for the conventional emulsion polymerization include the surfactant, sodium dioctyl sulfosuccinate (Aerosol® OT, Aldrich), and the initiator, 2,2′ azobis (2-amidinopropane dihydrochloride (V-50, Wako Pure Chemical Industries).
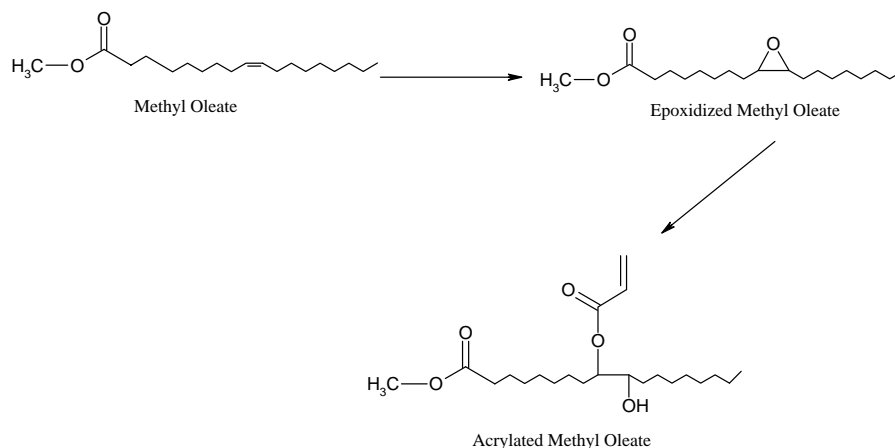
Fig. 2. Schematic diagram of the monomer synthesis steps.

Table 1
Emulsion compositions

Component	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Conventional
DDI H$_2$O (g)	40	40	40	40	40	30
SLS (15 wt%) (g)	1.33	1.33	1.33	1.33	1.33	2.25 g Aerosol® OT
AMO (g)	10	9	8.5	8.0	—	15
MMA (g)	—	1	1	1	1	0.5 g Acrylic Acid
BDDA (g)	—	-	0.5	1	—	—
2-EHA (g)	—	—	—	—	9	—
Vazo 67 (g)	0.1	0.05	0.05	0.05	0.05	0.05 g V-50
Emulsion droplet size (nm)	390	350	380	420	780	>1000
Particle diameter (nm)	350	350	380	400	800	>1000
K_{value}	26.8	42.7	NA	NA	NA	26.6
T_g (°C)	−49	−49	−50	−46	−58	−39

The monomer purity was examined using gas chromatography (GC)-Fourier transform infrared spectroscopy (FTIR) coupling technique as well as GC-mass spectroscopy (MS) in order to be able to clarify the structure of possible side products. To limit the interactions between the monomer and the GC column, the hydroxyl group of monomer was reacted with n-methyl-n-(trimethylsilyl)trifluoracetamid for 2 h at 80°C. A 1 µl sample was injected for the GC/IR coupling into a CP-Sil-5 CB 30 m column with a temperature profile 150°C/3 min/15°C/300°C/30 min. The GC/MS coupling was performed on a DB-1 30 m column with a temperature profile 150°C/3 min/15°C/300°C/30 min.

2.2. Polymerization techniques

2.2.1. Macroemulsion polymerization

In this work, the AMO monomer is polymerized using both macroemulsion (also referred to as conventional emulsion polymerization) and miniemulsion polymerization. The experimental conditions for the macroemulsion polymerization is outlined in detail in Bunker et al. [4]. The formulation of the macroemulsion is shown in Table 1. The reaction time was approximately 18 h at 70°C.

2.2.2. Miniemulsion polymerization

The specific formulations for each miniemulsion polymerization are listed in Table 1 (samples 1–5). The polymerizations were conducted in a 500 ml round bottom flask equipped with a reflux condenser, nitrogen inlet, and a Teflon stirrer. First, the initiator was combined with the monomer using a magnetic stirrer, to ensure its complete dissolution in the monomer phase. After the initiator dissolution, the surfactant and water were mixed into the system using a magnetic stirrer for approximately 10 min. The miniemulsion was then prepared by continuous ultrasonification for 5 min. During sonification, the emulsion was submerged in an ice bath to maintain a temperature below 50°C. This ensured that the initiator did not prematurely decompose. The glass reactor containing the monomer emulsion was then placed in an oil bath and heated to 85°C for 1 h.

2.3. Polymer characterization

The conversion of monomer to polymer was analyzed using FTIR spectroscopy. A Mettler-Toledo/ASI Applied Systems ReactIR™-1000 was used to collect an ATR spectrum at $2\,cm^{-1}$ in 64 scans at $80°C$. This technique collects the spectra in situ and therefore can be used to observe the reaction progression as a function of time. The peak associated with the polymerizable carbon–carbon double bond is located at $1406\,cm^{-1}$ and decreases in intensity during the reaction. Also during the reaction, the carbonyl group $(C=O)$ in the polymer shifts to the $1737\,cm^{-1}$ location and increases in intensity. Therefore, recording the development of these two peaks will allow the monitoring of the reaction progression.

Particle size of the monomer emulsions and polymer dispersions were examined using a Coulter® N4 Plus particle size analyzer. This instrument is based on the principle of dynamic light scattering [18] which takes advantage of the size dependence of the Brownian motion of colloidal particles as reflected in the intensity fluctuation correlations of scattered laser light. The mean diameters of the emulsions and dispersions are listed in Table 1.

The viscosity of a dilute polymer solution is a measure of the capacity of a polymer molecule to enhance the viscosity of the given solution. This increase of viscosity depends on the size and shape of the polymer molecule. Within a given series of polymer homologues, viscosity increases with the molecular weight. Accordingly, the average molecular weight can be determined from intrinsic viscosity measurements utilizing so-called Mark–Houwink relationships [7]. Here we have done a relative comparison of molecular weights based on a single concentration viscosity measurement. The viscometer was a Micro-Ubbelohde type M-Ic and the kinematic viscosity, v, calculated from the measured time of flow t_c as $v = 0.03119t_c$. Measurements were performed at $25°C$ with a polymer concentration of $1\,g/100\,ml$ in tetrahydrofuran. The viscosity, v, was converted to a representative K-value according to ISO 1628-1. The uncertainty in the K-values is about 1% (according to ISO 1628-1). This conversion allows for a comparison of samples with similar composition. Therefore, only the values for the polymers that were derived from AMO monomer are reported in Table 1.

The glass transition temperature was determined by differential scanning calorimetry (DSC) using a Mettler-Toledo 820. A temperature ramp between $-100°C$ and $150°C$ at $20°C/min$ was used. The system was calibrated using three standards: cyclopentane, water, and indium. The polymer in this analysis was obtained from the dispersion by evaporating the water. Therefore, the resulting sample includes the surfactant.

The linear viscoelastic properties were examined within the temperature range from $-60°C$ to $130°C$. From $-60°C$ to $-20°C$, a Rheometrics RDA (transducer 2 K STD) dynamic mechanical analyzer was used. The range from $-20°C$ to $130°C$ was covered with a Rheometrics ARES (transducer 2 K FRTN1). Both machines were necessary due to the limitations of their force transducers. In both cases a 8 mm parallel plate geometry was used. The linear viscoelastic moduli G' (storage modulus) and G'' (loss modulus) were determined at a fixed frequency of 1 Hz, and a strain of 0.01. Similar to the DSC characterization, the polymer was obtained from the dispersion by evaporating the water. No polymer purification technique was used.

The tack properties were measured using a Stable MicroSystems Taxt2i Texture Analyzer. Cylindrical probes (2 mm diameter) with flat ends made out of stainless steel and polyethylene, respectively, were used to examine the tack properties of approximately 50-μm-thick adhesive films. The measurements were carried out at $23°C$ with a contact time of 1 s and a contact pressure of 1.0 N. The rate of separation was 1 mm/s. Each sample was tested ten times in order to get reliable average values.

The application properties of the resulting polymers were analyzed using a 180° peel test and a 178° shear time to failure test. Both of these tests were performed on 80 μm thick adhesive films with Mylar® backing. The 180° peel tests were performed on a stainless-steel substrate in accordance with ASTM D903 [8]. The shear time to failure tests were also performed on a stainless steel substrate in accordance with ASTM D3654 [9].

3. Results and discussion

3.1. Monomer conversion

The monomer conversion as a function of time for a miniemulsion polymerization (sample 2, Table 1) is shown in Fig. 3. This plot tracks the intensity of the peak that corresponds to the carbon–carbon double bond of the monomer as well as the carbonyl group in the developing polymer. The results indicate that the reactive monomer group is completely depleted after 1 h of reaction time. This corresponds to the maximum intensity of the polymer carbonyl group. This is a significant improvement over the conventional emulsion polymerization. Fig. 4 depicts the typical conversion of monomer to polymer in a conventional emulsion reaction as a function of time, as recorded using gravitational analysis. This study indicates that 18 h of reaction is required to achieve 90% monomer conversion. Additional reaction time does not further increase this conversion.

3.2. Polymer properties

Table 1 reports the mean particle diameter of the dispersions, K-value, and glass transition temperature (T_g) of the resulting polymers. Typical dispersions prepared by miniemulsion have particle sizes between 50 and 500 nm [5]. Samples 1–4 are in this range whereas sample 5, prepared with EHA, has a somewhat larger diameter. The effect of additional sonification time and additional surfactant on the mean particle size was examined. The additional sonification time (up to 10 min) seemed to have little effect on decreasing the particle size. An increase in surfactant levels from 2 to 5 wt% also resulted in no decrease in particle size. Surfactant concentrations above this amount were not used due to the well-known detrimental effect of excess surfactant on adhesive properties [10–12]. However, in conventional emulsion polymerization, 15 wt% of surfactant was required to form a stable dispersion [4].

The K-value of the AMO homopolymer (sample 1) from miniemulsion polymerization is similar to that of the polymer synthesized using conventional emulsion polymerization. Examination of the effect of comonomer (sample 2) on the K-value indicates that the addition of comonomer greatly increases the molecular weight of the polymer. Previous research in thermosetting polymers from acrylated soybean oil (ASO) found that a comonomer is required to increase the conversion of the ASO [13]. The comonomer behaves like a chain extender as well as a reactive diluent and reduces the mass transfer limitations associated with the reaction of the bulky ASO.

All of the glass transition temperatures presented here are significantly below room temperature and are comparable to the T_g of Acronal® A220 at $-45°$C. Such low T_g is typical for PSAs and allows them to flow and quickly form a bond to a substrate at room temperature. All of the T_gs are similar except for the polymer made using conventional emulsion polymerization, which has a higher T_g. This is likely to be due to the large amount of surfactant used to stabilize the polymer particles. As previously stated, the polymers tested were not purified and therefore surfactant remained in the polymer.

3.3. Dynamic mechanical analysis (DMA)

The performance of a PSA is related to the viscoelastic response of the bulk adhesive. Storage and loss moduli for each polymer are shown in Fig. 5a and b, respectively. The storage modulus of the AMO

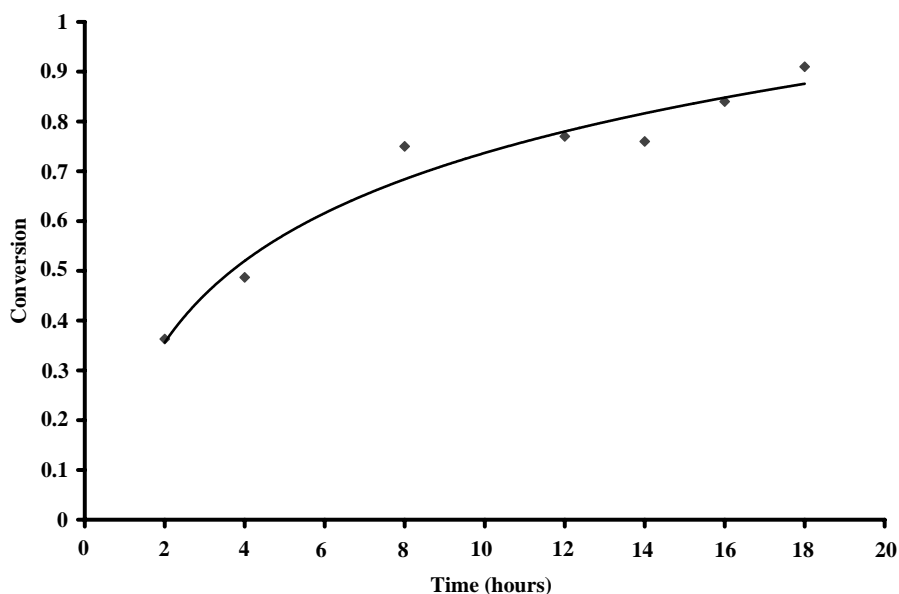Fig. 3. Conversion of monomer to polymer as a function of time (miniemulsion polymerization).

Fig. 4. Conversion of monomer to polymer as a function of time (conventional emulsion polymerization technique).
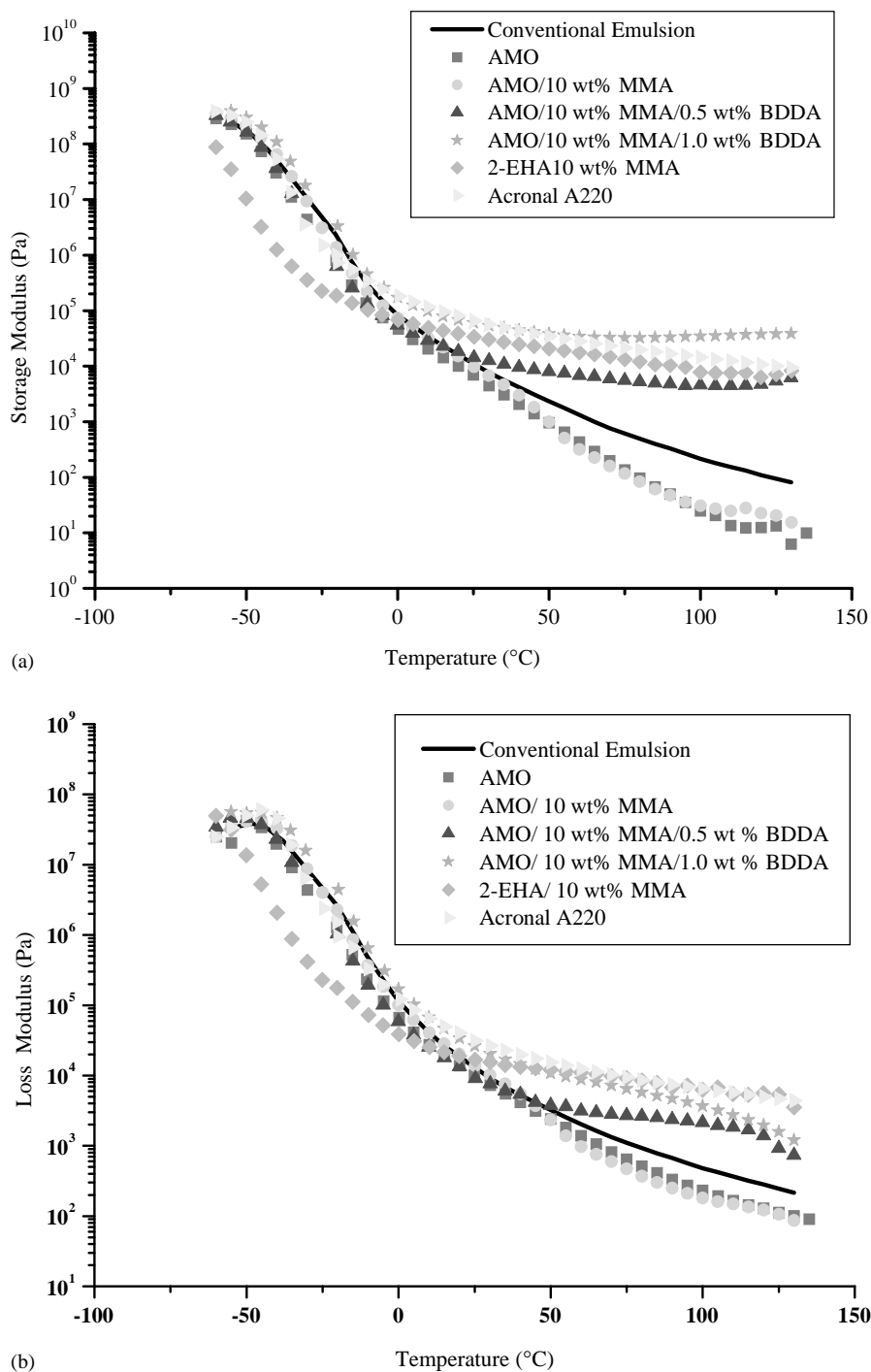
Fig. 5. The loss moduli of the polymers as a function of temperature. The descriptive labels correspond to the samples listed in Table 1. Specifically, AMO (sample 1), AMO/10 wt% MMA (sample 2), AMO/10 wt% MMA/ 0.5 wt% BDDA (sample 3), AMO/10 wt% MMA/1.0 wt% BDDA (sample 4), 2-EHA/10 wt% MMA (sample 5).

homopolymer and the AMO-co-MMA polymer are very similar. The lack of a plateau region indicates that the polymer is not crosslinked and has a molecular weight that is below or around the critical molecular weight required for physical entanglements to form. Correspondingly, the polymers will have very little cohesive strength and therefore poor shear properties, but can

easily wet even rough surfaces which is important to get good contact/adhesion.

In order to improve these properties, the molecular weight needs to be greater than the critical molecular weight for the formation of entanglements. The most obvious method to accomplish this is to decrease the initiator concentration. However, in this case the
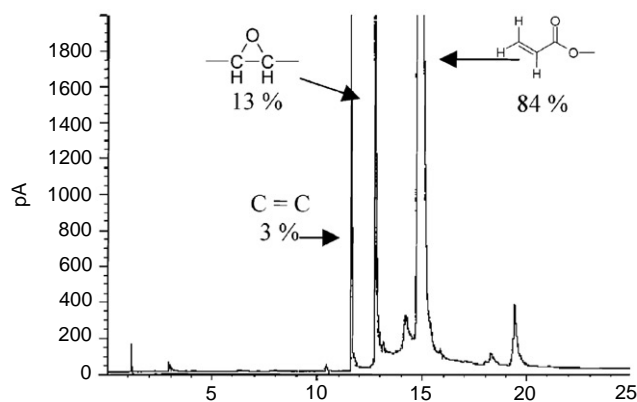
Fig. 6. GC spectra of the monomer, AMO. The monomer is composed of 84% acrylate species, 16% epoxidized species and 3% of original OME.

monomer limits the molecular weight. Although ^{1}H-NMR and ^{13}C-NMR of the AMO monomer indicated that the monomer contained 95% acrylate functionality, further analysis using GC showed that only 83% of the monomer had acrylate functionality. This discrepancy can be attributed to error in the NMR analysis. Fig. 6 shows the GC/FTIR coupling results, which give a structure for the different side products. The monomer is composed of 83% of the acrylated methyl oleate, 14% epoxidized methyl oleate (EMO), and 3% of the starting material, methyl oleate. These results were confirmed with the GC/MS analysis. As shown in Fig. 2, the EMO is the intermediate product in the monomer synthesis process. Therefore, the unreactable part, approximately 17%, will behave as a plasticizer in the polymer and reduce the mechanical and adhesive properties. Also, the unreactable components could limit the molecular weight of the polymer. Techniques to decrease the amount of EMO are currently being explored. However, even with this limitation, the polymers synthesized with the current monomer show acceptable PSA properties, as described.

Above the glass transition region, the storage modulus of 2-EHA-co-MMA (sample 5) exhibits a rubbery plateau with G' almost independent of temperature. Further, at high temperatures G' falls below G'', this behavior indicates a linear but physically entangled polymer. From G' in the rubbery zone, the mean molecular weight between entanglements is calculated to be $M_e = 60$ kg/mol, which is in good agreement with literature data [14].

The storage modulus of the polymer synthesized using conventional emulsion polymerization offers a slight improvement, indicated by the higher modulus values compared to the samples from miniemulsion polymerization. Although the K-value of the conventional polymer and the miniemulsion AMO homopolymer are similar, the differing rheological properties may be

explained by the different reaction times. As polymerization reaction times increase, branching will increase due to chain transfer to polymer via hydrogen abstraction of the tertiary backbone C–H bond [15,4]. Therefore this chain transfer and resulting branched structure will have an effect on the DMA properties as indicated in an increase in the storage modulus. Copolymerization of the stiff acrylic acid groups is another parameter expected to increase the storage modulus.

The addition of the crosslinking comonomer, 1,4-butanediol diacrylate (BDDA), to the miniemulsion system increased the modulus significantly. In fact, the resulting modulus of the AMO-MMA-co-BDDA (both the 0.5 and 1 wt%) is comparable to the commercial Acronal® A220. Comparing the modulus profiles for these samples with the uncrosslinked counterparts indicates that these polymers are indeed chemically crosslinked as G' is always higher than G'' even at high temperatures were the uncrosslinked materials start to flow. Nevertheless, the crosslink density is low enough that the plateau modulus still fulfills the Dahlquist criterion, which states that polymers to be used for PSA applications should have a plateau modulus below 3×10^5 Pa [16].

3.4. Tack

The adhesion performance of PSAs is determined by three main properties: tack, peel strength and shear resistance. Tack is a key property of PSAs and is defined as the ability of an adhesive to form a bond of measurable strength to another material under conditions of low contact pressure and short contact time [17]. Figs. 7 and 8 are bar charts of the tack properties of the polymers tested with a polyethylene and stainless-steel probe, respectively. In both cases, the conventional emulsion polymer displayed the lowest tack energy. It is well known that residual surfactant in the polymer migrates to the polymer–air surface, decreasing the tack and adhesive properties [17].

For both testing probes, the miniemulsion polymers display increasing tack values with the addition of comonomer. Against PE, the AMO-co-MMA copolymers show tack values almost as high as the petroleum-based polymers (2-EHA-co-MMA and Acronal® A220). Against stainless steel, the highest tack is observed for the sample with 0.5% BDDA. This may be due to the two carbonyl groups on the BDDA monomer that increase its attraction to a metal surface. However, there is a limit of the increase of tack with the increase of concentration of BDDA. The polymer with 1 wt% BDDA showed a significant decrease in tack value. Again, this is attributed to the balance between a polymer that has cohesive strength while at the same time flows to make an adhesive bond quickly. The 1 wt% BDDA polymer has a tight network as indicated
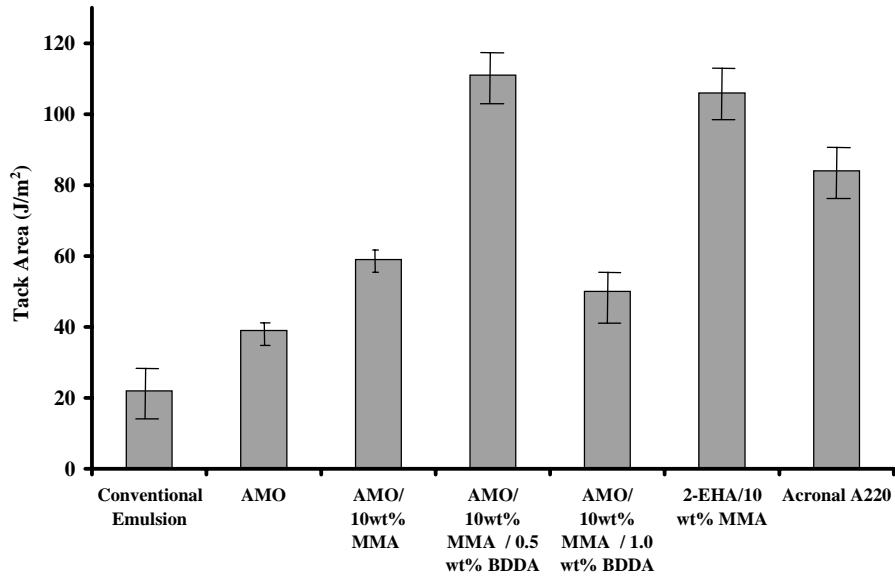
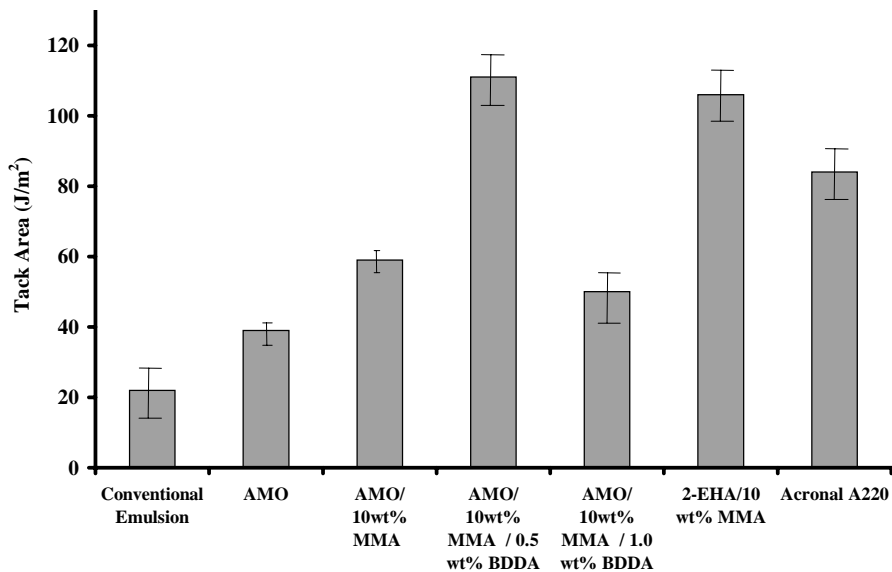Fig. 7. Tack of polymers to a polyethylene probe.

Fig. 8. Tack of polymers to a stainless-steel probe.

by the high storage modulus, providing good cohesive strength, but probably flow is so strongly restricted that it can not form a tight contact to the probe within the short dwell time. Overall, the AMO-co-0.5 wt% BDDA polymer shows comparable tack results to both the 2-EHA-co-MMA polymer and Acronal® A220.

3.5. Peel and shear strength

Fig. 9 shows the results of the peel and shear time to failure tests. The peel results of the conventional polymer, AMO-co-MMA and the 2-EHA-co-MMA are very comparable. The peel value for the conventional polymer is somewhat higher than for the other linear polymers, this is presumably due to the acrylic acid copolymerized in the conventional polymer. All of the linear polymers offer very little shear resistance, as observed with a time to failure on the order of minutes. These values are so low that they do not appear in Fig. 9b. This is even true for the 2-EHA-co-MMA polymer, which clearly had a physically entangled network based on the storage modulus, although the
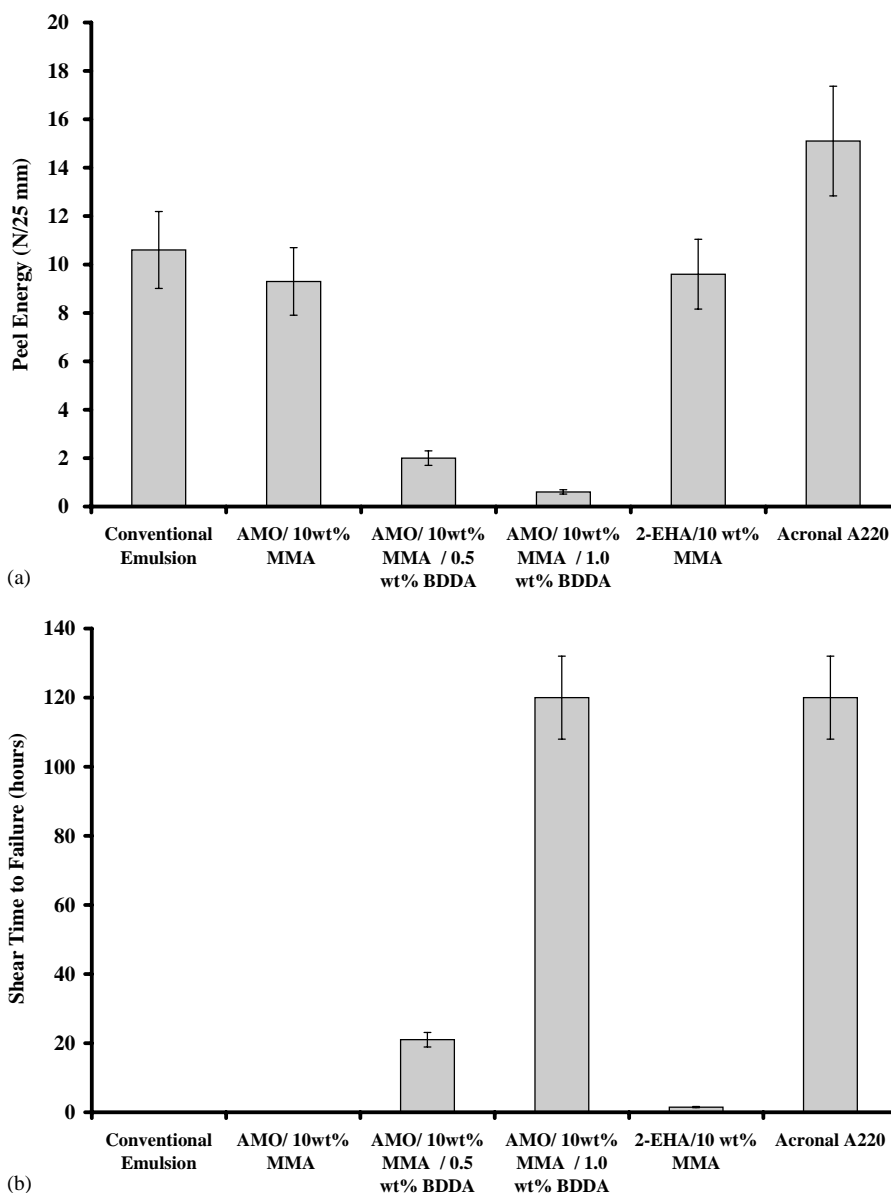
Fig. 9. (a) 180° peel test results. The peel energy is in units of N/25 mm. (b) Shear time to failure, recorded in hours.

time to failure is significantly longer than for the AMO linear polymers. Introducing chemical crosslinks is one strategy to improve the shear strength. Consequently, the chemically crosslinked AMO-copolymers did show a large increase in shear holding time, increasing from minutes to hours. However, with the increased amount of chemical crosslinking, the peel values decreased drastically. On the other hand the 2-EHA-co-MMA and Acronal® A220 show good balance between tack, peel, and shear properties, which is a result of an appropriate degree of crosslinking in combination with sufficiently high molecular weight. This clearly shows the future direction into which the development of the AMO polymers has to go, in order to yield competitive PSA materials.

4. Conclusions

Significant improvement of the polymerization of AMO latex has been achieved by using miniemulsion polymerization. The reaction time has been decreased from 18 to 1 h in addition to the surfactant concentration being reduced from 15 to 2 wt%. The resulting polymer has shown physical properties comparable to petroleum based polymers. Most importantly, the polymers derived from a renewable resource display typical PSA properties. While the AMO and petroleum based PSAs have comparable tack, shear strength and elasticity, the peel of the AMO-based polymers was lower. We believe a complete balance can be achieved by increasing the molecular weight of the AMO polymer

while maintaining an appropriate degree of crosslinking. This problem is likely to be overcome by improving the monomer synthesis technique and reducing the amount of initiator.

Acknowledgements

References

[1] Satas D, editor. Handbook of pressure sensitive adhesive technology. 2nd ed. New York: Van Nostrand Reinhold, 1989.

[2] Pryde EH. Fatty acids. Champaign: The American Oil Chemists' Society, 1979.

[3] Wool RP, et al., High modulus polymers and composites from plant oils. US patent, 6, 121, 398 (2000).

[4] Bunker SP, Wool RP. J Polym Sci: Part A: Polym Chem 2002;40:451.

[5] Lovell PA, El-Aasser M. Emulsion polymerization and emulsion polymers. New York: Wiley, 1997.

[6] Gilbert RG. Emulsion polymerization: a mechanistic approach. San Diego: Academic Press, 1995.

[7] Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook. 4th ed. New York: Wiley, 1999.

[8] ASTMD 903; Annual Book of ASTM Standards. West Conshohocken, PA: American Society for Testing and Materials, 1998.

[9] ASTM D3654; Annual Book of ASTM Standards. West Conshohocken, PA: American Society for Testing and Materials, 1998.

[10] Charmeau JY, Kientz E, Holl Y. Prog Org Coat 1996;27(1–4):87.

[11] Kientz E, Holl Y. Colloids Surf A-Physiochem Eng Aspects 1993;78:255.

[12] Zosel A, Schuler B. J Adhes 1999;70:179.

[13] Khot SN, et al. J Appl Polym Sci 2001;82:702.

[14] Zosel A. Int J Adhes Adhes 1998;18:265.

[15] Lovell PA, Shah TH. Polym Commun 1991;32(4):98.

[16] Chang EP. J Adhes 1997;60:233.

[17] Zosel A. J Adhes 1991;34:201.

[18] Berne BJ, Pecora R. Dynamic light scattering. New York: Wiley, 1976.