Formulation/Property Relationships in Radiation-Cured Poly(urethane methacrylate) Pressure-Sensitive Adhesives. II. Variation of the Chain Terminator Component

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Received 27 October 2000; accepted 5 December 2000

ABSTRACT: The synthesis of a series of radiation-curable poly(urethane methacrylate) oligomers are reported, which, on exposure to electron-beam irradiation, result in adhesive films with pressure-sensitive properties. Variation of the chain terminator component of the formulation and the effect of this on adhesive properties were investigated. Adhesive systems utilizing Dowfax 9N6 nonylphenolethoxylate, 1-(2-hydroxyethyl)-2-pyrrolidinone, 2-hydroxyethyl salicylate, or 4-(2-hydroxyethyl)morpholine as alternative chain terminators performed in a manner that may make them suitable for medical applications. Terminators with higher ethoxylation levels (Brij 35, 58) conferred high hydrophilicity on the resulting adhesives. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3321–3326, 2001

Key words: radiation curing; adhesive; poly(urethane methacrylate)

INTRODUCTION

Synthesis of commercially useful pressure-sensitive adhesives (PSAs) by solventless processes has clear environmental, energetic, and process attractions. Traditional solvent recovery techniques are rarely 100% effective, and solvent-based syntheses can be both labor intensive and lengthy. Previously, we reported the general synthesis of a new class of radiation curable PSAs[1] with properties appropriate for medical applications, and subsequently, in part one of the present series, we reported the development of this chemical system by systematic inclusion of hydrophilic species in the formulation.[2] In all the previous examples, the underlying chemistry involved the preparation of methacrylate-terminated oligourethanes followed by curing under an electron beam, producing loosely crosslinked urethane methacrylate networks. The oligourethanes were prepared by the nonstoichiometric reaction of polypropylene glycol and ethanediol, with an excess of aliphatic diisocyanate, followed by end-capping of all residual isocyanate functionalities with a mixture of hydroxyethyl methacrylate (2-HEMA) and hydroabietyl alcohol ("abitol") as a hydroxyl-functional terminator (Scheme 1). The relative proportion of 2-HEMA to abitol controls the crosslink density of the radiation-cured product and hence the performance of the cured adhesive. Thus, it will be clear from this procedure

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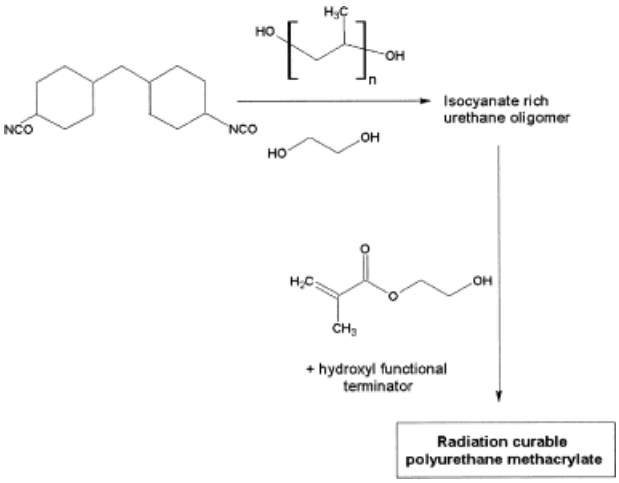
Journal of Applied Polymer Science, Vol. 81, 3321–3326 (2001)



Scheme 1 Synthetic route to radiation-curable oligomers.

that the scope for formulation modification (and hence performance control) is wide.

Abitol and esters of abietic acid can be used as blended components in traditional rubber–resin PSA formulations, where they function as tackifying additives.[3] These additives are not reacted into the adhesive in these systems, although polymers of methacrylic esters of abietic acid have been reported.[4] Abitol may cause local skin reactions in a few susceptible individuals.[5] In our previously reported formulations, we made use of the primary hydroxyl group to bind the abitol molecule to the polymer backbone. Commercial abitol is believed to contain variable amounts of nonhydroxyl functional species that may act as unbound plasticizers within our cured adhesive formulations. To eliminate this potential variable from our formulations, the present study was undertaken to evaluate other end-capping agents, available in commercial quantities, which might provide an alternative. The adhesives produced by electron-beam curing of the new poly(urethane methacrylate) oligomers were characterized by shear adhesion, peel force, and hydrophilicity tests.

EXPERIMENTAL

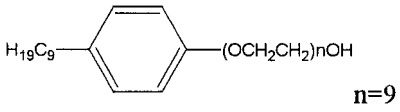
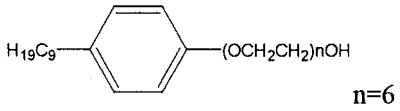
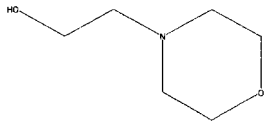
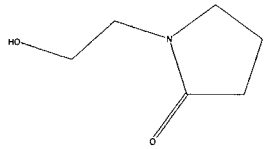
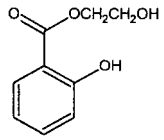
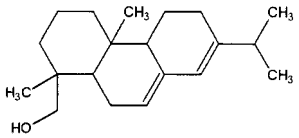
The general two-stage synthesis procedure, performed in the absence of solvent, was the same for all precursor oligomers and similar to that reported previously.[2] However, in the present study, the appropriate alternative end-capper to abitol was added in the second stage of the process. All hydroxyl functional materials were analyzed for water content and hydroxyl value before use, and all starting materials were used as received from the suppliers: PPG 2025 [α,Ω-dihydroxy-terminated poly(propylene glycol); number average molecular weight, 2025; BP Chemicals]; Desmodur W (4,4'-dicyclohexylmethane diisocyanate; Bayer AG); Abitol (Hercules Inc); Metatin 812ES (dioctyl tin dilaurate; Acima). Chain terminators were obtained from Dow Chemical Company (Dowfax range) and BP Chemicals (Brij range). Benzil dimethylketal (Irgacure 651) was obtained from Ciba-Geigy Chemicals. All other reagents were obtained from the Aldrich Chemical Company.

Oligomers were electron beam cured into thin-film form and laminated onto Melinex polyester film (average coating mass 30 $\pm$ 5 g/m^2), and the products were physically characterized as reported previously.[2] All adhesion, peel, and hydrophilicity measurements reported are the mean of three determinations. In every case, all replicate values were within 10% of each other. For hydrophilicity determinations, thicker samples were required and were cured at room temperature as bulk slabs of ~3-mm thickness under a Hanovia Fluorescence 16 UV lamp system and a nitrogen atmosphere, after being blended at 60 °C (to improve flow) with 1% w/w of benzil dimethylketal photoinitiator. The exposure time was 15 min. Samples were immersed in distilled water for 24 h, and their water uptake was measured as previously reported[2] by determination of mass increase after hydration.

Chain Terminators

A range of alternative terminators was selected. Candidates were selected on the basis of the following characteristics: primary hydroxyl monofunctionality, acceptable purity, and comparable molecular size to abitol. Linear and ring-containing species were both included. Additionally, the volatility of the terminator must be such as to preclude significant evaporative loss during oligomer synthesis at 90 °C. This requirement effectively rules out alkyl alcohols with lower boiling points, and only 1-hexanol (bp, 158 °C) was evaluated in the present study. The alternative terminators evaluated in this work are listed in Table I.

Table I Terminator Molecules

Terminator	Structure
Antarox CO 630 (ethoxylated nonylphenol)	 $n = 9$
Dowfax 9N6 (ethoxylated nonylphenol)	 $n = 6$
Brij 35 (ethoxylated lauryl alcohol)	$C_{12}H_{25}(OCH_2CH_2)_{23}OH$
Brij 58 (ethoxylated cetyl alcohol)	$C_{16}H_{23}(OCH_2CH_2)_{20}OH$
1-Hexanol	$CH_3(CH_2)_5OH$
4-(2-Hydroxyethyl)morpholine	
1-(2-Hydroxyethyl)-2-pyrrolidinone	
2-Hydroxyethyl salicylate	
Hydroabietyl alcohol (abitol)	

DISCUSSION

The aim of this work was to evaluate the direct mole-for-mole replacement of abitol with a range of possible alternative chain-terminator species and to assess their utility by measuring shear and peel adhesion performance. The control values against which this assessment is to be made for standard abitol terminated oligomers give, on cure, adhesive films with a peel force from steel of 1036 Nm^{-1} (AF) and shear adhesion value of 57 mins (Bloom). Both these values are normally reproducible to $\pm 10\%$. The control formulation had a water uptake at 24 h of 2.6% (mean of three determinations).

The formulations investigated in this study are listed in Table II. All weights take into account both the water and isocyanate contents of the respective reagents, and the mole value given represents the ratio of components used. Syntheses were conducted on a 200–300-g scale. All of the adhesives formulated with alternative terminators were colorless, of high subjective tack, and of high optical clarity. Quantitatively, it can be seen from the data in Table III that the mole-for-mole replacement of abitol with the new teminators

Table II Formulation Details for Terminated Oligomers

Sample	Terminator			PPG2025		Ethanediol		2HEMA		812ES		Desmodur W		MEHQ	
		Moles	Grams	Moles	Grams	Moles	Grams	Moles	Grams	% w/w	Grams	Moles of NCO	Grams	% w/w	Grams
T1	Dowfax 9N6	0.9	32.7	1.00	167.30	0.40	2.03	0.30	3.19	0.2	0.5	4.19	44.8	0.02	0.04
T2	Dowfax 9N6	0.9	27.62	1.00	131.40	0.40	1.59	0.40	3.34	0.2	0.4	4.19	36.06	0.02	0.04
T3	Dowfax 9N6	0.9	27.39	1.00	130.29	0.40	1.58	0.50	4.14	0.2	0.4	4.39	36.60	0.02	0.04
T4	Antarox CO630	0.9	43.09	1.00	159.13	0.40	1.93	0.30	3.03	0.2	0.5	4.21	42.83	0.02	0.05
T5	Brij 35	0.9	68.15	1.00	140.12	0.40	1.70	0.30	2.67	0.2	0.5	4.17	37.38	0.02	0.05
T6	Brij 58	0.9	66.95	1.00	135.56	0.40	1.64	0.30	2.58	0.2	0.5	4.99	43.28	0.02	0.05
T7	1-Hexanol	0.9	8.38	1.00	186.53	0.40	2.26	0.30	3.55	0.2	0.5	4.13	49.28	0.02	0.05
T8	4-(2-Hydroxyethyl)morpholine	0.9	10.63	1.00	184.41	0.40	2.23	0.30	3.51	0.2	0.5	4.17	49.20	0.02	0.05
T9	4-(2-Hydroxyethyl)morpholine	0.9	8.44	1.00	146.31	0.40	1.77	0.40	3.72	0.2	0.4	4.25	39.76	0.02	0.04
T10	4-(2-Hydroxyethyl)morpholine	0.9	8.36	1.00	144.96	0.40	1.76	0.50	4.60	0.2	0.4	4.35	40.32	0.02	0.04
T11	1-(2-Hydroxyethyl)-2-pyrrolidinone	0.9	8.38	1.00	147.63	0.40	1.79	0.30	2.81	0.2	0.4	4.17	39.38	0.02	0.04
T12	2-Hydroxyethyl salicylate	0.9	11.65	1.00	145.44	0.40	1.76	0.30	2.77	0.2	0.4	4.19	38.38	0.02	0.04

invariably resulted in lower performance values. The use of Antarox CO630 as terminator (sample T4) gave products after cure that were far too low in cohesive properties for useful application, and no quantification of performance was possible. 1-Hexanol produced an adhesive with lower peel force values than the control. However, 1-(2-hydroxyethyl)-2-pyrrolidinone (sample T11) results in performance values near to those of the abitol control, and is likely to be a useful candidate in future development work. None of the other terminators, when used in direct replacement, deliver matching performance [although Dowfax 9N6 (sample T1)-, 2-hydroxyethyl salicylate (sample T12)-, or 4-(2-hydroxyethyl)morpholine (sample T8,9)-based formulations may be acceptable in specific application areas where a milder adhesion is required]. The results support our earlier statement that in the control formulation, excess abitol acts as a plasticizer in the adhesive mass, improving the adhesion performance values. For both Dowfax 9N6 and 4-(2-hydroxyethyl)morpholine, a series of samples of increasing crosslink density were prepared by progressively increasing the amounts of 2-HEMA in the prepolymers. The purpose of this procedure was to try to improve the shear adhesion values. For the Dowfax 9N6-terminated samples, the effect is not clearly defined and there is no apparent effect on the mode of failure in any of the tests. The values for peel adhesion remain approximately half that of the abitol control. In the case of the 4-(2-hydroxyethyl)morpholine chain terminator, a trend is seen that is wholly consistent with increasing crosslink density in the adhesive. With increasing methacrylate concentration in the formulation, the peel strength falls from 854 to 356 to 264 Nm^{-1}, with a concurrent change in failure mode to adhesive failure. Similarly, the mean time to failure in the shear adhesion test rises, and again the failure mode switches from cohesive to adhesive failure. The performance figures cover a practically useful range of adhesive performance, although at lower values than the control. In this particular example, therefore, we have evidence that performance can be tuned by control of methacrylate concentration.

Several examples of the chain terminators chosen contained significant amounts of ethoxylation or polar groups. The effect of these groups on bulk adhesive hydrophilicity can be seen in Table IV. In biomedical applications, the presence of low levels of hydrophilicity in a skin contact adhesive

Table III Peel and Shear Test Results for the Electron-Beam Cured Formulations[a]

Terminator	Oligomer Formulation Reference	Mean Time to Fail (min)	Failure Mode	Mean Peel Strength (Nm^{-1})	Failure Mode
Abitol (control)	—	57	Bloom	1036	Bloom
Dowfax 9N6	T1	31	Bloom	443	Bloom
Dowfax 9N6	T2	37	Bloom	345	Bloom
Dowfax 9N6	T3	18	Bloom	410	Bloom
Antarox CO630	T4	—	Gross CF	—	Gross CF
Brij 35	T5	2	CF	171	Bloom
Brij 58	T6	2	CF	239	Bloom
1-Hexanol	T7	15	Bloom	322	Bloom
4-(2-Hydroxyethyl)morpholine	T8	20	CF	854	Bloom
4-(2-Hydroxyethyl)morpholine	T9	70	Bloom	356	S1 Bloom
4-(2-Hydroxyethyl)morpholine	T10	348	AF	264	AF
1-(2-Hydroxyethyl)-2-pyrrolidinone	T11	94	Bloom	882	Bloom
2-Hydroxyethyl salicylate	T12	22	Bloom	565	Bloom

[a] AF = adhesive failure; CF = cohesive failure.

is desirable, because this attribute allows the transmission of moisture away from the skin through the adhesive mass. With the following exceptions, all the samples showed bulk hydrophilicty of <10%: two examples have bulk hydrophilicities of 31.4% (Brij 58) and 59.8% (Brij 35). Such large water content values will equate to significant swelling in use and indicate that these particular formulations might be suited to specialist applications where large amounts of aqueous fluid must be accommodated. Therefore, this approach offers an alternative method to that reported in our previous paper[2] for the incorporation of hydrophilicity, where hydrophilic polyethylene glycol units were incorporated into the main chain of the urethane oligomer. Both the Brij-based adhesives had very low shear adhesion times (~2 min), indicating a low cohesive strength and a "soft" adhesive character.

This work has demonstrated that direct replacement of abitol with alternative chain terminators in electron-beam cured PSA formulations can result in PSAs with useful performance characteristics. Regardless of its utilization as a tackifying additive in other formulations, the use of abitol per se is not required to produce tacky adhesives from the formulations described in this study. Although exact duplication of the performance characteristics of the control has not been achieved, terminators Dowfax 9N6, 1-(2-hydroxyethyl)-2-pyrrolidinone, 2-hydroxyethyl salicylate, or 4-(2-hydroxyethyl) morpholine are all candidates worthy of further study for general purpose applications. After further optimization, formula-

Table IV Water Contents of UV-Cured Prepolymers

Terminator	Oligomer Formulation Reference	Water Content @ 24 h (%)
Abitol control	—	2.6
Dowfax 9N6	T1	4.7
Brij 35	T5	59.8
Brij 58	T6	31.4
1-Hexanol	T7	2.6
4-(2-Hydroxyethyl)morpholine	T8	7.6
1-(2-Hydroxyethyl)-2-pyrrolidinone	T11	8.3
2-Hydroxyethyl salicylate	T12	3.7

tions containing terminators 1-hexanol, Brij 35, and Brij 58 may find useful applications in specialist areas that capitalize on their particular performance characteristics.

REFERENCES

1. Ansell, C.W.G.; Butler, C. Polymer 1994, 35, 2001.
2. Millan, E.J.; Webster, I. J Appl Polym Sci 1999, 71, 2313.
3. Paiva, A.; Sheller, N.; Foster, M.D.; Crosby, A.J.; Shull, K.R. Macromolecules 2000, 33, No.5, 1878–1881.
4. Priem, J. J.; Devolder, N. J.; Gilliams, Y. K.; DeWinter, W. F. (assignee: Agfa-Gevaert NV). U.S. Pat. 4, 241, 159 (1977).
5. Tarvainen, K. Contact Dermatitis 1995, 32(6), 346–351.