Radiation-cured polyurethane methacrylate pressure-sensitive adhesives

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New oligomeric polyurethanes have been prepared from polyether diols, chain extender and 4,4'-dicyclohexylmethane diisocyanate or 4,4'-diphenylmethane diisocyanate, which are terminated with a mixture of 2-hydroxyethyl methacrylate (2-HEMA) and non-functional terminators such as n-propanol or technical hydroabietyl alcohol. The oligomers may be cured by electron beam or u.v. radiation to give pressure-sensitive adhesives.

(Keywords: radiation curing; adhesive; polyurethane methacrylate)

Introduction

Radiation processing is an area of growing importance in industry as pressures increase for more environmentally friendly production processes, in terms of reducing both solvent emissions and energy requirements[1]. Many reports of the chemistry and applications of u.v. curing technology have appeared in the literature[2], but electron beam (e.b.) curing has, until recently, received much less attention. In this preliminary paper we will describe the synthesis of new e.b.-curable polyurethane methacrylate oligomers that give rise to pressure-sensitive adhesives on curing. No additional tackifiers are required in the formulations. The oligomers are viscous liquids with little or no volatile components, which eases processing considerably. The new adhesives have adhesion and permeability characteristics that make them suitable for medical applications.

Experimental

Oligomer synthesis. The following is typical of synthetic techniques employed. As a matter of routine, water contents and hydroxyl values were obtained on all hydroxyl reactants. These values were used in the determination of total hydroxyl content in the calculation of reaction quantities, as given in *Table 1*. All reactions were performed in the absence of any solvent. All starting materials were obtained from the Aldrich Chemical Co., with the exception of 4,4'-dicyclohexylmethane diisocyanate (Bayer), hydroabietyl alcohol (Hercules Ltd) and Dowfax 63N10 (ethylene oxide (~10%) terminated poly(propylene oxide), number average molecular weight 2000; Dow Chemical Co.). A general reaction scheme is given in *Figure 1*.

Stage 1. Polyglycol, ethanediol and diisocyanate were mixed until homogeneous in a 700 cm^3 flange flask fitted with an air-driven stirrer, under an inert gas blanket. Dibutyltin dilaurate (DBTDL, catalyst) was added and the mixture warmed to 60°C with stirring. Once gas evolution had ceased the temperature was raised to 90°C and the mixture stirred at this temperature for 1 h to give an isocyanate-terminated oligomer.

Stage 2. The reactants were cooled to 60°C and 2-hydroxyethyl (meth)acrylate, followed by the selected chain terminator, was added and stirred in until homogeneous. *p*-Methoxyphenol stabilizer (500 ppm) was added in a similar manner. This mixture was allowed to cool to ambient temperature and stored for 3 days prior to use.

Oligomer curing. 1. Electron beam curing. Oligomers were heated to ~70°C to reduce their viscosity prior to spreading on silicon release paper. Spread thicknesses were adjusted to approximately 40 $g\,m^{-2}$. Coating was effected using a doctor blade system. Samples were then passed under an e.b. generator (ESI model M0175) in a nitrogen atmosphere (<200 ppm oxygen) at a conveyor speed of 30 $m\,min^{-1}$. The cathode voltage was held at 165 keV and the dose at 4 Mrad for each sample. The cured adhesive film could then be transferred onto Estane 5714 polyurethane film for measurement of moisture vapour transmission rates (MVTRs) or Melinex polyester film for adhesion testing.

2. Ultraviolet light curing. Oligomers were heated to ~70°C to reduce their viscosity. Benzildimethylketal (Irgacure 651, Ciba-Geigy; 1% w/w) was blended into the oligomer, which was then sandwiched, at a thickness of ~1 mm, between two layers of Melinex film prior to irradiation for 5 min under a hand-held Hanovia u.v. lamp system.

3. Physical testing. MVTRs were determined by a cup method based on ASTM E96-92, at 37°C and 10% relative humidity. Water contents were determined at full hydration on u.v.-cured samples that had been immersed in distilled water for 24 h. The relation:

$$\text{water content} = \frac{\text{wet mass} - \text{dry mass} \times 100\%}{\text{wet mass}}$$

was used.

Peel strength was determined from a standard stainless steel surface at a peel angle of 180° and a machine crosshead speed of 300 $mm\,min^{-1}$. The backing film was 36 μm Melinex polyester. All failures were adhesive at the peel front.

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Table 1 Formulation data for the radiation-curable oligomers

Sample	Polyglycol[a] (mol, g)	Diisocyanate[b] (mol, g)	Chain extender (mol, g)	Acrylic terminator[c] (mol, g)	Chain terminator (mol, g)
A	PPG2025 (0.1, 202.5)	DCMD (0.203, 53.25)	Ethanediol (0.04, 2.48)	2-HEMA (0.03, 3.9)	n-Propanol (0.09, 6.66)
B	PPG2025 (0.1, 202.5)	DCMD (0.203, 53.25)	Ethanediol (0.04, 2.48)	2-HEMA (0.04, 5.2)	*N*,*N'*-dimethylethanolamine (0.08, 7.1)
C	PPG2025 (0.1, 202.5)	DCMD (0.203, 53.25)	Ethanediol (0.04, 2.48)	2-HEMA (0.04, 5.2)	Hydroabietyl alcohol (0.08, 22.64)
D	Dowfax 63N10 (0.066, 136.6)	DCMD (0.14, 35.9)	Ethanediol (0.026, 1.64)	2-HEMA (0.02, 2.58)	Hydroabietyl alcohol (0.08, 22.64)
E	Dowfax 63N10 (0.066, 136.6)	DCMD (0.14, 35.9)	Ethanediol (0.026, 1.64)	2-HEA (0.02, 2.3)	Hydroabietyl alcohol (0.08, 22.64)
F	PPG2025 + PEG1500; 9:1 (114.7 + 9.84)	DCMD (0.14, 35.9)	Ethanediol (0.026, 1.64)	2-HEA (0.02, 2.58)	Hydroabietyl alcohol (0.08, 22.64)
G	PPG2025 + PEG1500; 4:1 (101.9 + 19.67)	DCMD (0.137, 36.02)	Ethanediol (0.026, 1.64)	2-HEMA (0.02, 2.58)	Hydroabietyl alcohol (0.08, 22.64)
H	PPG2025 + PEG1500; 1:1 (63.7 + 49.2)	DCMD (0.146, 38.42)	Ethanediol (0.026, 1.64)	2-HEMA (0.02, 2.58)	Hydroabietyl alcohol (0.09, 25.8)
I	PPG2025 (127.4)	DPMD (0.136, 34.12)	Ethanediol (0.026, 1.64)	2-HEMA (0.02, 2.58)	Hydroabietyl alcohol (0.08, 22.64)

[a] PPG, poly(propylene glycol); PEG, poly(ethylene glycol); Dowfax 63N10, see text
[b] DCMD, dicyclohexylmethane diisocyanate; DPMD, diphenylmethane diisocyanate
[c] 2-HEMA, 2-hydroxyethyl methacrylate

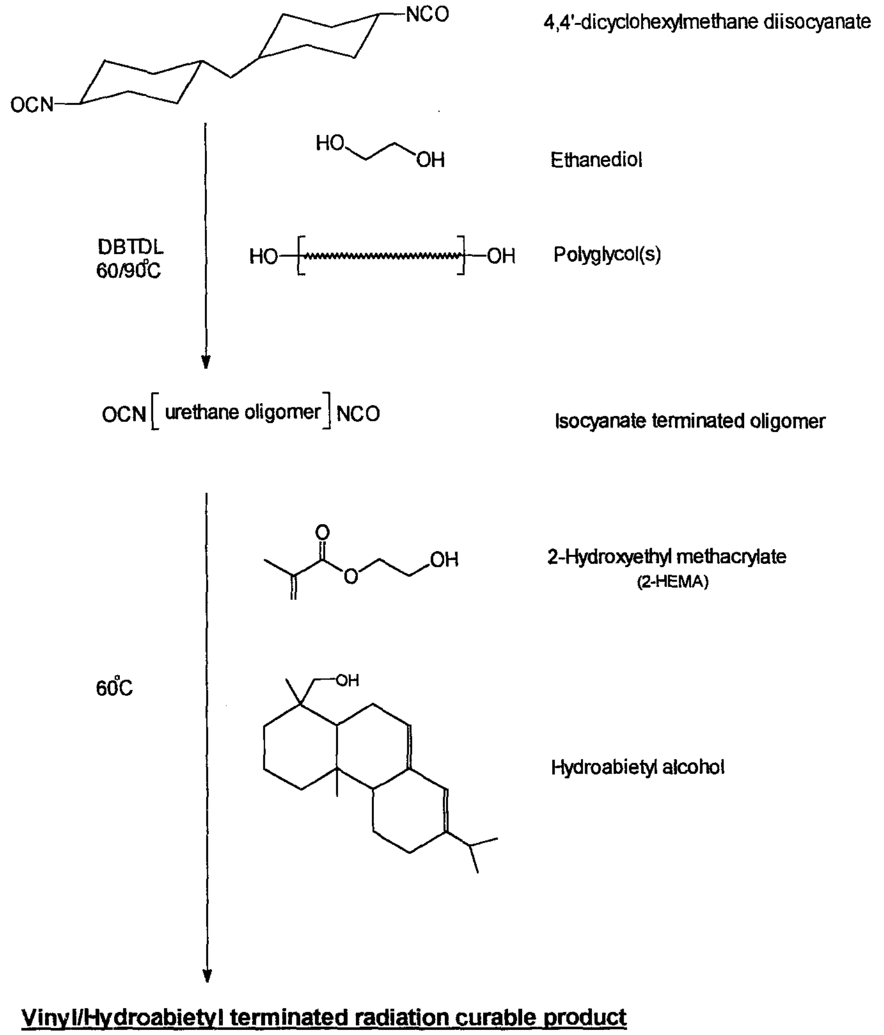

Figure 1 Generalized reaction scheme

Table 2 Water content at full hydration

Oligomer sample	Water content at full hydration (%)
D	4
E	4
F	5
G	8
H	22
I	<1

Results

Table 1 summarizes formulation data for the new adhesive oligomer systems. In addition, all samples were made using 0.25% w/w DBTDL catalyst and 500 ppm *p*-methoxyphenol stabilizer. Although the overall isocyanate to hydroxyl ratio in each system is unity, the stoichiometry of the (meth)acrylate and chain terminator inevitably results in a complex mixture of oligomers. In order to achieve pressure-sensitive adhesives it is necessary to react approximately 25% of available isocyanate groups after stage one of synthesis with the hydroxymethacrylate. The remainder are reacted with chain terminator. Notwithstanding any side reactions that may occur under the e.b., the product, after radiation curing, must be a loosely crosslinked network which is swollen with oligourethanes not containing radiation-reactive groups. These are likely to be of central importance in conveying pressure-sensitive characteristics.

Subjectively, all the above formulations are aggressive, high-tack systems when cured, which show little or no tendency to cohesive failure on peeling. The peel strength from steel plates for sample E, a $40\,g\,m^{-2}$ spread on a Melinex supporting backing, was determined at $246\,N\,m^{-1}$ with a typical variation between samples of +/− 10%. The same example gave an MVTR figure of $1075\,g\,m^{-2}\,(24\,h)^{-1}$ when exposed to water vapour, rising to $1248\,g\,m^{-2}\,(24\,h)^{-1}$ when exposed to liquid water. These values are significantly higher than those associated with traditional surgical acrylic pressure-sensitive adhesives[3] and are a consequence of a high polyether content of the adhesives. We have prepared formulations using a variety of different polyether systems, and for the most hydrophilic (derived from oligomers G and H) increasing water uptake values were observed. In order to produce samples of sufficient thickness for convenient handling, samples were cured by u.v. irradiation as described in the Experimental section. *Table 2* summarizes the results obtained in determining bulk water content at full hydration.

On full hydration, examples G and H showed complete loss of adhesive character, which was restored on drying out. This feature may have advantages in wound care applications, when adhesion to the moist wound surface is undesirable[4].

Conclusions

This preliminary work has shown that novel radiation-curable urethane (meth)acrylate systems, which lead to pressure-sensitive adhesives on curing, can be prepared easily and in the absence of solvent. The wide range of formulations possible in these systems, resulting from the use of polyurethane chemistry, promises further developments.

References

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