

# Studies in Water-Vapor Transmission Rate of Nonocclusive Acrylic Adhesive Tape

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## SYNOPSIS

Various homopolymers, copolymers, and terpolymers based on 2-ethylhexyl acrylate (2-EHA), *n*-butyl methacrylate (nBMA), and acrylic acid (AA) were synthesized using the well-known free-radical polymerization technique. The polymers were analyzed by <sup>1</sup>H-NMR and IR spectroscopy to identify and confirm the presence of the monomers in the copolymer and also to check the absence of monomer impurities. A water-vapor transmission rate (WVTR) study of the synthesized adhesives coated on nonwoven polyester fabric was undertaken using the desiccant method. The water-vapor permeability of the various copolymers changed with the change in monomer concentration. The higher the AA content in the copolymer, the higher was the permeability. The trend shown by various copolymers and terpolymers of 2-EHA with respect to their WVTR is 2-EHA-co-AA > 2-EHA-co-nBMA > 2-EHA-co-AA-co-nBMA. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Nonocclusive or breathable tapes show better adhesion to the skin surface since moisture does not accumulate at the skin interface, causing a decrease or loss in adhesion. The nonocclusive tapes allow moisture to diffuse through the adhesive, providing a superior water-vapor transmission rate (WVTR) and adhesive performance, which ultimately leads to a healthier skin. Since the acrylic polymers do not irritate the skin and are physiologically harmless, they are particularly suitable for these types of medical tapes.<sup>1</sup>

In our laboratory, while working on 2-ethylhexyl acrylate (2-EHA)-based copolymers, it was observed that with the change in the monomer concentration the adhesive characteristics also changed.<sup>2,3</sup> It was therefore thought that it would be worthwhile to check whether the WVTR of the synthesized acrylic polymers would also change with the change in monomer concentration. The literature survey revealed that although voluminous work has been reported on the adhesive properties of acrylate-based

adhesive tapes very little attention has been paid with respect to their WVTR study. Probably, due to its commercial importance, the patent literature does not disclose the details of the commercial product.<sup>4</sup> However, quite a number of reports are available about the water-vapor permeability of various polymeric films.<sup>5-15</sup> Lorant<sup>5</sup> studied the characteristic features of isothermal and thermal water-vapor transmission of hydrophilic polymers. Bhattacharyya and Malda<sup>8</sup> reported the specific permeability of water vapor through styrene and acrylamide grafted on cellulose acetate films at various humidities. Acrylamide is a polar molecule; the permeability increases with the increase in the grafting of acrylamide at all humidities, but in case of styrene, which is a nonpolar molecule, the permeability showed a reverse order. The present article reports the WVTR of various homo-, co-, and terpolymers based on 2-EHA coated on a nonwoven polyester fabric.

## EXPERIMENTAL

### Materials

2-EHA (Fluka) and *n*-butyl methacrylate (nBMA) (E. Merck, India) were washed with 5% sodium hy-

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**Table I WVTR at Relative Humidity 90.2% and Temperature 38°C of Various Homopolymers**

Polymer	Monomer (Mol)	Solvent (Mol)	Permeability (g/m <sup>2</sup> /24 h)
P (2-EHA) <sup>a</sup>	0.162	0.340	2077.90
P (nBMA) <sup>a</sup>	0.210	0.340	1454.53
P (AA) <sup>b</sup>	0.416	1.667	2671.59

<sup>a,b</sup> Polymerization conditions. <sup>a</sup> Initiator: Benzoyl peroxide (0.5% by weight of monomers). Temperature: 78 ± 0.1°C. Solvent: Ethyl acetate. Nonsolvent: Methanol. Conversion: Greater than 90%. Period: 8 h. <sup>b</sup> Initiator: Potassium persulfate. Temperature: 60 ± 0.1°C. Solvent: Distilled water. Nonsolvent: Petroleum ether (40–60). Period: 8 h. Conversion: Greater than 90%.

dioxide solution to remove the inhibitors, viz., monomethyl ether of hydroquinone and hydroquinone, followed by distilled water. After drying over anhydrous calcium chloride, it was distilled under reduced pressure. Acrylic acid (AA) (Sisco-chem, India) was purified by distilling it under reduced pressure. All other solvents and chemicals used were of analytical grade and were used without further purification.

### Polymerization

The well-known free-radical polymerization technique was used for the polymerization of acrylic monomers. A predetermined amount of monomer, solvent (ethyl acetate), and initiator (benzoyl peroxide) were charged in a three-necked reaction flask equipped with condenser and a nitrogen gas inlet and kept in a thermostatically controlled water bath maintained at 78 ± 0.1°C with constant stirring (Tables I–IV). The polymerization reactions were carried out for a period of 8 h to obtain greater than 90% conversion. The reaction was stopped by adding a large excess of methanol to the polymer solution. The precipitated polymer was further purified by repeated reprecipitation from ethyl acetate into methanol, so as to remove traces of unreacted monomer and initiator. The purified polymer was dried in a vacuum desiccator to constant weight for 12–13 days.

Acrylic acid (AA) was polymerized at 60 ± 0.1°C with potassium persulfate as the initiator and distilled water as the solvent for a period of 8 h. The purification of the polymer was done in a similar manner as that given for other acrylic polymers.

### Analysis

The polymers were analyzed by <sup>1</sup>H-NMR and IR spectroscopy to identify and confirm the presence

**Table II WVIR at Relative Humidity 90.2% and Temperature 38°C of Various 2-EHA-co-nBMA Copolymers<sup>a</sup>**

2-EHA (Mol)	nBMA (Mol)	Permeability (g/m <sup>2</sup> /24 h)
0.081	0.105	1484.22
0.098	0.084	1632.95
0.114	0.063	1791.37
0.130	0.042	1870.11
0.147	0.021	2018.53

<sup>a</sup> Polymerization conditions: Same as those given in footnote a, b to Table 1 for 2-EHA and nBMA.

of the monomers in the copolymer and also to check the absence of monomer impurities. The <sup>1</sup>H-NMR spectra were recorded using a Varian 60 MHz spectrophotometer. The samples were used in the form of solution (10–15% w/v) in deuterated chloroform, at ambient temperature with tetramethyl silane as the internal standard. A thin film of the polymer solution (0.5 mg/cm<sup>3</sup>) in spectroscopic-grade chloroform was cast on a NaCl pellet which was used for recording infrared spectra on a Shimadzu FT-4200 Fourier transform infrared spectrophotometer.

### Tape Preparation

A 25% solution of the polymer in ethyl acetate was coated (20 × 10<sup>-6</sup> m thick) on a nonwoven polyester fabric (120 × 10<sup>-6</sup> m thick) using the roller coat technique. This technique is based on the transference of adhesive material from a trough, by means of a pick-up roller partially immersed in it, to a contacting transfer roller sheet. Nonwoven fabric is continuously coated with adhesive when fed between the transfer roller and a pressure roller, which is adjusted to determine the coat thickness. The sol-

**Table III WVTR at Relative Humidity 90.2% and Temperature 38°C of Various 2-EHA-co-AA Copolymers<sup>a</sup>**

2-EHA (Mol)	AA (Mol)	Permeability (g/m <sup>2</sup> /24 h)
0.081	0.208	2641.92
0.098	0.166	2523.19
0.114	0.125	2493.50
0.130	0.083	2403.21
0.147	0.041	2315.39

<sup>a</sup> Polymerization conditions: Same as those given in footnote a, b to Table 1 for 2-EHA and nBMA.

**Table IV WVTR at Relative Humidity 90.2% at Temperature 38°C of Various 2-EHA-co-AA-co-nBMA Terpolymers**

2-EHA (Mol)	AA (Mol)	nBMA (Mol)	Permeability (g/m <sup>2</sup> /24 h)
0.081	0.004	0.103	1454.53
0.081	0.016	0.097	1513.90
0.081	0.029	0.090	1573.27
0.081	0.041	0.084	1662.32
0.081	0.083	0.063	1781.06
0.081	0.125	0.042	1879.48
0.081	0.166	0.021	1928.24
0.098	0.004	0.082	1615.32
0.098	0.016	0.076	1674.69
0.098	0.029	0.060	1732.32
0.098	0.041	0.063	1840.43
0.114	0.004	0.061	1762.30
0.114	0.016	0.054	1856.51
0.114	0.029	0.046	1881.24
0.114	0.041	0.042	1931.95

<sup>a</sup> Polymerization conditions: Same as those given in footnote a, b to Table I for 2-EHA and nBMA.

vent was evaporated by drying the tape in an oven at 80°C. The mass weight of the adhesive coated was 20 g/m<sup>2</sup> (approximately).

### WVTR Test Method

The Pressure Sensitive Tape Council (PSTC) and American Society for Testing and Materials (ASTM) have set a standard test method for the determination of the WVTR.<sup>16-17</sup> An open-mouth cup made up of noncorroding, nonpermeable, aluminum metal (opening of  $8.085 \times 10^{-4}$  m<sup>2</sup>) was used in the WVTR determination. The cup was filled to within 0.003 m of the opening with 8 mesh anhydrous calcium chloride. The test specimen was applied, adhesive face down, over the opening to allow a minimum of 0.01 m of tape to be in contact with the sides of the flange and 0.02 m to be in contact with the ends. The tape sample was brought into intimate contact with the flange using ample finger pressure. The assembly was kept in a desiccator having a saturated barium chloride solution in it. A relative humidity of 90.2% (approximately) is maintained in the desiccator due to the saturated BaCl<sub>2</sub> solution.<sup>18</sup> The desiccator was then placed in an oven maintained at 38°C. The weight gain in 24 h is used to calculate the WVTR through the tape under the specified conditions.

## RESULTS AND DISCUSSION

### <sup>1</sup>H-NMR and IR Spectral Analysis

The absence of peaks due to unsaturated protons between 5 to 6 ppm in the <sup>1</sup>H-NMR spectral scan indicated that the polymers under study were free from monomer impurities. The spectral scan of the homopolymer of 2-EHA and nBMA showed peaks at 0.9–2.5 ppm and at 4.0 ppm. The peak due to the —CH<sub>3</sub> group in the alkyl pendant group appears at 1.0 ppm and is resolved well with the peaks due to backbone methylene groups at 1.1–2.5 ppm. However, the peaks of the methylene groups due to stereoirregularities are overlapped, forming a broad peak, and, hence, individual assignment of the peaks is impossible. The characteristic peak due to the α-CH<sub>3</sub> group in nBMA was found to be overlapped by the peaks due to the methylene groups. The —OCH<sub>2</sub> peak at 4.0 ppm does not show multiplicities due to stereoeffects.<sup>19</sup> The NMR spectrum of poly(acrylic acid) [P(AA)] shows three peaks at 1.5, 2.2, and 11.9 ppm. The doublet at 1.5 ppm and triplet at 2.2 ppm are due to —CH<sub>2</sub> and —CH groups, respectively. A weak signal at 11.9 ppm arises due to the carboxylic (—COOH) group. The differences in the chemical shift observed for the homopolymers persists when the monomers are co- and terpolymerized.

All the infrared spectra of the polymers showed an absence of a band at 1600 cm<sup>-1</sup> corresponding to C=C, indicating that no monomer impurities were present in the copolymers. The bands due to carbonyl group of 2-EHA, nBMA, and AA appear at 1730–1740 cm<sup>-1</sup>. As a result, in the copolymers, the carbonyl bands due to respective comonomers were found to be overlapped. The O—H stretching vibration of the —COOH group showed a broad absorption band centering near 3000 cm<sup>-1</sup>, which is superimposed on the C—H stretching bands at 2850–2960 cm<sup>-1</sup>. The characteristic C—O bending of the acrylic ester group appeared at 1080–1300 cm<sup>-1</sup>. All the copolymers of the same series showed more or less similar spectra.

### WVTR Study

In the WVTR studies, successive weighing of the cup covered with the nonwoven tape coated with the sample to be tested was undertaken at an interval of 1 h. A plot of successive weighing against elapsed time was drawn; a straight line passing through the origin indicated the existence of a nominal steady state. The slope of the straight line gave the WVTR

for the test area ( $8.085 \times 10^{-4} \text{ m}^2$ ). Further, the WVTR for  $1 \text{ m}^2$  for a period of 24 h was calculated as shown below:

$$\text{WVTR} = \frac{1 \times (\text{slope}) \times 24}{8.085 \times 10^{-4}} \quad (1)$$

Also, the WVTR is calculated from the weight gain in 24 h by the equation

$$\text{WVTR} = \frac{1 \times (\text{weight gain in 24 h})}{8.085 \times 10^{-4}} \quad (2)$$

An excellent agreement was obtained between the WVTR values calculated by eq. (2) and those evaluated graphically using eq. (1). The results obtained from the permeability experiments for the various polymers coated on nonwoven polyester fabric are listed in Tables I–IV.

### Homopolymers

The homopolymers themselves are not suitable as pressure-sensitive adhesives, but their permeability was checked for the purpose of comparison among themselves and that with the other copolymers. From Table I, it is clear that the permeability shown by P(AA) is highest followed by P(2-EHA) and then P(nBMA). This high value shown by P(AA) may be assigned probably to the high polarity of AA in comparison with the other two monomers. The nBMA, because of its  $\alpha$ -methyl group, is less polar than is 2-EHA and, hence, correspondingly shows a decrease in WVTR.

### Copolymers

#### 2-EHA-co-nBMA

The results obtained from the WVTR studies of various 2-EHA-co-nBMA are listed in Table II. A careful study of the results indicate that as the 2-EHA content in the copolymers increases the permeability increases, whereas as the nBMA content increases in the copolymer, the permeability decreases, in consonance with their individual polarity. It is interesting to observe that the permeability shown by the various 2-EHA-co-nBMA copolymers lie in between those shown by the corresponding homopolymers (Tables I and II).

#### 2-EHA-co-AA

A comparison between Tables I and III clearly indicates that the permeability shown by the various

2-EHA-co-AA copolymers also lies in between those of corresponding homopolymers. With the increase in 2-EHA content in the copolymers, the permeability decreases in contrast to what was observed in case of 2-EHA-co-nBMA (Table II). But, as the AA concentration in the copolymer increases, the permeability increases. Thus, the hydrophilicity shown by the various polymers increase with increase in AA content. Comparing the two copolymer systems, viz., 2-EHA-co-nBMA and 2-EHA-co-AA, the latter is found to be more permeable than is the former.

### Terpolymers

#### 2-EHA-co-AA-co-nBMA

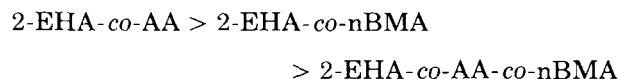
It is interesting to study the results obtained from the permeability experiments of various terpolymers where the monomer concentration is widely varied (Table IV). A glance at Table IV clearly indicates that all the three sets show a similar pattern of the WVTR. It is also clear that with increase in AA concentration in the terpolymer the permeability increases. Thus, the higher the carboxylic content, the higher is the hydrophilicity. An exactly reverse trend is observed with increase in nBMA content in the terpolymer. As the nBMA content increases, the permeability decreases. Comparing the three sets of terpolymers, it is observed that with increasing 2-EHA content from 0.081 to 0.114 mol through 0.098 mol the permeability increases.

### Nonocclusive Tape

During the preparation of a nonocclusive tape, not only the permeability but also the adhesive characteristics of the synthesized polymers should be taken into account. It is known that an optimum balance among adhesion, cohesion, and tack characteristics is obtained in the case of 2-EHA-co-nBMA and 2-EHA-co-AA-co-nBMA, where the 2-EHA content is 0.081 mol.<sup>2</sup> It should also be noted that human skin has an average water-vapor emission of  $240 \text{ g/m}^2/24 \text{ h}$ .<sup>20</sup> Based on the above observations, one can definitely argue a positive case for the use of 2-EHA-co-nBMA and 2-EHA-co-AA-co-nBMA, where the 2-EHA content is 0.081 mol, as pressure-sensitive adhesives in the preparation of a nonocclusive adhesive tape.

## CONCLUSIONS

Based on the preceding observations, the trend shown by various copolymers and terpolymers of 2-EHA with respect to their WVTR appears to be



It can also be concluded that the higher the AA content in the copolymer the higher is the permeability. Thus, AA helps in enhancing the hydrophilicity of the polymers. It is also seen that with the change in monomer concentration in the copolymer the permeability changes. Hence, the optimum concentration should be selected to fulfill the particular end-use requirement.

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