Studies on the Sorption of Lipids in Segmented Polyurethanes. III. Effects of Stretching at Room Temperature

K. SREENIVASAN,[1,*] M. JAYABALAN,[1] and K. V. C. RAO[2]

[1]Biomedical Technology Wing, Sree Chitra Tirunal Institute for Medical Sciences & Technology, Poojapura, Trivandrum 695 012, India; [2]ABR Organics Ltd., 2-2-3/B/7/1 Durgabai Deshmukh Colony, Hyderabad - 500 007, India

SYNOPSIS

Diffusion and absorption of a few representative lipids in amorphous segmented polyurethanes subjected to stretching to various elongations were carried out. Stretching was found to influence the extent of the absorption of lipids. The variation in absorption was traced to the morphological alterations like phase mixing induced by stretching. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that orientation can cause considerable changes in the transport properties of polymers. The origin of such an effect has both theoretical and practical interest and has been studied for many years. Peterlin[1] first reported on the reduction of sorption and diffusion of organic vapors in drawn high-density polyethylene. Subsequently, several studies[2-6] were made on the effect of drawing on the transport of various molecules in semicrystalline polymers. Orientation in polymers was found to reduce the transport rate when diffusion occurred mainly perpendicular to the draw direction. This behavior is attributed to the loss of chain mobility after drawing. Most of the reported studies are related to the diffusion of gases or organic vapors through polyethylene, polypropylene, poly(ethylene terephthalate), etc. Similar studies on polyurethanes have not been reported to the best of our knowledge.

Polyurethanes are known to absorb lipids.[7-10] We have attempted to probe into the intricacies of lipid absorption by polyurethanes, particularly stressing the structural features of the polymers.[11-13]. These studies undoubtedly pointed out that lipid absorption is confined to the soft-segment domains of the polyurethanes. Our effort in this communication was to understand the diffusional behavior of lipids in drawn polyurethanes with the aim to correlate stretch-induced morphological changes with diffusion and also to know how physical modification like stretching affect the diffusion of lipids.

EXPERIMENTAL

The polyurethanes used in this study are derived from methylene bis(*p*-cyclohexyl diisocyanate) (H_{12}MDI), poly(tetramethylene glycol) 1000 (PTMEG), and 1,4-butanediol (BD). The polyurethane was synthesized by a two-stage process as reported elsewhere.[14] By changing the composition of H_{12}MDI/PTMEG/BD, polymers having 23, 33, and 47 wt % hard-segment contents were synthesized. Polymer films cast from dimethylacetamide solution were extracted with ethyl alcohol and then *n*-hexane to remove residual reactants and impurities. The vacuum-dried polymers were used for further studies. The relevant parameters of the polymers are shown in Table I.

A DuPont 1090 thermal analyzer system with a 910 DSC cell as an accessory was used to determine

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 59, 1009–1014 (1996)
 CCC 0021-8995/96/061009-06

Table I Relevant Parameters of the Polymers

Polymer	Weight % HS	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	D	T_g of SS (°C)	Ultimate Stress (MPa)	Ultimate Strain (%)
PU-1	23	2.10	1.05	2.01	−53	39 ± 0.8	690 ± 16
PU-2	33	2.32	1.09	2.12	−42	44.5 ± 1.2	498 ± 13
PU-3	47	1.93	1.03	1.87	−31	57.8 ± 1.4	456 ± 5

the glass transition temperature of the polymers using liquid nitrogen as a coolant. An Instron 1193 universal testing machine was used for drawing the polymers to varied degrees of elongation at room temperature (25°C). The polymers (6×2 cm^2) after drawing to the desired elongation were at the stressed state for 15 min and then allowed to relax. The polymer strips were then kept for 48 h at room temperature. The central portion of films was used for the diffusion studies. Stearic acid, cholesterol, cholesteryl acetate, and triolein, all from Sigma Chemicals, USA, were used as representative lipids.

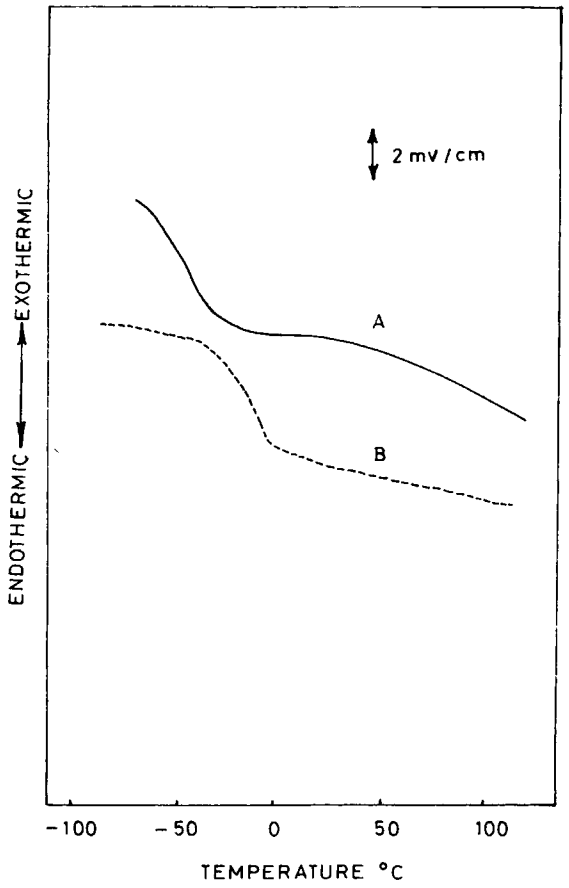

Figure 1 DSC thermogram of (A) PU-2 and (B) PU-2. Stretched to 480% elongation.

GLC-grade silicone oil (BDH, Poole, UK) was used for dissolving the lipids.

For estimating the diffusion coefficient of the lipids, an immersion-weighing method was adopted as reported elsewhere.[15] Briefly, the conditioned polymer strips (3×2 cm^2) placed in the respective lipid solution at 37°C were taken out, plotted with filter paper strips, and weighed to obtain the mass uptake at time $t(M_t)$.

The process was continued until equilibrium absorption was attained (M_∞). Alternatively, an infrared spectroscopic method was also used to estimate the amount of diffused lipids, as detailed elsewhere.[11] Diffusion coefficients were estimated from the slope of the M_t/M_∞ vs. $t^{1/2}$ plots.

RESULTS AND DISCUSSION

We attempted to elucidate the morphological changes induced by stretching[11,16,17] in these materials. Wide-angle X-ray diffraction studies[16] showed the orientation of hard-segment (HS) domains at lower elongation. At higher elongation, however, the HS domains disrupted and mixed with the soft-segment (SS) matrix. Both thermogravimetric[17] and mechanical studies[18] further pointed out stretch-induced morphological changes. Figure 1 depicts a typical DSC thermogram of PU-2 (33 wt % HS content) unstretched and stretched to 400% elongation. The traces apparently indicate an increase in SS T_g, reflecting the dissolution of HS in SS. Table II sum-

Table II Effect of Stretching on the T_g of Soft Segment

Polymer	Elongation (%)	T_g of Control (°C)	T_g of Stretched (°C)
PU-1	600	−53	−50
PU-2	480	−42	−34
PU-3	450	−31	−17

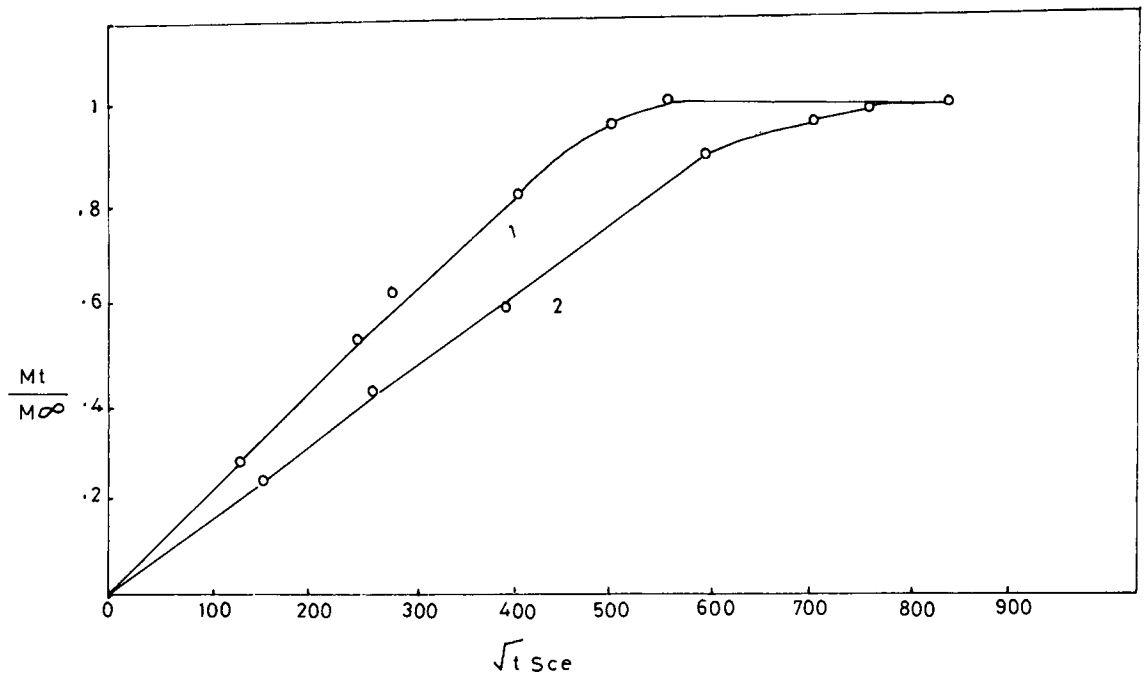

Figure 2 Typical M_t/M_∞ vs. $t^{\frac{1}{2}}$ plots for stearic acid in (1) unstretched PU-1 and (2) stretched to 400% elongation.

marizes the T_g of the stretched and unstretched polymers.

Figure 2 illustrates representative Mt/M_∞ vs. $t^{\frac{1}{2}}$ plots for stearic acid in stretched and unstretched PU-1. The curves favorably support the Fickian nature of the diffusion of lipids in polyurethanes.

The diffusion coefficients (D) of the diffusants in PU-1, PU-2, and PU-3 with the extent of stretching are shown in Tables III–V, respectively. In general, D decreases with the extent of stretching. Diffusion in semicrystalline polymers is termed[19]

$$D = \frac{D^*}{TB} \tag{1}$$

Table III Effect of Stretching on Diffusion Coefficient of Lipids in PU-1

Elongation (%)	Stearic Acid	Diffusion Coefficient Cholesterol	Cholesteryl Acetate	($\times 10^9$ cm^2/s) Triolein
0	3.4 ± 0.03	1.62 ± 0.02	1.35 ± 0.03	0.73 ± 0.01
200	3.36 ± 0.06	1.38 ± 0.04	1.14 ± 0.04	0.66 ± 0.02
400	2.85 ± 0.04	0.94 ± 0.01	0.86 ± 0.05	0.42 ± 0.04
600	2.66 ± 0.07	0.91 ± 0.03	0.77 ± 0.06	0.31 ± 0.04

Table IV Effect of Stretching on Diffusion Coefficient of Lipids in PU-2

Elongation (%)	Stearic Acid	Diffusion Coefficient Cholesterol	Cholesteryl Acetate	($\times 10^9$ cm^2/s) Triolein
0	2.37 ± 0.04	1.16 ± 0.04	0.72 ± 0.03	0.56 ± 0.04
200	2.17 ± 0.05	0.86 ± 0.05	0.47 ± 0.04	0.42 ± 0.02
400	1.56 ± 0.05	0.57 ± 0.06	0.22 ± 0.02	0.18 ± 0.04
480	1.54 ± 0.02	0.49 ± 0.01	0.17 ± 0.01	0.14 ± 0.02

Table V Effect of Stretching on the Diffusion Coefficient of Lipids in PU-3

Elongation (%)	Diffusion Coefficient ($\times 10^9$ cm^2/s)			
	Stearic Acid	Cholesterol	Cholesteryl Acetate	Triolein
0	2.01 ± 0.02	0.63 ± 0.03	0.57 ± 0.05	0.42 ± 0.01
200	1.56 ± 0.05	0.32 ± 0.01	0.22 ± 0.02	0.19 ± 0.01
400	1.04 ± 0.05	0.14 ± 0.02	0.09 ± 0.01	0.03 ± 0.002
450	0.98 ± 0.03	0.12 ± 0.03	0.06 ± 0.02	0.03 ± 0.001

where D is the diffusion coefficient in the semicrystalline polymer; D^*, the diffusion coefficient in the same polymer which is completely amorphous; T, the tortuosity factor; and B, the chain immobilization factor. HS domains in PU have been shown to be impermeable[11,15,20] and the diffusion is governed by the nature of the SS. In that case, eq. (1) could be used to estimate the diffusion coefficient in PU assuming D^* as equivalent to the diffusion coefficient of a diffusant in 100% SS. As seen from the equation, an increase in T should decrease D. At higher elongation, however, HS aggregates disrupt, and this, in fact, should reduce T, thereby enhancing D. Interestingly, however, D decreases at higher elongation, indicating that the chain immobilization factor B has an important role in controlling the diffusion in drawn polyurethanes. Unlike small molecules, the diffusants encountered here are all big and need substantial segmental mobility to find their way. The HS domains present in the SS acting as physical crosslinks reduce the segmental mobility of the SS matrix, resulting in numerical enhancement in B, which, in turn, reduces the diffusion coefficient.

In PU-1, D decreases slowly with stretching for all four diffusants. This polymer contains relatively less HS content (23%). The reduction in D is negligibly small for molecules like stearic acid in 200% elongated polymer. For rigid and bulky molecules like cholesterol, the change in D is slightly high. However, from a practical point of view, the extent of diffusion can be considered invariant in the 200% elongated PU-1. The oriented SS chains relax immediately after removing the stress. Orientational effects were apparent only for the HS which do not have any influence on the diffusion. However, the reduction is apparent in 400 and 600% stretched materials. The hard domains disrupt at higher elongations[16] and mix with the SS, enhancing the viscosity of the SS. Further, the HS acting as multifunctional crosslinks constrains the SS movement, preventing the relaxation, and apparently retains the orientation. The reduction in the diffusion coefficient in 600% drawn PU-1 is about 22% and that of a rigid molecule like cholesterol is as high 44%. The reduction in D, in fact, confirms the morphological changes revealed by WAXD and other techniques.

PU-2 and PU-3 showed similar behavior. However, the reduction in the diffusion coefficient were more in the order PU-1 < PU-2 < PU-3. Higher HS contents in these materials reduce the relaxation and thereby retain the orientation more. Higher HS domains further enhance the phase mixing possibility, favoring the retention of orientation as well as substantially reducing the segmented mobility. The reduction in D of two representative linear and rigid molecules, e.g., stearic acid and cholesterol, in these materials drawn close to the breaking points is shown in Table VI. The parameter evidently suggests morphological alterations induced by stretching. Depending upon the HS content, the diffusion decreases drastically, particularly for rigid molecules, and it is as high as 85% for cholesterol in PU-3 drawn to 450%.

Tables VII-IX provide the % equilibrium absorption of the diffusing species with the degree of elongation in PU-1, PU-2, and PU-3, respectively. Sim-

Table VI Reduction in D and % Absorption of Stearic Acid and Cholesterol in Stretched Polyurethanes

Polymer	Elongation (%)	Reduction in D (%)		Reduction in Absorption	
		Stearic Acid	Cholesterol	Stearic Acid	Cholesterol
PU-1	600	22	44	36	54
PU-2	480	35	58	47	68
PU-3	450	51	81	56	85

Table VII Effect of Stretching on Absorption of Lipids in PU-1

Elongation (%)	Absorption (%)			
	Stearic Acid	Cholesterol	Cholesteryl Acetate	Triolein
0	4.25 ± 0.05	3.05 ± 0.06	2.42 ± 0.07	1.81 ± 0.06
200	3.96 ± 0.06	2.40 ± 0.03	1.97 ± 0.06	0.98 ± 0.06
400	3.20 ± 0.01	1.90 ± 0.01	1.06 ± 0.02	0.58 ± 0.02
600	2.73 ± 0.02	1.39 ± 0.02	0.98 ± 0.04	0.55 ± 0.01

Table VIII Effect of Stretching on Absorption of Lipids in PU-2

Elongation (%)	Absorption (%)			
	Stearic Acid	Cholesterol	Cholesteryl Acetate	Triolein
0	3.35 ± 0.07	2.04 ± 0.03	1.57 ± 0.08	1.21 ± 0.04
200	2.74 ± 0.05	1.37 ± 0.06	1.12 ± 0.02	0.71 ± 0.01
400	1.88 ± 0.04	0.70 ± 0.03	0.64 ± 0.03	0.43 ± 0.04
480	1.76 ± 0.03	0.66 ± 0.04	0.36 ± 0.04	0.46 ± 0.04

ilar to D, the absorption also reduces depending upon the extent of stretching and the nature of the polymer. The % reduction in absorption for a linear molecule (stearic acid) and a rigid one (cholesterol) is also summarized in Table VI. The absorption change is also more or less in the same pattern observed in the case of D. Figure 3 illustrates the relation between equilibrium mass uptake of the four diffusants with the respective diffusion coefficients. The variation is linear, indicating that the diffusion coefficients are inherently related to the mass uptake. Indirectly, it reflects the lack of substantial deviation in the structural factors of the SS by the absorption of lipids.

Orientation of the polymeric chains can certainly influence the diffusion characteristics. To a large extent, however, the effect depends upon the crystallinity which is ruled out in the present system. Orientation in an amorphous polymer can result in a reduction of absorption around 10–15%.[21] Interestingly, here, the reduction in absorption is between 36 and 85%, depending on the nature of the diffusant and, of course, the HS content. The HS undoubtedly plays a major role in reducing the absorption by controlling the SS movement, which has been stated in previous sections. The stronger interchain interaction through altered structural features in the drawn materials is reflected in the enhanced thermal stability.[17] As the diffusion process takes place by the passage of molecules through the interstices between adjacent molecular chains, the orientation and separation between them will control the process. The decrease in absorption with drawing reflects structural changes incurred by deformation. The changes are attributable to the decrease of the amount of free volume present in the SS. In oriented polymers, additional flow resistance could develop due to the change of chain mobility.

Table IX Effect of Stretching on Absorption of Lipids in PU-3

Elongation (%)	Absorption (%)			
	Stearic Acid	Cholesterol	Cholesteryl Acetate	Triolein
0	2.27 ± 0.1	1.26 ± 0.07	0.86 ± 0.06	0.60 ± 0.03
200	1.48 ± 0.05	0.74 ± 0.04	0.49 ± 0.07	0.36 ± 0.05
400	1.12 ± 0.04	0.48 ± 0.04	0.28 ± 0.01	0.26 ± 0.05
450	1.01 ± 0.02	0.25 ± 0.03	0.19 ± 0.05	0.19 ± 0.02

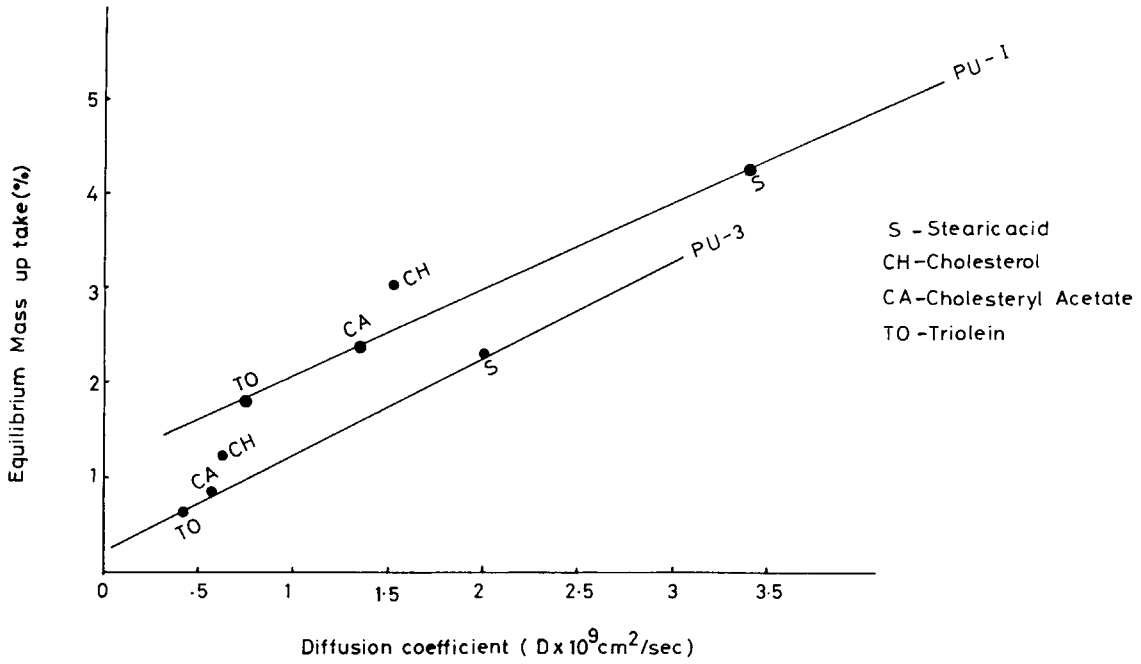

Figure 3 Correlation between equilibrium mass uptake and diffusion coefficients of the diffusants in PU-1 and PU-3.

Though the orientation of the segment can influence the absorption, the remarkably high degree of reduction could possibly be traced to the reduced segmental mobility of SS in the drawn materials illustrated in Figure 1, and Table II suggests the considerable degree of phase mixing in these materials. This is in close agreement with our earlier study.[16] It seems that the sluggishness in SS mobility resulting from phase mixing is the major factor responsible for the substantial reduction in diffusion and absorption.

CONCLUSION

The results emerged from the study indicate that the SS content as well as its purity are the major factors governing the absorption of lipids in polyurethanes. The presence of more HS domains in the SS phase drastically decreases the extent of absorption. The present study favors that lipid absorption in polyurethanes can be controlled by simple stretching.

REFERENCES

1. A. Peterlin, J. L. Williams, and J. Stannett, *Polym. Sci. A2*, **5**, (1967).
2. J. L. Williams and A. Peterlin, *J. Polym. Sci. A*, **29**, 1493 (1971).
3. A. Peterlin, *J. Macromol. Sci. B*, **11**, 57 (1978).
4. F. De Candia, R. Russo, V. Victoria, and A. Peterlin, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 2083 (1980).
5. Y. Takagi, *J. Appl. Polym. Sci.*, **9**, 3887 (1965).
6. Y. J. Molsan, *Eur. Polym. J.*, **16**, 997 (1980).
7. D. L. Coleman, D. Lim, T. Kessler, and J. D. Andrade, *Trans. Am. Soc. Artif. Intern. Org.*, **27**, 97 (1981).
8. D. Owen and R. M. Zone, *Trans. Am. Soc. Artif. Intern. Org.*, **27**, 528 (1981).
9. K. Hayashi, T. Matsuda, M. Takano, and M. Umezu, *J. Biomed. Mater. Res.*, **18**, 939 (1984).
10. A. Takahara, A. Tashita, T. Kajiyama, and M. Takayanagi, *J. Biomed. Mater. Res.*, **19**, 13 (1985).
11. K. Sreenivasan, PhD Thesis, Sree Chitra Tirunal Institute for Medical Sciences & Technology, 1990.
12. K. Sreenivasan, M. Jayabalan, and K. V. C. Rao, *J. Appl. Polym. Sci.*, **45**, 2105 (1992).
13. K. Sreenivasan, M. Jayabalan, and K. V. C. Rao. *J. Appl. Polym. Sci.*, to appear.
14. K. Sreenivasan, *Polym. J.*, **22**, 620 (1990).
15. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, New York, 1968.
16. K. Sreenivasan, *J. Polym. Sci. Polym. Phys. Ed.*, **31**, 1983 (1993).
17. K. Sreenivasan, *Acta Polym.*, **43**, 189 (1989).
18. K. Sreenivasan, *Polym. Deg. Stab.*, **32**, 115 (1991).
19. A. S. Michaels and R. B. Parker, *J. Polym. Sci.*, **41**, 53 (1959).
20. J. S. McBride, J. A. Massaro, and S. L. Cooper, *J. Polym. Sci.*, **23**, 201 (1979).
21. A. J. Ashley, in *Polymer Permeability*, Comyn, Ed., Elsevier, Amsterdam, 1985, p. 286.

Received February 18, 1995
Accepted July 29, 1995