

## STUDY OF THE COMPRESSION PROPERTIES OF POLYURETHANES BASED ON DIBENZYL MONOMERS AND 1,4-BUTANEDIOL AS COMPARED TO OTHER DIOL CHAIN EXTENDERS

Cristina PRISACARIU and Elena SCORTANU\*

Institute of Macromolecular Chemistry "Petru Poni", Aleea Grigore Ghica Voda 41A, 700487, Iasi, Roumania

*Received January 17, 2007*

A systematic study of the compression properties for a series of polyurethane elastomers (PUs) was made by varying the type of chain extender and using the same diisocyanate of variable geometry, 4,4'-dibenzyl diisocyanate (DBDI). The compression set and Young Modulus at variable temperature was followed for the family of PUs with dibenzyl structures as compared to the conventional PUs based on classical rigid diisocyanates 4,4'-diphenyl diisocyanate (MDI) and 1,5-naphthalene diisocyanate (NDI). The lowest compression set values were found in the case of PUs derived from dibenzyl monomers. In the case of PUs based on the chain extender (CE) 1,4 – butanediol (BG), increasing the hard segment (HS) weight percentage from 32% to 40% had no significant effect on the residual elongation but determined changes in the values of the Young Modulus at a 25% compression ( $E_{25}$ ). Changing the type of CE also determined variations of the  $E_{25}$  Young Modulus.

### INTRODUCTION

As mentioned elsewhere,<sup>1</sup> in our previous compression experiments effected on PUs we have shown that for the same elastomeric material it obtain different load–deflection curves if changing the shape and/or size of PUs specimens. The Shape Factor ( $\theta$ ) function was introduced and calculated as the ratio between the charged area and the sum of free areas of specimen when compressed.<sup>1</sup> The stress-strain diagrams of compression were determined for a series of PUs when approaching a large scale of  $\theta$  numbers which we varied from the values 0.1 to 4. The variation of the Young Modulus ( $E$ ) as a function of the  $\theta$  factor was determined. In the present paper we envisaged a sub-set of PUs based on flexible diisocyanate DBDI and different chain extenders (CE). The effect of increasing the hard segment weight percentage on the residual elongation and Young Modulus was studied. The compression set values when replacing the flexible DBDI with conventional diisocyanates were followed.

### RESULTS AND DISCUSSION

#### 1. The effect of increasing the hard segment weight percentage on the compression properties of DBDI based PUs with chain extender 1,4-butanediol (BG)

The effect of increasing the hard segment weight percentage from 32% to 40% BG on the compression set was undertaken. The evolution of the Young Modulus was followed. As shown in Table 1 in the case of PUs based on the chain extender 1,4–butanediol (BG), increasing the hard segment weight percentage (wt%) at temperature  $t=20^{\circ}\text{C}$ , from 32% to 40% had no significant effect on the compression set after 30 min. The compression set values decrease with increasing temperature to  $t = 80^{\circ}\text{C}$  as follows: for a 32 wt % from 4.3% at  $20^{\circ}\text{C}$  to 1.8% at  $80^{\circ}\text{C}$ ; for a 37 wt % from 4.8% to 2.8% at  $80^{\circ}\text{C}$ ; and for a 40 wt % from 4.7% to 2.7% at  $80^{\circ}\text{C}$ . The increase of hard segment content determines a slight enhance of the PUs compression set data as depicted in Table 1.

\* Corresponding author: nutiscor@yahoo.com

Changing the type of CE also determined variations of the  $E_{25}$  Young Modulus. The modifications of the Young Modulus data at a 25% compression ( $E_{25}$ ) were followed as a function of temperature. As a general observation, it observes a dramatic decrease of  $E_{25}$  at temperatures of 80°C. At temperature  $t=20^\circ\text{C}$  the highest  $E_{25}$  values (60 MPa) were found as corresponding to PUs of 40 wt%. This is due to the fact that increasing the hard segment weight percent from 32wt% to 40wt % determines the enhance of polymer toughness by the increase of the number of hydrogen bonds.<sup>2,3</sup>

## 2. Compression set and $E_{25}$ Young Modulus at $t=20^\circ\text{C}$ for DBDI based PUs with chain extender 1,4-butanediol (BG) as compared to other CE.

The compression set data were followed for some PUs derived from dibenzyl monomers when replacing the BG chain extenders with other diol CEs. As seen in Table 2, the compression set values are higher for PUs based on the couples BG 40 – DBDI and EG 40 – DBDI. As previously shown this is due to the special spatial structure of DBDI when the EG-DBDI and BG-DBDI hard segment crystallization performs in a high proportion (88.7%), this process being not affected by the presence of the soft segments. As a result, in such polymers there perform high phase separations which were confirmed by the X-ray experiments.<sup>2,3</sup> That also explains the significantly higher  $E_{25}$  data in the case of PUs based on the chain extenders BG and EG, in contrast to dibenzyl based PUs derived from the chain extender diethylene glycol (DEG) which was proved to inhibit crystallization.<sup>2,3</sup>

## 3. Compression set at $t=20^\circ\text{C}$ for DBDI based PUs as compared to other conventional PUs

The compression set values when replacing the flexible DBDI with conventional diisocyanates were followed also. All PUs depicted in Table 3 were synthesized with PEA ( $M = 2000 \pm 50$ ) macrodiol and 1,4 butanediol (BG). As observed, the compression set value of the polymer with DBDI is significantly smaller than the data found for the conventional similar polymers derived from the rigid MDI and NDI. The lower compression set for PUs are attributed to the BG-DBDI couple where the variable geometry of this isocyanate favours the polymer crystallization.

## 4. Young Modulus ( $E_{25}$ ) as a function of $\theta$ shape factor at 25% compression

Young Modulus ( $E_{25}$ ) as a function of  $\theta$  shape factor at a 25% compression was followed for three DBDI based PUs with different CE but the same HS of 40wt%. The adopted chain extenders were BG, DEG and ethylene glycol (EG) respectively. The specimens compression was employed in three different ways as follows: (a) specimen located in a seat; (b) specimen not located in seat and compressed between dried surfaces; (c) specimen not located in seat but compressed between lubricated surfaces (Figure 1).

As seen in Figure 1 the E dependence on the  $\theta$  factor varies significantly according to the adopted compression conditions: polymer 1 with BG display higher Young Modulus with increasing the value of  $\theta$  number. The highest E value is seen when  $\theta = 1$  when the compression was made with specimen located in a seat and also for the same polymer but for  $\theta = 4$  but when compression was achieved between dried surfaces. As expected the BG based materials display the highest E values. The E values corresponding to compression between lubricated surfaces are significantly lower. As observed in Figure 1, the  $E_{25} - \theta$  curves differ for the same polymer if changing the value of  $\theta$  factor and/or when approaching different compression conditions.

## EXPERIMENTAL

### 1. Synthesis

For synthesis the following procedure was followed: polymers with molar ratios DI:MD:CE = 4:1:2.64 were achieved; 100g (0.05 mol) of macrodiol poly (ethylene adipate) (PEA) was dehydrated by stirring at  $110^\circ\text{C}$  under vacuum ( $< 1\text{ mm Hg}$ ) for 2 hours. 52.8 g (0.2 mol) of DBDI was added to the anhydrous macrodiol with intense mixing, and vacuum was restored. After 30 minutes of mixing under vacuum at  $100^\circ\text{C}$  the temperature was reduced to  $90^\circ\text{C}$  and vacuum was removed. A prepolymer was obtained with final NCO groups in a mixture with the excess of isocyanate. Then the CE was added quickly with rapid stirring. The proportion of the CE was chosen so to get the above mentioned constant molar ratio. For example, when employing 1,4-butanediol (BG 40) as a CE with 40 % hard segment weight percentage, it was used 0.132 mol of CE. The mixing was continued for a maximum of 30-40 seconds. After addition of the CE the prepolymer melt was poured into a sheet mould and cured by heating for 24 h at  $110^\circ\text{C}$ . PUs prepared with a deficit of CE ( $I=110$ ) were postcured by holding for two weeks under ambient humidity, so as to obtain a further increase of the molecular weight as a result of the NCO excess transforming into urea linkages and allophanate crosslinks. All polyurethanes mentioned in Tables 1-3 were synthesized in this manner.

Fig. 1 – Young Modulus ( $E_{25}$ ) as a function of  $\theta$  shape factor at 25% compression for 3 DBDI based PUs based on the different CE but with same 40 wt%: 1. polymer based on butanediol (BG); 2. polymer with diethylene glycol (DEG); 3. polymer derived from ethylene glycol (EG); (a) specimen located in a seat; (b) specimen not located in seat with compression between dried surfaces; (c) PU compression between lubricated surfaces.

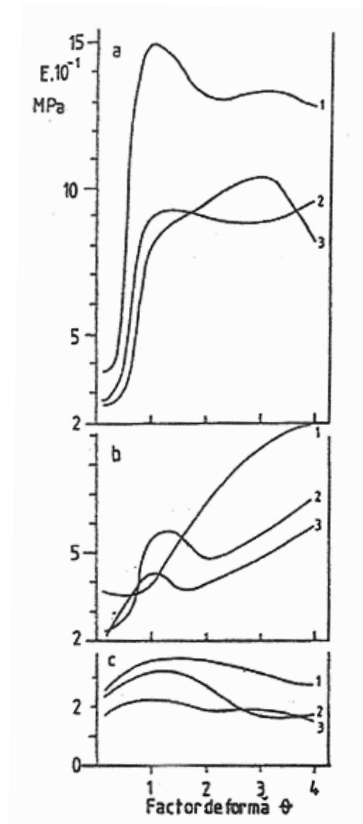


Table 1

Compression set and Young Modulus at a 25% compression ( $E_{25}$ ) for PUs based on DBDI and chain extender BG of variable hard segment weight percentage

Type of CE hard segment percentage, (wt %)	T <sup>0</sup>	Compression set after 30 mins, [%]	$E_{25}$ , [MPa]
BG 32	20	4.3	44.0
BG 32	50	4,3	42,0
BG 32	80	1,8	34,8
BG 37	20	4,8	37,2
BG 37	50	4,2	35,8
BG 37	80	2,8	33,7
BG 40	20	4,7	60.0
BG 40	50	3,6	40.0
BG 40	80	2,7	36.2

Table 2

Compression set and  $E_{25}$  Young Modulus at  $t=20^{\circ}\text{C}$  for DBDI based PUs with chain extender 1,4-butanediol (BG) as compared to other CE.

Type of CE hard segment percentage (wt %)	T ( $^{\circ}\text{C}$ )	Compression set after 30 mins, [%]	$E_{25}$ [MPa]
BG 40	20	3.7	60.0
DEG 40	20	2.29	22.8
EG 40	20	3.75	55.9

Table 3

Compression set at  $t=20^{\circ}\text{C}$  for DBDI based PUs  
as compared to other conventional PUs

	T ( $^{\circ}\text{C}$ )	NDI	MDI	DBDI
Compression set, [%]	20	21.3	13.2	5.0

## 2. Mechanical tests

Elastomer compression set measurements were made for a 25% compression for a given time and variable temperatures from  $20^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ . The cross-section was measured after the load was removed. Elastomer compression set was determined as the percentage of the original compression (25%) that was not recovered. The tests were conducted on cylindrical specimens of diameter  $\varnothing = 20$  mm and height  $H = 20$  mm according to the ISO 815-1972 standard. At the end of the test, the samples were removed and allowed to cool at room temperature for 30 minutes before measuring. After a load was released from an elastomer, the difference between the final dimensions and the original dimensions was considered the compression set. The experiments were made on employing an in-house made hydraulic press previously described.<sup>1</sup>

## CONCLUSIONS

The compression set and Young Modulus at variable temperature were followed for a series of PUs with dibenzyl structures as compared to two conventional similar polymers but based on classical rigid diisocyanates 4,4'-diphenyl diisocyanate (MDI) and 1,5-naphthalene diisocyanate (NDI). The lower compression set for polyurethanes with DBDI were attributed to their BG-DBDI couple where the variable geometry of DBDI favors the polymer crystallization. When replacing the chain extender BG with other diol

chain extenders, the compression set data are higher for PUs based on the couples BG 40 – DBDI and EG 40 – DBDI. In such polymers there perform high phase separations and differences in hard phase plastic flow stress, resulting from crystallinity in the DBDI phase. Significantly higher Young Modulus  $E_{25}$  data were found in the case of PUs based on the chain extenders BG and EG, in contrast to similar polymers but derived from DEG which was proved to inhibit crystallization. The compression set values decrease with increasing temperature. The enhance of the hard segment content determines a slight increase of the PUs compression set data. The  $E_{25} - \theta$  shape factor dependence differ for the same polymer if changing the value of the  $\theta$  factor and/or when approaching different compression conditions.

## REFERENCES

1. C. Prisacariu, *Polytechnical Inst. "Gh. Asachi", Bull. Iasi-Vol. XLVII, (LI), Section I, Mathematics, Theoretical Mechanics Physics*, **2001**, 3-4, 106-118.
2. C. Prisacariu, C. P. Buckley and A. Caraculacu, *Polymer*, **2005**, 46, 3884-3894.
3. C. P. Buckley, C. Prisacariu, A. Caraculacu and C. M. Martin, *4<sup>th</sup> European Conference on Constitutive Models for Rubber*, Stockholm, June 27-29, 2005, 324-329.