Novel polyurea polymers with enhanced mechanical properties

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ABSTRACT: The present work describes the preparation of a set of new polyurea polymers suitable for ballistic protection applications by employing different aromatic diamines derivatives with different flexibility degrees. This modification would allow the synthesis of polymers with both enhanced and controllable mechanical properties through the combination of aliphatic and aromatic molecules. Besides the classical methylene diphenyl diisocyanate and polypropylene glycol bis(2-aminopropyl ether) (PPG), benzidine, 4,4'-diaminodiphenylmethane and 3,6-diamino carbazole were chosen as the third monomer and used in different ratios toward PPG, in order to optimize the polymer properties. The proportions between the polyurea components were selected as such to achieve the total consumption of the monomers. The different types of polyurea obtained have been characterized by Fourier transform infrared spectroscopy, thermal measurements (differential scanning calorimetry and thermogravimetric analysis), tensile tests, and scanning electron microscope. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43967.

INTRODUCTION

Polyurea is an elastomeric polymer suitable for applications in ballistic protection due to its characteristic set of properties: light weight, high elasticity, high flexibility, heat resistance, impact resistance, and high energy absorbing capacity. Recent studies showed that polyurea is a promising material in military applications where its coating on a steel plate changes the response under dynamic impulsive loadings,[1,2] favoring the delay of the "bottleneck" phenomenon of the metal. Thus, a polyurea layer deposited on a steel plate could lead to an enhanced blast-mitigation performance,[3] but it could also retain the fragments/debris coming from the structure failure.

Polyurea is also one of the most successful materials used in the coating industry, having multiple applications in many fields of activity due to fast curing, chemical resistance, low flammability, good stability and durability, excellent bonding properties to all type of surfaces, especially metals.[4] The synthesis of polyurea elastomeric films consists in a rapid polyaddition reaction between two oligomeric species: a diamine and a diisocyanate. The spray-on technique is the most commonly used method for obtaining polyurea coatings on different types of surfaces.[4] The polyurea

films described in literature are generally obtained by simply mixing two commercial components: an isocyanate component (Isonate 143L,[4–11] Basonat HI-100,[12] Vestanat IPDI[13]) and an oligomeric diamine (Versalink P-1000,[4–11,14] Jeffamine D-2000 and D-400,[12,14] Jefflink 754,[13] Clearlink 1000[13]).

The aforementioned polyureas have an unusual morphology, consisting in two distinct microphases, with different characteristic: aromatic rings regions (hard domains) which are chemically bonded and homogenously distributed through the aliphatic polymer chains matrix (soft domains).[4,15] This special structure ensures good mechanical properties and makes these materials suitable for ballistic protection applications. Depending on the composition, the properties of a polyurea coating change dramatically. Thus, a higher aliphatic chain content increases the flexibility, but decreases the strength, whereas higher aromatic rings content leads to increased strength but lower elasticity. Another important aspect related to polyurea coatings used in ballistic protection is represented by their transition from glassy to rubbery state, during the deformation process, which occurs earlier in case of high impact forces. The large energy absorption induces the glass transition of the

polyurea, improving the resistance of the hard substrate concerning fragmentation or ballistic penetration.[15] The amount of energy dissipated through the polyurea film is comparable to its loading-unloading behavior, being related to the hysteresis area under stress–strain curve.[16]

The design of polyurea properties for a certain type of application can be obtained by choosing the right components and the adequate proportions between them. Thus, the behavior of these materials can be controlled by the synthesis parameters. A such parameter is represented by the addition of chain extenders, like, for example, 3,3′-dichloro-4,4′-diamino-diphenylmethane, 3,5-diethyltoluene-2,4-diamine, m-phenylene diamine, di(methylthio) toluene diamine, 4,4′-methylenebis(2,6-diethylaniline), 4,4′-methylenebis(cyclohexyl amine), 4,4′-methylenebis(2-methyl cyclo-hexylamine), 4,4′-methylenebis(2-methyl 6-ethyl cyclo-hexyl amine), which have already been mentioned in previous studies.[17,18]

The present work deals with the synthesis and characterization of some novel polyureas obtained by the addition of new aromatic amines as chain extenders, with possible applications in the ballistic protection field. As the flexibility of the aromatic amine may bring an important contribution to the polyureas film mechanical properties, to the best of our knowledge we report here for the first time an example of how the chain extender structure may affect the resulting polyurea properties. We will show within the article that the addition of more aromatic rings to the chemical structure of polyurea, leads to higher deformation energies. Therefore, an improvement of the energy dissipation capacity and limitation of the structure damage should be brought by the strengthening effect induced by these aromatic compounds. Also, the influence of the ratio between the amines and polypropylene glycol bis(2-aminopropyl ether) (PPG) on the final properties of the material was studied.

EXPERIMENTAL

Materials

Poly (propylene glycol) bis(2-aminopropyl ether)—$M_n \approx 2000$ Da (PPG, Sigma Aldrich), benzidine (BZ, Sigma Aldrich), 4,4′-diaminodiphenylmethane (DADPHM, Sigma Aldrich), 3,6-diaminocarbazole (DAC, TCI), diphenylmethane-4,4′-diisocyanate (MDI, technical product Desmodur® 44V20L, Bayer), acetone (Sigma Aldrich) and N,N-dimethylformamide (Sigma Aldrich, Germany) were used as received. Zinc tetra amino phthalocyanine (ZnPc) was synthesized according to literature data.[19]

Methods

Preparation of the Polyurea Films. For the synthesis of each type of polyurea films, two different solutions were prepared. First, PPG and the other diamines (BZ, DADPHM, or DAC) were solubilized in acetone in the right proportions (Composition A, Table I) while the second solution was obtained by dissolving MDI in the same solvent (Composition B). The molar ratio between the isocyanate groups and the primary amino groups was always 1:1. The polyurea containing ZnPc was obtained by using N,N-dimethylformamide as the solvent.

In order to obtain a homogenous polyurea film, the two solutions (Composition A and Composition B) were stirred vigorously for a few seconds and the mixture was then transferred

**Table I.** . Mole Ratios between the Amines used in the Synthesis of Polyurea

Sample	Composition	Molar ratio between amines
PU-0 (blank)	PPG	—
PU-1-a	PPG:BZ	1:3
PU-1-b	PPG:BZ	1:2
PU-1-c	PPG:BZ	1:1
PU-2-a	PPG:DADPHM	1:3
PU-2-b	PPG:DADPHM	1:2
PU-2-c	PPG:DADPHM	1:1
PU-3-a	PPG:DAC	1:3
PU-3-b	PPG:DAC	1:2
PU-3-c	PPG:DAC	1:1
PU-4	PPG:DADPHM + ZnPc	1:2 + 1% (wt %)

in a Petri dish placed on a flat surface at 25 °C and 50–55% relative humidity. After the complete reaction and solvent evaporation, films of about 0.4 mm thickness were obtained.

Characterization. The IR (infra red) spectra were obtained using a Bruker VERTEX 70 Spectrometer with ATR (Attenuated total reflection). Data were collected by averaging 32 scans, at a resolution of 4 cm^{-1}, from 500 to 4000 cm^{-1}. The transition glass temperature (T_g) was determined by differential scanning calorimetry (DSC) measurements performed with a NETZSCH DSC 204 F1 Phoenix instrument, under nitrogen flow, at 10 °C/min heating rate. The tests were carried out on samples having around 10 mg, in two heating/cooling cycles, between −80 and 200 °C. T_g was determined from the inflection point obtained during the second heating cycle. The thermogravimetric analysis (TGA) of the synthesized polyureas was executed using a Thermal Analysis Q500 instrument. Samples of about 2 mg were heated from room temperature to 700 °C, at 10 °C/min heating rate, under nitrogen flow. Tensile tests were carried out by using a Titan - Universal Strength Tester by James H. Heal & Co. Ltd testing machine. The tests were carried out according to the international standard ISO 37:2005. Tensile samples were prepared by cutting standard dumbbell tensile specimens (5 mm width of the narrow parallel part, 100 mm total length, distance between gauge marks 20 mm). Tests were performed at 500 mm/min rate of extension, starting with 50 mm jaw separation (plain jaw faces). For each polymer film, five tensile tests were performed and the average value was reported. In order to make a comparison between these polyurea films, the stress–strain plots displayed within the "Results and Discussion" section show only the curve having the closest parameters to the mean values from each set of specimens. The scanning electron microscopy analyses were performed using a FE-SEM (field emission scanning electron microscope) RAITH e Line at 10 kV acceleration voltage.

RESULTS AND DISCUSSION

In order to analyze the influence of the third monomer (BZ, DADPHM, DAC, or ZnPc) on the final properties of the
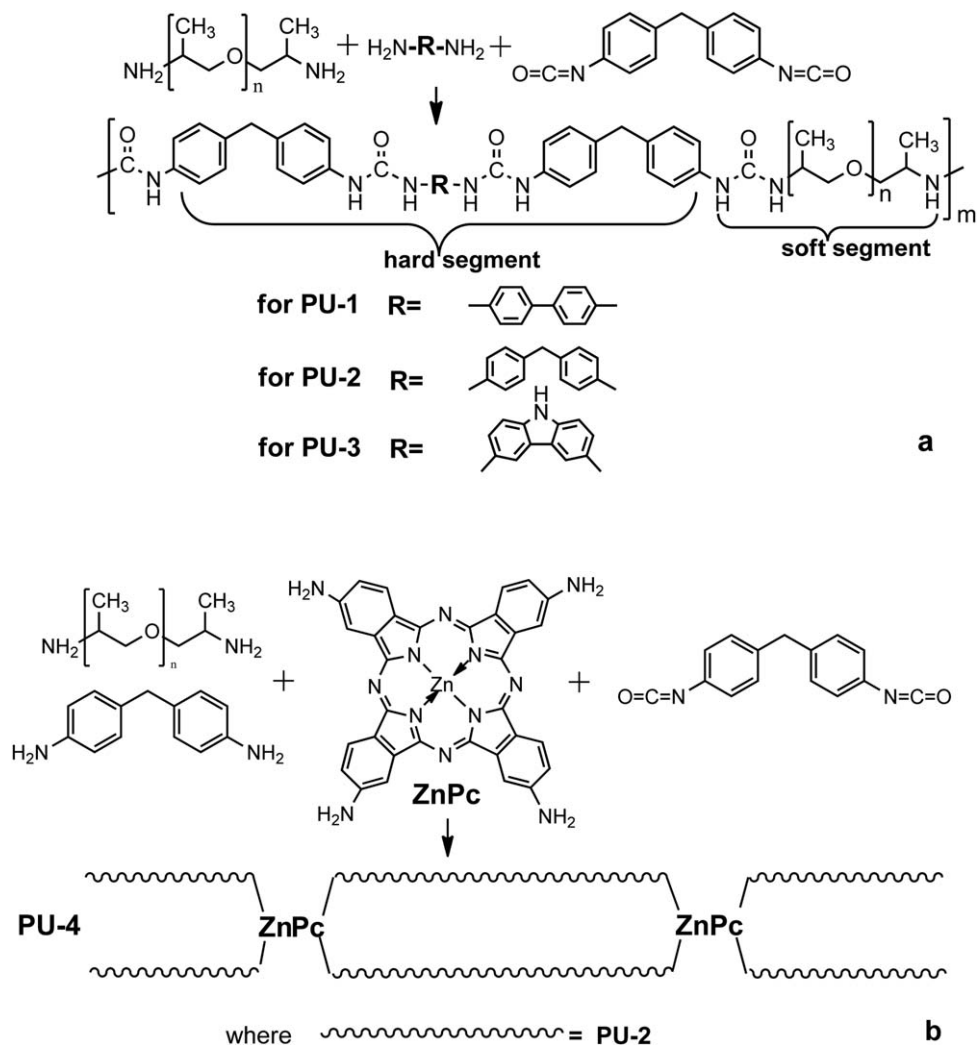
Figure 1. (a) Synthesis of polyurea; (b) Synthesis of polyurea with ZnPc.

polyurea films and to establish an optimal composition for ballistic applications, samples using different molar ratios between the components were prepared (Table I). The simplified reaction schemes are presented in Figure 1. In this figure, the MDI monomer functionality is equal to 2, in agreement with the approximate average functionality reported by the manufacturer.

The first step of our study consisted in the investigation of the reaction between PPG and MDI (sample PU-0, Table I). Due to the relatively increased viscosity of the two reactants, respectively, the high rate of the reaction, it was not possible to obtain a homogenous polyurea film, without using a solvent. Acetone represented a good choice in this case because it is a good solvent for all the reactants and it has a low boiling point which allows its fast evaporation. For PU-4 it was necessary to use *N,N*-dimethylformamide because of the poor solubility of ZnPc in other solvents. However, even in the presence of the solvent the reactions occurred quite fast, making very difficult to control or monitor the reaction profile.[8]

The blank polyurea film showed poor mechanical strength due to the extended long aliphatic chains regions and only few aromatic rings reinforcing areas. Therefore, the addition of the aro-

matic diamine as the third monomer [Figure 1(a)] was mandatory, taking into account our aim of preparing polyurea films with superior mechanical properties. Obviously, the ratio between the amine components should influence the mechanical behavior of the polymer films.

The polyurea films prepared with various compositions (Table I) were characterized structurally by Fourier transform infrared spectroscopy (FTIR), while their thermal behavior and mechanical properties were investigated by TGA and DSC, and tensile tests, respectively.

The FTIR analyses were performed in order to highlight the formation of the urea groups and the total consumption of the monomers. The FTIR spectra obtained (Figure 2), were quite similar and confirmed the formation of the specific urea linkage (R—NH—CO—NH—R) by the presence of the N—H stretching vibrations around $3330 \ cm^{-1}$ and carbonyl stretching band at 1655 and $1105 \ cm^{-1}$. The only difference between the IR spectra is represented by the intensity of the peaks at $1540 \ cm^{-1}$ ($\nu_{C—N}$) and $1508 \ cm^{-1}$ ($\nu_{C=C}$ in the aromatic ring), which changed in agreement with the aromatic diamines/PPG ratio. Also, the specific peak of the isocyanate stretching band (around
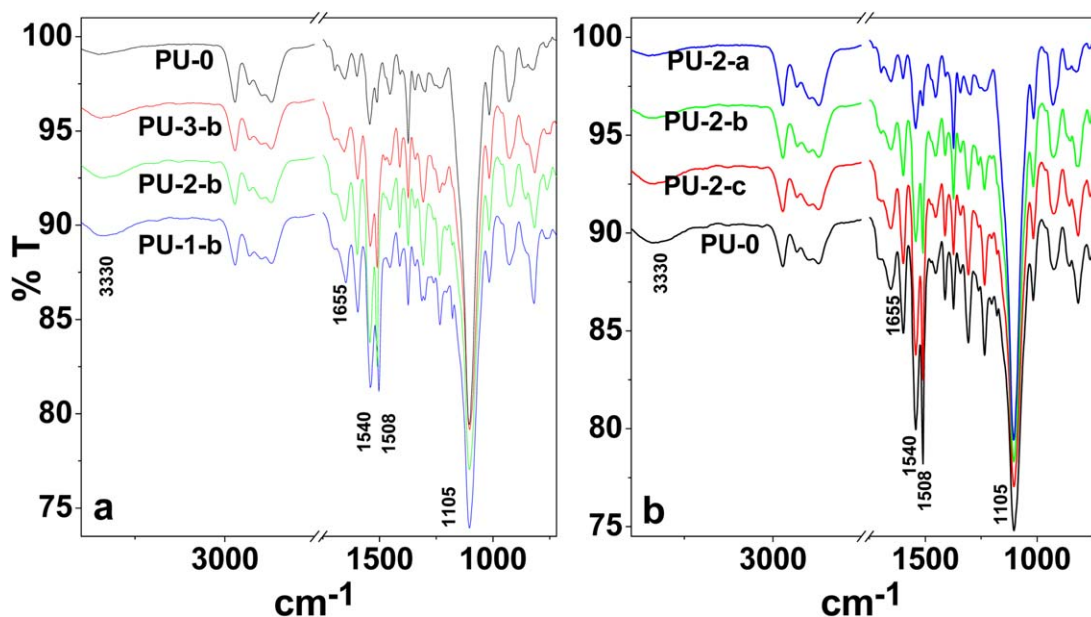
Figure 2. FTIR spectra of the synthesized polyureas using. (a) 1:2 aromatic diamine:PPG mole ratio; (b) different molar ratios between PPG and DADPHM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2280 cm^{-1}) and the two peaks specific for the primary amine groups (in the range 3600–3400 cm^{-1}) disappeared as a result of their complete consumption.

The thermal behavior of the polyureas designed for ballistic applications is a very important characteristic because the thermal radiation brought by the gaseous products generated from an explosion could lead to the degradation of the polymer coating. In the case of our polymers, the thermogravimetric analyses revealed that all synthesized polyureas were stable up to 300 °C, but after this temperature they displayed a drastic weight loss due to the decomposition process. The weight loss values for each type of polyurea are shown in Table II. Thus, below 300 °C there was no significant change, but above this temperature the weight loss increased due to the initiation of the polymer decomposition process. According to literature data, polyureas decomposition begins with the degradation of the hard domains because of the relatively low thermal stability of the urea group, but it also depends on the isocyanate nature. The decomposition process continues then with the degradation of the soft segments.[11]

Table III shows that the decomposition process started in the 314–331 °C temperature range (See Supporting Information S3). The polyureas containing DAC displayed a slower degradation process having a higher T_{max} than the blank sample.[8] Also, A higher concentration of BZ, DADPHM, DAC and the addition of ZnPc led to higher percentages of char residue at 700 °C.

The glass transition temperature of polyurea is also an important property in ballistic applications because at high temperatures (impact tests), polyurea tends to have high ductility, maintaining its rubbery state, but at lower temperatures (but still above the glass transition temperature) polyurea tends to turn into the glassy-state during the deformation due to the energy-dissipation process.[3]

According to literature data, polyurea polymers should display two glass transition temperatures due to the microphase segregated structure (Figure 3). The first one is associated with the polymer chains from the soft nanodomains (PPG), while the second one may be attributed to the aliphatic polymer chains

**Table II.** TGA Measurements for Polyureas at Different Temperatures

Sample	Weight loss (%)								
	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C	550 °C	600 °C
PU-0	0.2	0.8	4.9	21.0	83.9	94.4	95.3	95.7	95.9
PU-1-a	1.0	1.4	5.5	22.4	71.4	82.3	85.3	87.3	87.9
PU-1-c	0.5	1.0	5.1	20.9	79.0	88.3	89.9	91.0	91.4
PU-2-a	0.9	1.3	5.9	24.3	68.2	79.7	83.4	85.9	87.1
PU-2-c	1.1	1.6	6.3	21.4	78.0	88.8	90.8	92.1	92.4
PU-3-a	0.8	1.3	4.9	17.1	63.6	79.4	83.1	85.6	86.5
PU-3-c	0.2	0.8	4.4	17.0	76.6	88.5	90.4	91.6	92.0
PU-4	0.3	1.8	7.4	25.8	71.7	84.4	86.8	88.3	88.8

Table III. Thermal Properties of Polyurea

Sample	$T_{10\%}$ (°C)	T_{max} (°C)	Char residue at 700 °C (wt %)
PU-0	330	373	3.7
PU-1-a	317	367	11.5
PU-1-c	324	371	8.3
PU-2-a	319	365	12.6
PU-2-c	319	373	7.1
PU-3-a	329	378	12.7
PU-3-c	331	379	4.1
PU-4	314	368	10.6

$T_{10\%}$ = onset temperature (measured at 10% weight loss).
T_{max} = maximum degradation temperature.
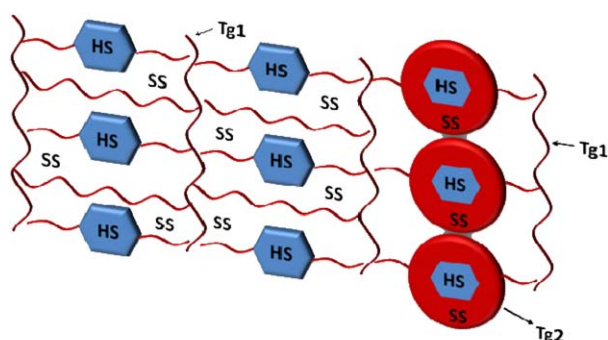
Figure 3. Schematic representation of the microphase segregated structure of polyurea. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

located in the proximity of the hard nanodomains formed by the aromatic rings sequences, whose mobility is restricted and, therefore, they require a higher energy for flexibility. Consequently, their glass transition temperature is higher than for the
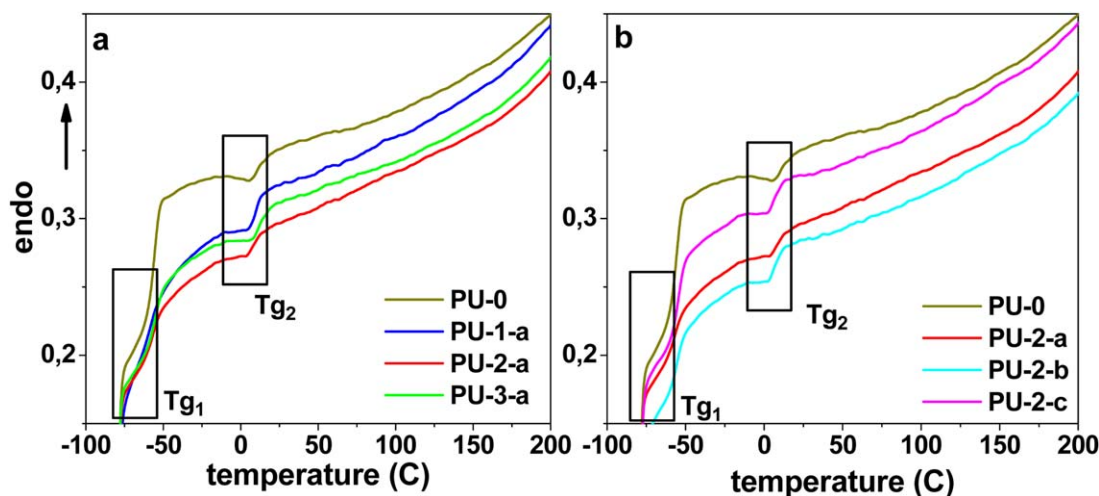
Table IV. T_g Values for the Synthesized Polyureas

| Sample	T_{g1} (°C)	T_{g2} (°C)
PU-0	−55.60	10.38
PU-1-a	−57.70	9.80
PU-2-a	−56.60	6.96
PU-3-a	−55.69	12.20
PU-2-b	−55.6	5.6
PU-2-c	−54.5	5.4

polymer chains situated at a longer distance from hard nanodomains, which have a higher mobility.[12]

The T_g values and the DSC traces of the synthesized polyureas are displayed in Table V and Figure 4(a), respectively. The first inflection point (T_{g1}), located between −56 and −58 °C was very similar for all the synthesized polyureas. T_{g1} corresponds to the transition from glassy to rubbery state of the polypropylene glycol sequences which were relatively far from the hard phase, therefore, having a higher mobility. The second inflection point (T_{g2}) was different for each type of polyurea, and it was ascribed to the glass transition of the lower mobility polymer chains located in the proximity of the hard nanodomain.[15] The T_{g2} values shown in Table V were in agreement with the flexibility/rigidity of the third monomer used by taking into account the chemical structure of the diamines presented in Figure 1(b), that is, DADPHM is the most flexible, followed by BZ and DAC. Increasing amounts of aromatic diamine led to higher T_{g2}, indicating a hardening effect due to the supplementary aromatic rings introduced in the polymer chain [Table IV, Figure 4(b)].

The tensile tests are mandatory for polyureas designed for ballistic applications. Thus, it is very important to estimate how the material would react when subjected to impulsive loadings. Being designed to be energy absorbing materials, the synthesized polyureas should present a high deformation energy. Thus, the best mechanical properties were obtained for the polyureas with

Figure 4. DSC traces for the synthesized polyureas using. (a) 1:2 aromatic diamine:PPG mole ratio; (b) different molar ratios between PPG and DADPHM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
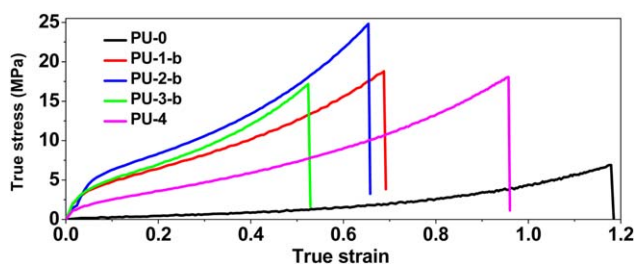
Figure 5. True stress–true strain curves for the synthesized polyureas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1:2 mole ratio between PPG and the other diamines, namely for PU-1-b, PU-2-b, PU-3-b, and PU-4 samples. Figure 5 shows the stress–strain curves obtained for these polyureas films. The maximum tensile stress was reached by the PU-2-b sample, while the maximum strain by PU-0. This means that the PU-2-b was a strong material but with lower ductility, while PU-0 was very ductile but it had a lower tensile strength.

The mechanical tensile tests revealed that the addition of DAC (PU-3-b sample) led to a polyurea with the highest modulus of elasticity, while DADPHM (PU-2-b sample) allowed for the highest deformation energy to be reached. PU-4 showed an interesting mechanical behavior due to the improved strain value while keeping a high tensile toughness, comparable with the one of PU-2-b (Table V). In this case, the PU-4 sample could absorb almost the same quantity of energy like PU-2-b, but it took longer to break. PU-4 combined both high stress and high strain and this property makes it a good candidate for ballistic applications. This type of polyurea may be used as coating for metal surfaces in order to delay the bottleneck phenomenon of the metal, thus postponing its fracture for a longer period of time.

In order to assess the morphology of the polyurea films, SEM analyses have been performed. Figure 6 confirmed that the films obtained were non-porous materials, presenting a homogenous surface aspect with no defects.

CONCLUSIONS

The degree of flexibility and the ratio between the components play a crucial role in the mechanical properties of the polyurea films designed for ballistic protection.

In order to find an optimal composition for this type of application, new polyurea terpolymer films involving three types of aromatic dia-
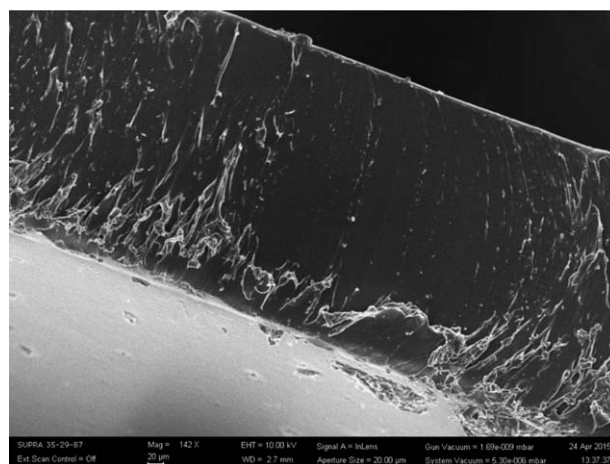
Figure 6. SEM images of PU-4 sample (side view).

mines derivatives (benzidine, 4,4′-diaminodiphenylmethane and 3,6-diamino carbazole) and zinc tetra amino phthalocyanine, with different degrees of flexibility, were synthesized.

The formation of the urea groups and the complete reaction between the three monomers was confirmed by FTIR analysis. TGA results revealed that all synthesized polyureas were stable up to 314 °C. From the three aromatic diamines added as the third monomer, 3,6-diamino carbazole led to higher onset temperatures for the decomposition process of the polyurea.

According to the DSC analyses, all the synthesized polyureas displayed two inflection points, the first one being attributed to the glass transition temperature of the soft nanodomains, while the second one being ascribed to the glass transition temperature of the polymer chains located near the hard nanodomains. The mechanical behavior of these polyureas demonstrated that these materials are suitable for ballistic applications due to their high capacity of absorbing energy. From all the synthesized polyureas, the one obtained using zinc tetra amino phthalocyanine seemed to have the optimal composition, showing simultaneously high stress and high strain values, therefore, high deformation energy. This means that this polymer can absorb a large amount of energy without breaking, therefore, protecting the structure on which it may be applied.

In conclusion, we may say that the unique set of properties of the synthesized polyureas makes them very good candidates for ballistic protection purposes.

Table V. Tensile Tests Results for the Synthesized Polyureas

Sample	Young's modulus[a] (MPa)	Maximum tensile stress (MPa)	Deformation energy (tensile toughness) (J m^{-3})
PU-0 (blank)	17.7 ± 0.4	6.89 ± 0.4	2.50 ± 0.2
PU-1-b	135.0 ± 2.6	18.78 ± 0.9	6.63 ± 0.3
PU-2-b	153.7 ± 1.5	24.81 ± 1.8	8.00 ± 0.5
PU-3-b	158.5 ± 0.7	17.17 ± 0.5	4.64 ± 0.2
PU-4	54.0 ± 1.1	18.06 ± 2.0	7.57 ± 0.4

[a] Young's modulus was calculated according to the mathematical model described in Ref. 20.

REFERENCES

1. Amini, M.; Isaacs, J.; Nemat-Nasser, S. In Proceedings of the 2006 SEM Annual Conference and Exposition on Experimental and Applied Mechanics; Saint Louis (MO, United States), **2006**; pp 1323–1326.

2. Mohotti, D.; Ngo, T.; Raman, S. N.; Ali, M.; Mendis, P. *Mater. Des.* **2014**, *56*, 696.

3. Grujicic, M.; Pandurangan, B.; He, T.; Cheeseman, B. A.; Yen, C. F.; Randow, C. L. *Mater. Sci. Eng. A* **2010**, *527*, 7741.

4. Nussinovitch, A. *Int. J. Innov. Mater. Sci. Eng.* **2009**, *1*, 295.

5. Holzworth, K.; Jia, Z.; Amirkhizi, A. V.; Qiao, J.; Nemat-Nasser, S. *Polymer (United Kingdom)* **2013**, *54*, 3079.

6. Roland, C. M.; Fragiadakis, D.; Gamache, R. M.; Casalini, R. *Philos. Mag.* **2012**, *93*, 468.

7. Ackland, K.; Anderson, C.; Ngo, T. D. *Int. J. Impact Eng.* **2013**, *51*, 13.

8. Mariappan, T.; Wilkie, C. A. *Polimery* **2013**, *58*, 371.

9. Casalini, R.; Bogoslovov, R.; Qadri, S. B.; Roland, C. M. *Polymer (Guildf)*. **2012**, *53*, 1282.

10. Cai, L.; Al-Ostaz, A.; Li, X.; Fowler, C.; Cheng, A. H. D.; Alkhateb, H. *Int. J. Impact Eng.* **2015**, *75*, 1.

11. Awad, W. H.; Wilkie, C. A. *Polymer (Guildf)*. **2010**, *51*, 2277.

12. Reinecker, M.; Soprunyuk, V.; Fally, M.; Sánchez-Ferrer, A.; Schranz, W. *Soft Matter* **2014**, *10*, 5729.

13. Posey, M. L.; Hillman, K. M.; Klein, H. P. *Development* **2003**, *1000*.

14. Qian, X.; Song, L.; Yu, B.; Yang, W.; Wang, B.; Hu, Y.; Yuen, R. K. K. *Chem. Eng. J.* **2014**, *236*, 233.

15. Fragiadakis, D.; Gamache, R.; Bogoslovov, R. B.; Roland, C. M. *Polymer (Guildf)*. **2010**, *51*, 178.

16. Shim, J.; Mohr, D. *Mech. Mater.* **2011**, *43*, 349.

17. Schmelzer, H. G.; Mafoti, R. M.; Sanders, J.; Slack, W. E. *J. Prakt. Chem.* **1994**, *336*, 483.

18. Samson, N.; Mechin, F.; Pascault, J. *J. Appl. Polym. Sci.* **1997**, *65*, 2265.

19. Diacon, A.; Rusen, E.; Boscornea, C.; Pandele, A. M.; Cincu, C. *UPB Sci. Bull. Ser. B Chem. Mater. Sci.* **2011**, *73*, 87.

20. Xue, Z.; Hutchinson, J. W. *Mech. Mater.* **2007**, *39*, 473.