Study of structural changes in thermoplastics using dynamic mechanical analysis

M Kohutiar\textsuperscript{1}, R Janík\textsuperscript{1}, M Pajtášová\textsuperscript{1}, D Ondrušová\textsuperscript{1}, I Labaj\textsuperscript{1} and V Zvoláneková Mezencevová\textsuperscript{2,3}

\textsuperscript{1} Department of Materials Technologies and Environment, Faculty of Industrial Technologies in Púchov, Alexander Dubček University of Trenčín, I. Krasku 491/30, 020 01 Púchov, Slovakia

\textsuperscript{2} Technical University of Košice, Faculty of Mechanical Engineering, Letná 9, 042 00 Košice, Slovakia

\textsuperscript{3} M-Science Group, Ltd., Gogolova 2, 040 01 Košice, Slovakia

E-mail: marcel.kohutiar@fpt.tnuni.sk

Abstract. Diffuse coplanar surface barrier discharge (DCSBD) is an innovative plasma source that finds application in industrial practice and also in the surface treatment of various types of materials. The presented paper deals with the investigation of structural changes in selected thermoplastic materials that have occurred after their treatment with plasma discharge. The structural changes were investigated by using dynamic mechanical analysis, where the changes between the unmodified material samples and the thermoplastic material samples exposed to the plasma discharge, were compared, based on the obtained data of the storage modulus, the loss modulus and the loss tangent. For the experiment, thermoplastic materials were chosen, which are widely represented in the production of packaging materials, namely polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET).

1. Introduction

The Plasma is an ionized gas, referred to as the fourth state of matter [1]. The word "ionized" means that at least one electron does not bind to an atom or molecule and converts the atoms or molecules into positively charged ions [2, 3]. As temperature increases, molecules become more energetic and transform matter in sequence: solid, liquid, gaseous, and finally plasma, which explains the term "fourth state of matter" [4, 5]. Plasma occurs either naturally or can be effectively produced in laboratories. Plasma is commonly used in industrial practice, which provides opportunities for numerous applications [6, 7].

DCSBD (Diffuse Coplanar Surface Barrier Discharge) is a type of plasma with a high concentration of chemically reactive particles along with neutral particles. It is a type of low temperature atmospheric plasma, operating at room temperature, suitable especially for surface treatment of materials [7]. DCSBD can be used to treat a wide variety of materials from wood, metal, glass to polymers. Possible structural changes in materials that may occur after plasma discharge treatment can be investigated by dynamic mechanical analysis (DMA) [8, 9].

DMA is one of the most commonly used type of sample loading when investigating the viscoelastic behavior of polymers [10, 11]. In a dynamic experiment, the sample is cyclically stressed by varying stresses or cyclically deformed to a degree of deformation. As with static tests, the specimen can be loaded in tension, compression, bending or shear. Possible changes between the unmodified material...
samples and the material samples exposed to the plasma discharge, can be compared based on the obtained data of the storage modulus, the loss modulus and the loss tangent [10, 12].

2. Materials and methods
For the experiment, six test samples were used. Two polypropylene samples (PP1 and PP2) gained from plastic food containers, two low density polyethylene samples (LDPE1 and LDPE2) gained from plastic foil, and two polyethylene terephthalate samples labeled PET1 and PET2 gained from plastic bottle samples of carbonated beverages. All samples were taken from household municipal waste (figure 1).

The samples from foils, bottles and containers were manually cut and then abraded to be smooth on the edge. The thickness of the individual samples was not the same and for that reason it was necessary to adjust the width so that the samples could be correctly measured. To compare the results, the samples were measured in basic form and subsequently treated with a DCSBD plasma discharge. Figure 2 shows samples treated by plasma discharge, in particular PP1-DCSBD and PP2-DCSBD polypropylene, LDPE1-DCSBD and LDPE2-DCSBD polyethylene, PET1-DCSBD and PET2-DCSBD polyethylene terephthalate.

![Figure 1. Samples used for experiment.](image1.png)  
![Figure 2. Samples treated by plasma discharge.](image2.png)

Surface modification of samples was performed on a diffuse coplanar barrier discharge line (DCSBD). DCSBD measurements were made at atmospheric pressure and at room temperature. Plasma discharge is characterized by high power density at low plasma thickness. 350 W unit power was determined, exposure time was 30 seconds for both sides of the sample. The plasma electrode area was 200 × 70 mm. Samples were attached with a slide on the plasma electrode surface to ensure sample surface alignment. The electrode did not burn homogeneously throughout the sample surface due to the natural properties of the material, such as thickness, chemical composition, surface unevenness).

The DMA analysis was performed on a DMA Q800 from TA Instruments. The samples were clamped between the two jaws using the tension-film geometry (figure 3), with one jaw moving and the other static.

![Figure 3. Sample attachment for DMA analysis.](image3.png)

To measure polypropylene samples, a temperature range of -70 °C to 120 °C, for polyethylene samples from -70 °C to 100 °C and for polyethylene terephthalate samples from -70 °C to 170 °C, was determined.
The samples were initially cooled to -70 °C and subsequently heated to the required temperature, at a rate of 3 °C min⁻¹, at frequency 10 Hz. The dimensions of samples are shown in table 1.

| Dimension (mm) | PP samples | LDPE samples | PET samples |
|----------------|------------|--------------|-------------|
| Length         | 50         | 50           | 50          |
| Width          | 10         | 10           | 10          |
| Thickness      | 0.17       | 0.13         | 0.22        |

All measurements were carried out at the CEDITEK (Center for quality testing and diagnostics of materials) workplace at Faculty of Industrial Technologies in Púchov.

3. Dynamic mechanical analysis
Dynamic mechanical analysis (DMA) was performed on polypropylene, polyethylene and polyethylene terephthalate samples. Elastic modulus (E') were measured and compared. The elastic modulus is the temperature at which the material begins to lose its strength, i.e. the material is no longer able to withstand the stress without causing its deformation [10, 12]. The measured curves PP1 and PP1-DCSBD are compared in figure 4. As can be seen, there is a gradual decrease in the elastic modulus at approximately -70 °C to -15 °C. From -11 °C to 42 °C, the elastic modulus decreased significantly.

The elastic modulus for PP2, PP2-DCSBD is shown in figure 5. The PP2-DCSBD sample has a higher elastic modulus values than PP2 after plasma discharge treatment. At a temperature of about -70 °C to 5 °C, the elastic modulus of PP2-DCSBD is significantly reduced. From about 10 °C to 120 °C, the samples have roughly the same elastic modulus and there is a gradual decline. Sample PP2-DCSBD showed higher values of elastic modulus at negative temperatures than sample PP2.

![Figure 4](https://via.placeholder.com/150)

**Figure 4.** Elastic modulus of PP1 samples.

![Figure 5](https://via.placeholder.com/150)

**Figure 5.** Elastic modulus of PP2 samples.

The elastic modulus for LDPE1 and LDPE1-DCSBD is shown in figure 6. The LDPE1 sample has a higher elastic modulus value than LDPE1-DCSBD. At a temperature of about -70 °C to -30 °C, the elastic modulus is significantly reduced and also at a temperature of from -17 °C to 25 °C for LDPE1. The gradual decrease in the elastic modulus occurs from 60 °C to 100 °C for LDPE1-DCSBD.

The elastic modulus for LDPE2 and LDPE2-DCSBD is shown in figure 7. The LDPE2 sample has significantly higher elastic modulus values than the LDPE2-DCSBD sample. It can be concluded that in this case, the effect of plasma discharge treatment significantly influenced the values of the elastic modulus. At a temperature of about -30 °C to about 10 °C, the elastic modulus for LDPE2 is significantly reduced, with a gradual decrease after 21 °C. For the LDPE2-DCSBD sample, the elastic modulus decreases slowly.
An elastic modulus for PET1 and PET1-DCSBD is shown in figure 8. The elastic modulus of both samples exhibits well-defined peaks that may be associated with the glass transition temperature of PET. The peak for PET1 was measured at 76.2 °C and for PET2-DCSBD at 70.7 °C.

The elastic modulus for PET2 and PET2-DCSBD is shown in figure 9. The elastic modulus of PET2 has a well-defined peak that can be associated with the glass transition temperature. The elastic modulus for PET2-DCSBD is not well-defined, it can be concluded that the plasma discharge treatment significantly reduced the values of the elastic modulus.

From the obtained tan δ values, the glass transition temperature ($T_g$) can be determined [10]. The tan δ for PP1 and PP1-DCSBD samples is shown in figure 10. The glass transition temperature for the PP1 sample was measured at approximately 11.4 °C. The glass transition temperature for the PP1-DCSBD sample was measured at approximately 10.3 °C.
The tan δ for PP2, PP2-DCSBD is shown in figure 11. The glass transition temperature for the PP2 sample was measured at approximately 2.1 °C. The glass transition temperature for the PP2-DCSBD sample was measured at approximately 4.1 °C.

The tan δ for LDPE1 and LDPE1-DCSBD is shown in figure 12. The characteristic α-transition for low-density polyethylene starts at about 45 °C to 60 °C for LDPE1 with a peak at 56.1 °C and for LDPE1-DCSBD from about 40 °C to 60 °C with a peak at 51.6 °C.

The tan δ for LDPE2 and LDPE2-DCSBD is shown in figure 13. The insignificant characteristic α-transition peak for LDPE2 is at approximately 48.9 °C. The significant α-transition peak for LDPE2-DCSBD starts from approximately 10 °C to 30 °C with peak at 23.9 °C.

The tan δ for PET1 and PET1-DCSBD is shown in figure 14. The glass transition temperature (T_g) for the PET1 sample was measured at approximately 109.6 °C. The glass transition temperature for PET1-DCSBD was measured at approximately 106.7 °C.

The tan δ for PET2 and PET2-DCSBD is shown in figure 15. The glass transition temperature (T_g) for the PET2 sample was measured at approximately 120.9 °C. The glass transition temperature for PET2-DCSBD was measured at approximately 102.5 °C.

4. Conclusions
The aim of given paper was to study thermal properties of selected thermoplastic materials before and after modification of their surface by plasma discharge DCSBD treatment. Measurements were carried on six samples, two samples of polypropylene, two samples of polyethylene and two samples of polyethylene terephthalate.

Values of elastic modulus (E') were measured and compared. For samples PP1, LDPE1, LDPE2, PET1, PET2 there was a gradual decrease of elastic modulus and for samples PP1-DCSBD, LDPE1-DCSBD, LDPE2-DCSBD, PET1-DCSBD, PET2-DCSBD reduced plasma discharge (DCSBD) elastic
modulus values. In the PP2-DCSBD sample, plasma discharge (DCSBD) increased the elastic modulus value of PP2-DCSBD. It can be concluded that the glass transition temperature values decrease after the plasma discharge treatment (DCSBD) in all six thermoplastic samples. Based on the above-mentioned findings, it can be concluded that the plasma discharge caused structural changes in the studied thermoplastics.

5. References
[1] Kutz M 2017 *Applied Plastics Engineering Handbook: Processing, Materials and Applications* (Edinburgh: Elsevier) p 759 ISBN: 978-0-323-39040-8
[2] Thomas M and Mittal K L 2013 *Atmospheric Pressure Plasma Treatment of Polymers: Relevance to Adhesion* (New Jersey: Wiley) ISBN: 9781118747308
[3] Černák M, Černáková Ľ, Hudec I, Kováčik D and Zahoranová A 2009 Diffuse Coplanar Surface Barrier Discharge and its applications for in-line processing of low-added-value materials *European Physical Journal: Applied Physics* 47 1–6
[4] Bárdos L and Baránková H 2010 Cold atmospheric plasma: Sources, processes, and applications *Thin Solid Films* 518 6705–6713
[5] Fridman A 2008 *Plasma Chemistry* (Cambridge: Cambridge University press) ISBN-13 978-0-511-39857-5
[6] Řáheľ J 2014 *Homogeneous high-pressure discharges for surface treatment of materials* Inaugural dissertation (Brno: Masaryk University)
[7] Roth J R 2001 *Industrial Plasma Engineering, Applications to Nonthermal Plasma Processing* (London: London Institute of Physics Publishing) ISBN 0-7503-0544-4
[8] Seshan K 2002 *Handbook of thin-film deposition processes and techniques, Principles, Methods, Equipment and Applications* (New York: Noyes Publications) ISBN 0-8155-1442-5
[9] Šuťa K 2017 Modification of the surface properties of fibers used in the production of clutch linings using DCSBD plasma discharge (Púchov: Alexander Dubček University of Trenčín) Diploma thesis (in Slovak)
[10] Menard K P 2008 *Dynamic mechanical analysis: A practical introduction* (Boca Raton: CRC Press) ISBN 0849386888
[11] Robertson G L 2012 *Foodpackaging: Principles and practice* (Boca Raton: CRC Press) ISBN 978-1-4398-6242-1
[12] Liptáková T 2012 *Polymeric Construction Materials* (Žilina: Edis) ISBN 978-80-554-0505-6 (in Slovak)

Acknowledgments
This work was supported by the Slovak Grant Agency – projects KEGA 007TnUAD-4/2017, VEGA 1/0649/17 and VEGA 1/0589/17. This publication was created with the support of the project „Advancement and support of R&D for “Centre for diagnostics and quality testing of materials“ in the domains of the RIS3 SK specialization“, code NFP313010W442 and project „New materials and technologies for the industry of the 21st century “NOMATECH”, ITMS: 313011T546“, co-financed from the European Regional Development Fund.