

PAPER REF: 4013

A MECHANICAL ANALYSIS OF POLYDICYCLOPENTADIENE WITH METAL INSERTS THROUGH FLEXURAL LOAD

André Camboa^{1(*)}; Bernardo Ribeiro²; J. P. Nunes³; Jorge Lino Alves⁴

¹ Faculty of Engineering, University of Porto, Porto, Portugal;

² CEIIA - Centre for Excellency and Innovation in Mobility Industry, Maia, Portugal;

³ Institute of Polymers and Composites/I3N, Minho University, Portugal

⁴ INEGI, Faculty of Engineering, University of Porto, Porto, Portugal

(*)Email: andrekamboa@gmail.com

ABSTRACT

Polydicyclopentadiene (PDCPD) is being used in several products with particular success regarding to weight reduction and surface finish improvement. Despite the enough good mechanical properties presented by this thermosetting polymer, it needs to be adequately reinforced in applications requiring extra structural stability. This work studies the improvement of mechanical properties that may be achieved in PDCPD components reinforced with over-moulded steel wires by using the reaction injection moulding (RIM). Specimens, with and without metal inserts, were produced by using a special dedicated developed prototype RIM mould to be submitted to three point bending test, according to EN ISO 178:2003 standard. This paper presents and discusses the results obtained from the flexural tests, which allow concluding that the solution could be industrially used in feasible and advantageous conditions.

Keywords: Polydicyclopentadiene, over-moulding, metal inserts, flexural tests.

INTRODUCTION

The polydicyclopentadiene (PDCPD), introduced in 1980, is a thermoset polymer resulting from the combination of two monomers of dicyclopentadiene (DCPD). The material is usually processed into final products by reaction injection moulding (RIM), a technique that allows mixing both monomers and introducing them into a mould under low pressure. Today, further research is being carried out to study the use of other manufacturing processes to produce PDCPD parts, such as, resin transfer moulding (RTM), near shape casting and rotational moulding (Toplosky and Walsh 2006).

Before RIM process injection, the two DCPD monomers are maintained separately stored in different tanks, as component A and B. Being almost identical, component A contains a mixture of DCPD ethylenic co-monomers, co-catalysts and additives and, component B a monomer combined with organometallic catalysts. After mixing components A and B, at high pressure, in mixing head of the RIM equipment, they are finally injected into a closed mould where the final polymerization (cure) takes place under controlled pressure and temperature. The accurate ratio of components in the mixture must be monitored and set in order to control its viscosity and the impact properties of the final produced part, which usually presents a colour varying from colourless to light yellow or orange, depending on the catalysts content and curing temperature (Yang, Lafontaine et al. 1997, Weijun Yin Weijun, Kniajanski et al. 2010). After an overall production cycle that only takes few minutes (4-6 min), the final cross-linked polymer component can be removed from the mould and, when necessary,

submitted to a post-cure process (Constable, Lesser et al. 2004). Due to the low inherent viscosity, pressure and temperature, a small investment in tooling is required, which makes the PDCPD an attractive low cost solution to manufacture small to medium series of plastic parts. The RIM technique presents also as advantage allowing the easily manufacture of medium to large size parts.

PDCPD parts present good mechanical properties, such as, impact strength and fracture toughness, corrosion resistance and low density (Abadie, Dimonie et al. 2000, Barnes, Brown et al. 2005, Weijun Yin Weijun, Kniajanski et al. 2010). Such properties made PDCPD parts to be successfully used in several transportation applications, such as external panels for trucks, trains and agricultural machinery (Toplosky and Walsh 2006, Alexandre Teixeira and Ribeiro 2010).

Considering this application field, the CEIIA (Portuguese Centre for Excellency and Innovation in Mobility Industry) is studying the feasibility of using PDCPD in the production of exterior body panels for electric vehicles. After analysing the mechanical performance of PDCPD, it was possible concluding that the material, by itself, did not offered enough stiffness for these applications. An appropriate solution to solve the problem requires reinforcing the PDCPD with higher stiffness materials, which can be assembled together or even over-moulded during the RIM processing. Over-moulding allows easily combining together different stiffener materials into one piece and, it is a technique often used to produce, at low cost, rather complex parts made from different constituents (Marta Gomes, Júlio C. Viana et al. 2010). To assess this solution and the mechanical improvement achieved, PDCPD reinforced with steel wires over-moulded specimens were processed by RIM and submitted to mechanically testing.

The design of the aluminium mould used and the RIM processing of standard shaped specimens were tasks carried out at CEIIA. To produce the over-moulded specimens, stainless steel wires with appropriate length were carefully placed in the mould cavity previously to injection.

EXPERIMENTAL

Production of Specimens

For this experimental work were used DCPD components from Telene® 1650 series. Both components, A and BK (3a,4,7,7a-tetrahydro-4,7-methanoindene) were combined through the RIM process.

Two types of rectangular flexural testing specimens, having dimensions of $200 \times 10 \times 4$ (mm), were manufactured according to the EN ISO 178:2003 standard. One type of specimens were integrally in PDCPD, while the other was manufactured using that polymer reinforced with stainless steel wires. To distinguish both groups, the conventional PDCPD specimens were referenced as “FDC” and the other ones as “FDCST”. Fig. 1 shows the geometry used in both specimens.

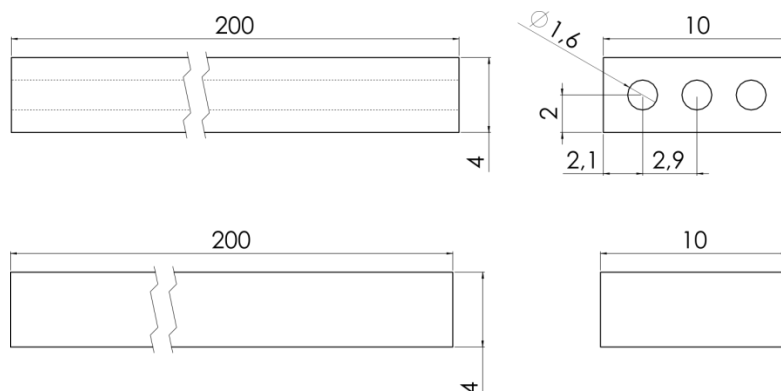


Fig. 1 Geometry of "FDC" and "FDCST" flexural specimens

The conventional steel wire initially used proved to be totally inappropriate to be used in the fabrication of the PDCPD/steel because it presented an initial residual curvature so pronounced and difficult to flatten that was very hard placing it adequately in the interior of the mould cavity (see Fig. 2). As this solution was time-consuming and threatened the good quality of specimens to be produced, it was decided replacing the initial conventional steel wire by a much flatten one, a welding grade stainless 316L AWS with a 1.6 mm diameter.

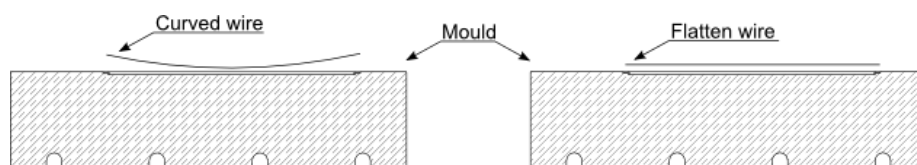


Fig. 2 Curved and flatten wire cases

Before insert three 220 mm long steel wires in the mould cavity, five indentations equally spaced along their length were made using a plier to ensure an adequate PDCP/wire adhesion. (Marta Gomes, Júlio C. Viana et al. 2010, Perring, Long et al. 2010). As it may be seen in Fig. 3, an interval of 30 mm was used between the indentations that were made with a depth of about 0.2 mm. The stainless steel wires were then carefully placed into the mould cavity, well aligned and centred along each specimen.

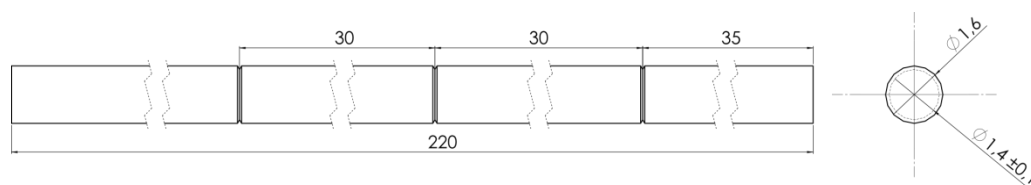


Fig. 3 Indentations along the wire length

To produce the specimens, an aluminium mould was machined with different cavities (Fig. 4). These cavities were designed in order to allow producing two specimens' types for being submitted to different mechanical tests, such as, tensile, shear and flexural.

Regarding the flexural specimens, an additional feature was machined to allow inserting the stainless steel wire reinforcements. These features placed on the extremities of each specimen's cavity length consist in three half circular holes (half diameter of each wire) with 1.6 mm of diameter to allow placing and hold the steel wires upon the mould closing.

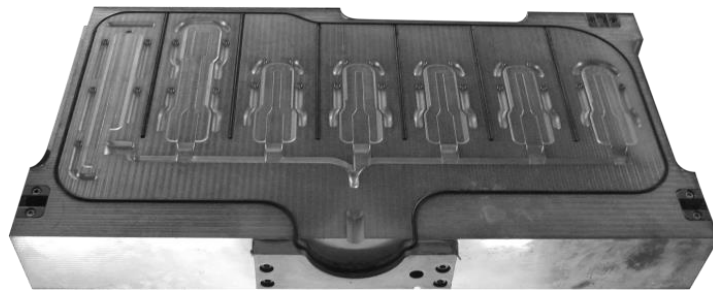


Fig. 4 Injection mould cavity

During injection, temperatures of 60°C and 70°C were set and monitored in heating water circuits of the mould cavity and core, respectively. Such heating water circuits were mounted in upper and bottom outer exterior ribs of the mould in order to allow reducing costs of this designed experimental research tool. The difference of temperature between cavity and core allows PDCPD to be in contact with the much warmer part of mould, in order to better control the processing and final part removal. Similar injection pressures were applied to each component A and B to balance and control the amount of material introduced in the cavity.

Several specimens were produced in the above described conditions, including the four ones of two types used in the flexural tests described in this paper.

Tests and Results

The three point flexural tests were made in a universal mechanical testing equipment Shimadzu AG-X-100KN using a 100 kN load cell. The specimens were tested using a span of 80mm between supports and a testing head speed of 2 mm / min. Radii of 3 mm and 5 mm were used in both supports and machine head puncture, respectively.

Figs. 3 and 4 show the results obtained with each specimen series. As expected, Table 1 shows that an improvement in flexural load was obtained in specimens containing metal inserts.

Table 1 Cross sectional areas of specimens and experimental results obtained in the flexural tests

Names	Area (mm ²)	Max Stress (MPa)	Flexural Modulus (MPa)
FDC1	39.76	33,98	1062
FDC2	39.19	38.82	1168
FDC3	39.25	33.58	990
FDC4	39.48	36.06	1035
FDCST1	40.45	112.50	6314
FDCST2	39.45	115.98	5805
FDCST3	40.24	111.48	5492
FDCST4	39.76	127.66	6911

As Table 1 shows, average flexural strengths of 35.6MPa and 116.9MPa were obtained in the non-reinforced and steel reinforced PDCPD specimens, respectively. This represents an improvement of around 3 times in flexural loading strength for the steel reinforced materials.

The better mechanical behaviour of the steel reinforced specimens may be also clearly seen through the experimental curves stress versus displacement obtained in the flexural tests that are depicted in Fig. 5.

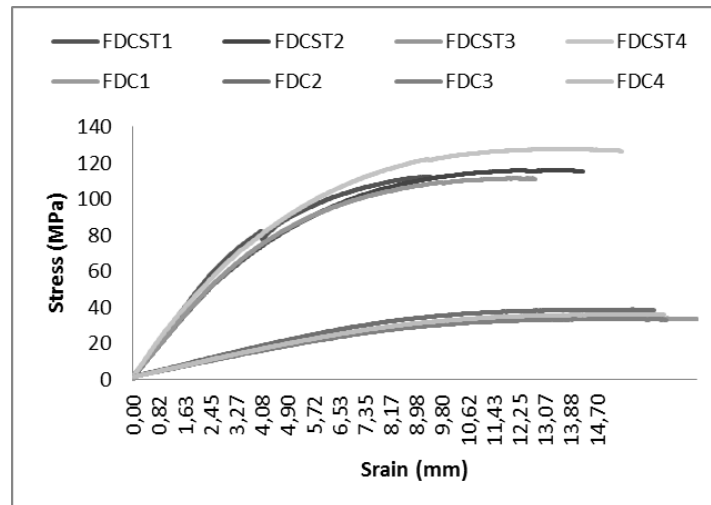


Fig. 5 Experimental curves of stress vs displacement obtained from the flexural tests

Regarding the flexural modulus, a substantial improvement was also obtained in the steel wire reinforced samples. As it may be seen in Table 1 and Fig. 6, average moduli of 6131 MPa and 1064 MPa were obtained in the reinforced and non-reinforced specimens, respectively. This means that the use of the steel reinforcements allowed improving the flexure stiffness by around 6 times.

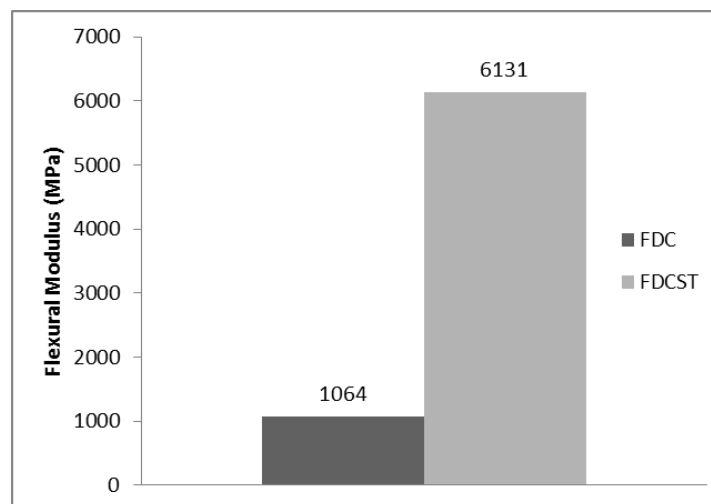


Fig. 6 Mean Young modulus of both tested samples

The overall values obtained for PDCPD specimens are below the typical values expected for this material. PDCPD presents a typical flexural modulus value around 1850MPa, while an average result of 1064MPa has been achieved in this study (Noveon). A lower average value for flexural strength (35.6 MPa) than the typical expected one (67 MPa) was also obtained in the experimental tests (Noveon).

Such unexpected values obtained for the flexural properties seem to result from an insufficient amount of material injected in the RIM process. To achieve high quality PDCPD parts, at least a minimum amount of material must be injected during the RIM process. The use of smaller quantities of material than the minimum necessary value usually results in lack of PDCPD, presence of voids or in a deficient consolidation of the final part, which also contributes to reduce its mechanical properties.

Therefore, to verify the hypothesis of absence of injected PDCPD, the density was determined on the manufactured specimens. In order to do that, the weight and volume were determined in both types of specimens. Fig. 7 shows two types of samples cut with 100 mm length used in the density determinations.

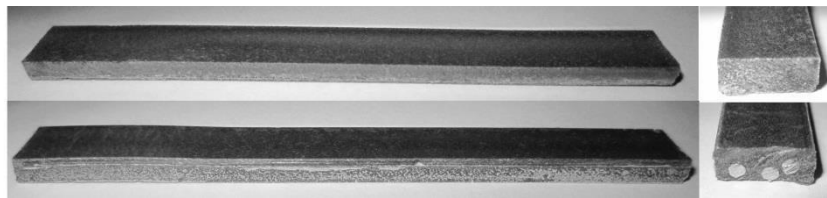


Fig. 7 Lateral and front view of both specimens (non-reinforced and reinforced) used in density determination

Fig. 8 shows the densities determined in both specimens. While the non-reinforced specimen presented a density of 0.8 Mg/m^3 , the reinforced specimen presented, as expected, a higher density, 2 Mg/m^3 . These values allow concluding that steel reinforced specimens are 2.5 times heavier than the non-reinforced ones, and also confirm the possibility of lack of injected PDCPD during RIM processing. In fact, the non-reinforced specimens presented lower density than the typical expected one for PDCPD parts that is of 1.03 Mg/m^3 , (Noveon). However, in spite of the problems regarding the amount of PDCPD injected in the mould may influence the mechanical properties obtained, the tests made clearly demonstrate that the steel wire reinforcements improved significantly the mechanical properties of PDCPD.

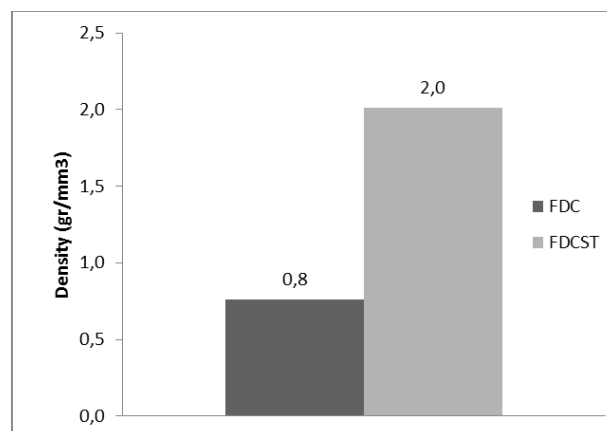


Fig. 8 Densities obtained on reinforced and non-reinforced specimens

CONCLUSIONS

PDCPD is a light-weight thermoset polymer which allows manufacturing parts by using cost efficient processing methods, such as, reaction injection moulding. In addition, it may be

easily reinforced with metal wires through the use of over-moulding techniques in order to produce much high performance structural parts at lower cost.

The present study with over-moulding technique demonstrates to the difficulty in placing the wire inside the mould cavity, especially if it presents an initial curvature (not flat). It was also concluded that is better adopting pre-formed wires or even spacers to keep them in the correct place and at the proper distance from the mould cavities' wall. Such solution could increase the costs and not becoming suitable for several products.

In terms of reinforcements, it seems that there are no restrictions to the use wires from different materials. To improve the adhesion to the PDCPD, the reinforcement should be mechanically indented or, preferably, submitted to an appropriate surface treatment. Despite the cost increasing, the final mechanical behaviour is significantly improved.

The flexural study carried out demonstrated that the PDCPD flexural strength and modulus may be increased by more than 3 times and 5.7 times, respectively, by reinforcing it with stainless steel wires. Concerning the weight gain obtained in the final component, it was verified that the use of the steel reinforcements doubles its original density.

ACKNOWLEDGMENTS

This work is financed by FEDER Funds, through the Operational Program for Competitiveness Factors – COMPETE under the project 13844. André Camboa thanks FCT (Fundação para a Ciência e Tecnologia) for his PhD scholarship (SFRH / BD / 51119 / 2010) under the scope of the MIT Portugal Program in Engineering Design and Advanced Manufacturing – Leaders for Technical Industries focus area.

REFERENCES

- Abadie, M. J., M. Dimonie, C. Couve and V. Dragutan (2000). "New catalysts for linear polydicyclopentadiene synthesis." European Polymer Journal 36(6): 1213-1219.
- Alexandre Teixeira and B. Ribeiro (2010). "Use of DCPD-RIM on exterior panels for the automotive industry." Rapid Product Development Event.
- Barnes, S. E., E. C. Brown, N. Corrigan, P. D. Coates, E. Harkin-Jones and H. G. Edwards (2005). "Raman spectroscopic studies of the cure of dicyclopentadiene (DCPD)." Spectrochim Acta A Mol Biomol Spectrosc 61(13-14): 2946-2952.
- Constable, G. S., A. J. Lesser and E. B. Coughlin (2004). "Morphological and Mechanical Evaluation of Hybrid Organic–Inorganic Thermoset Copolymers of Dicyclopentadiene and Mono- or Tris(norbornenyl)-Substituted Polyhedral Oligomeric Silsesquioxanes." Macromolecules 37(4): 1276-1282.
- Marta Gomes, Júlio C. Viana and A. J. Pontes (2010). "Hybrid injection moulding: Overmoulding of metal inserts with pp." Semana de Engenharia 2010: 8.
- Noveon, I. Retrieved Accessed in February 2013, from <http://www.matweb.com/search/DataSheet.aspx?MatGUID=e678eab2121244db837b865f056e9e7d&ckck=1>.

Perring, M., T. R. Long and N. B. Bowden (2010). "Epoxidation of the surface of polydicyclopentadiene for the self-assembly of organic monolayers." Journal of Materials Chemistry 20(39): 8679 – 8685.

Toplosky, V. J. and R. P. Walsh (2006). "Thermal and Mechanical Properties of Poly-Dicyclopentadiene (DCPD) at Cryogenic Temperatures." AIP Conference Proceedings 824(1): 219-224.

Weijun Yin Weijun, Y., S. Kniajanski and B. Amm (2010). "Dielectric properties of polydicyclopentadiene and polydicyclopentadiene-silica nanocomposite." Ieee International Symposium On Electrical Insulation. Proceedings: 1-5.

Yang, Y.-S., E. Lafontaine and B. Mortaigne (1997). "Curing study of dicyclopentadiene resin and effect of elastomer on its polymer network." Polymer 38(5): 1121-1130.