Materials Physics and Mechanics 47 (2021) 864-871
Research article

Received: November 28, 2020
Accepted: November 17, 2021

INVESTIGATING FAILURE OF AUTOMOTIVE COMPONENTS MADE OF POLYDICYCLOPENTADIENE

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Abstract. Today, polydicyclopentadiene (PDCPD) is a promising polymeric material for automotive components. It is a liquid moulding resin that is processed via a reaction injection moulding system. PDCPD is used to make a kit of parts for KAMAZ vehicle "lower belt", bumper face guards, air intakes. It was found during the operation that the KAMAZ side step frame made of PDCPD failed. The comprehensive investigation revealed that the causes of the part failure were environmental factors, thermal degradation, quality of the raw materials, as well as failure to comply with the production process. The study of the IR spectra of PDCPD samples showed that the failed part (unlike the standard samples) featured a more intensive peak at around 1745 cm^{-1}, which corresponded to the vibrations of carbonyl groups –C=O, which was indicative of the formation of the oxidized structures. The probability of formation of these structures can be a result of the thermal oxidation of the end product due to violation of the production process, operation at increased temperatures, and UV exposure, as well as low-quality raw materials.

Keywords: polydicyclopentadiene, automotive components, failure, defects

Acknowledgements. *No funding has been received for this research.*
The group of authors expresses gratitude to the Laboratory of Non-Metallic Materials in KAMAZ Technological Centre for the opportunity to perform the investigations.

Citation: Romanova N.V., Shafigullin L.N., Erofeev V.T. Investigating failure of automotive components made of polydicyclopentadiene // Materials Physics and Mechanics. 2021, V. 47. N. 6. P. 864-871. DOI: 10.18149/MPM.4762021_6.

1. Introduction

The major challenge of today's automotive industry is to reduce fuel consumption in vehicles, which leads to a decrease in polluting emissions [1]. In order to comply with the requirements for quality performance criteria of materials used in current automotive and military vehicles to reduce vehicle weight, the effective solution is to use polymeric materials.

Today, polydicyclopentadiene (PDCPD) is a promising polymeric material for automotive components. It is a liquid moulding resin that is processed via a reaction injection moulding system. This material has high strength and rigidity, features higher insulating properties, contains no abrasive components or fillers that affect the final external quality of products [2-6]. The material is easily processed, glued, and painted. Moreover, PDCPD parts have a high-quality surface for further surface painting with low-temperature enamels [7].

http://dx.doi.org/10.18149/MPM.4762021_6

However, polymer automotive components have shortcomings as well, among which is the presence of defects that occur during production and operation, hygroscopy, and toxicity during operation [8-9].

One of the key factors having a significant impact on the physical-mechanical properties of polymeric materials and hence the service life of polymer products in a vehicle is the presence of technological defects. Therefore, analysis of causes of failures of automotive products is a crucial task and involves describing the defects and identifying their causes. That is why, the purpose of this paper is to study the defects, as well as to analyze the causes of the catastrophic failure of PDCPD products in order to prevent these defects from happening in the future.

Polydicyclopentadiene is one of the most important thermosets, which is formed through ring-opening metathesis polymerization (ROMP) in the presence of transition metal-based complexes such as Ti, Mo, W, Ta, Re, Ru complexes. For example, the process involves polymerizing a mixture of dicyclopentadiene (DCPD) and TiCl4 with a mixture of DCPD and Al(C2H5)3 by the ROMP reaction, results in the formation of a cross-linked thermoset with a high elastic modulus, impact resistance, and chemical resistance. PDCPD is an industrially attractive material not only due to its excellent physical-mechanical properties but also due to its production method, which consists of reaction injection molding (RIM), which makes it a promising material for automotive parts [7-15].

2. Materials and methods

The studies were conducted on the standard PDCPD samples (Sample S) and on the samples cut out of the actual KAMAZ vehicle parts, namely the side step frames made of PDCPD:

- sample F: samples cut out of the defective product which had been returned by the user;
- sample N: samples cut out of the intact and undamaged product.

The photomicrographs were captured using the DigiMicro Mobile 500x digital microscope.

The physical-mechanical properties were determined according to GOST 4648 [16], GOST 24621-91 [17], GOST 11262 [18].

The IR spectra were determined by the PerkinElmer Spectrum 100 FT-IR spectrometer using the ATR ZnSe crystal.

3. Results and discussion

KAMAZ automotive components made of PDCPD are produced mainly from Telene and Metton monomers, which are polymerized by the ROMP process. PDCPD is used to make a kit of parts for KAMAZ vehicle "lower belt" (headlamp panel, spoiler, panel of front fender front part, sidestep frame, fender extension, panel of front fender rear part), bumper face guards, air intakes (Fig. 1). The material features a low density, high strength, resistance to chemical agents and temperature changes [19].

It is known [20] that the combination of residual stresses and influence of an external force, temperature, and continuous operation may have a negative impact on material and cause catastrophic consequences.

The most common failure mode of KAMAZ vehicle side step frame is the formation of a crack in the corners of the part due to continuous loading (Fig. 2) because corners are stress concentrations. The tensile stress is highest at such locations and exceeds the tensile stress when there are no corners. The inner corners in products should have a significant rounding radius [21].

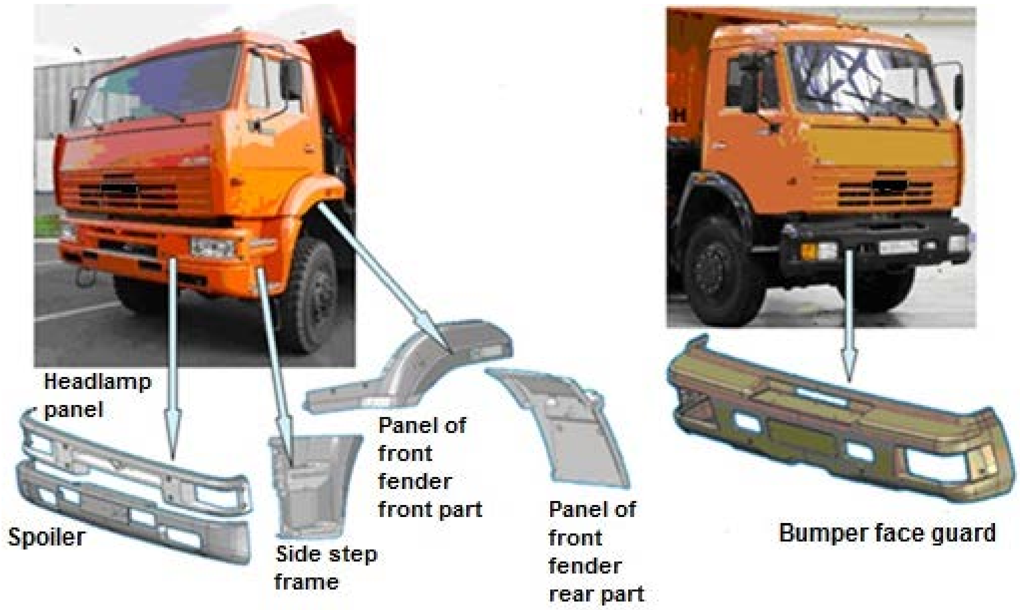

Fig. 1. Parts made of PDCPD

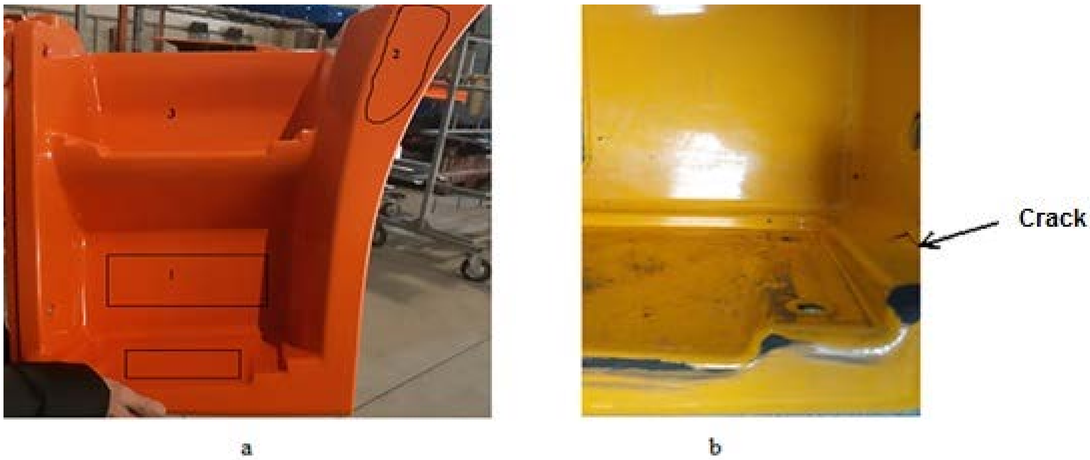

Fig. 2. The sample of the side step frame without any defects (a) and with a defect (b)

The common causes of the failure of this part include environmental stress failure, thermal degradation, formulation of the composition, and quality of the raw material, improper processing conditions.

The analysis of the crack showed the presence of brittle failure in the corner of the part. It is known [22] that cross-linked thermosetting plastics fail mainly due to mechanical fatigue (a polymer fails if the temperature increases insignificantly during cyclic loading), which depends on various factors such as stress level and geometry of a part. Breaking of a molecular chain and sliding of molecules can weaken the material and initiate cracks.

The study of the cross-section of the crack showed that the product had minimal thickness in the failure area. The average product thickness in the failure area was 2.8 mm. According to Telene documentation [23], the minimum thickness of an end product should be not less than 3 mm to achieve the maximum degree of polymerization and to make a product with the best properties. A decrease in the product thickness can lead to the effects of thermal oxidation.

Figure 3 shows the cross-section of the crack which has visible traces of material degradation and irregular areas, which is indicative of a catastrophic failure of the material. The common cause of this product failure is excessively fast cooling or overheating of a mold, which results in fast polymerization or short molding. As a result, the strength properties decrease due to a stress concentration in the areas of weakness.

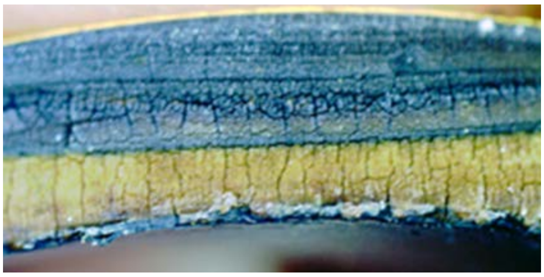

Fig. 3. Photomicrograph of the crack in the defective part

Irregularities due to low-quality raw materials can lead to thermal degradation of a product. Overheating can also cause polymer degradation. At high temperatures, polymer molecules may start breaking down into the constituents which react with each other, and it eventually leads to a gradual change in the material properties. Thermal degradation can be caused by overheating of material during production. Thermal degradation leads to changes in an average molecular mass, and, as a result, the plasticity decreases, the color changes, and all the physical properties deteriorate [20]. Due to degradation, a crack can appear in a product even at a low load.

Therefore, one of the failure causes is thermal-oxidative degradation. In order to prove this assumption, the PDCPD samples (sample F: samples cut out of the defective product, and sample N: samples cut out of the intact and undamaged product) were studied using IR spectrometry (Fig. 4).

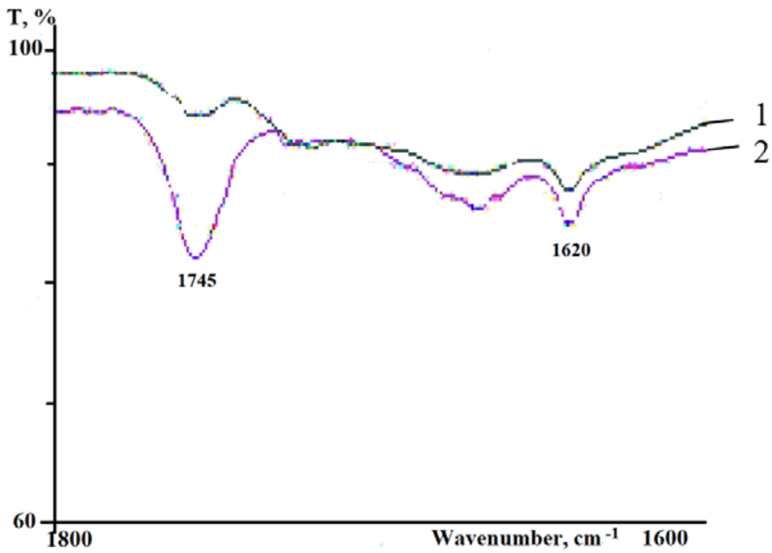

Fig. 4. IR spectra of samples N (1) and F (2)

It is known [23] that PDCPD ageing processes are associated with oxidation processes. When oxygen diffuses into polymer it interacts with double bonds and forms oxide groups. Oxidation processes depend on polymer exposure to temperature and UV light. As PDCPD is synthesized by ring-opening metathesis polymerization of dicyclopentadiene, polymer with a glass transition temperature of 155°C is formed after thermal cross-linking, which contains reactive double bonds in its structure [24]. Dicyclopentadiene is separated from C5 fraction of pyrolysis products, which contains reactive double bonds. The high degree of unsaturation of DCPD also determines the oxidation and polymerization ability [25].

The study of the IR spectra of PDCPD samples showed (Fig. 4) that sample F (unlike sample N) featured a more intensive peak at around 1745 cm^{-1}, which corresponded to the vibrations of carbonyl groups –C=O. It indicates that oxidized structures were formed. The probability of formation of these structures can be a result of the thermal oxidation of the end product due to violation of the production process, operation at increased temperatures, and UV exposure, as well as low-quality raw materials.

It is likely that oxidized raw materials were used during the polymerization process. It is known [26] that DCPD monomer oxidizes during the storage and carbonyl groups are formed, probably aldehyde and ketone groups, which corresponds to the vibrations at around 1700 cm^{-1} in the IR spectrum. The presence of active double bonds in DCPD monomer encourages the addition of oxygen when subjected to atmospheric oxygen, UV light, and heat. It leads to the formation of oxygen-containing impurities which can suppress or inhibit polymerization.

Therefore, the presence of reactive double bonds in a monomer and polymer encourages the active behavior of thermal-oxidative degradation processes, as evidenced by the IR spectra of the failed PDCPD sample. Thus, the presence of an intensive peak at around 1745 cm^{-1}, which corresponds to the vibrations of carbonyl groups–C=O, is evidence of the formation of oxidized structures.

The physical-mechanical tests of the samples were conducted at the next stage. The defective products, which had been returned by the user, were subjected to mechanical tests to determine the intactness of the part. For this purpose, the actual part (i.e., the samples cut out of this part) was subjected to tensile and flexural tests. The results were compared with the data of the similar measurements which were conducted on the parts that remained intact (Table 1, Table 2).

Table 1. Physical mechanical properties

Properties	PDCPD [27] Telene	Sample N	Sample F
Specific weight of polymer, g/cm^3	1.03	1.03	1.04
Shore D hardness	65	65	66
Flexural strength, MPa	70.0	75.5	71.4
Tensile strength, MPa	46.8	48.3	47.6

Table 2. Flexural strength of the samples cut out of the part areas as shown in Fig. 2a

Area number	Property	RH side step frame	LH side step frame	Sample F
1	Thickness, mm	3.3	3.3	3.2
	Flexural strength, MPa	73.0	71.9	71.4
2	Thickness, mm	8.4	8.0	7.8
	Flexural strength, MPa	90.1	92.3	91.0
3	Thickness, mm	3.4	3.4	3.2
	Flexural strength, MPa	61.5	61.6	62.4

The results of the physical-mechanical tests of the samples (Tables 1 and 2) showed that the tensile strength at break and flexural strength of the standard PDCPD samples and the samples cut out of the defective part corresponded to the reference data for Telene-based PDCPD with the similar thickness of the samples. The flexural tests of the samples cut out of the different areas of the side step frame showed that the system featured nonuniform physical-mechanical properties. Thus, the flexural strength varied in the range from 61.5 to 73.0 MPa in different areas with a similar thickness in one part when the guideline is minimum 70.0 MPa (Table 2), and this property is 62.4-71.4 MPa with a thickness of 3.2 mm in the defective part.

Therefore, the flexural strength can differ by 12-15% in one part, which is indicative of polymer heterogeneity throughout the end product.

4. Conclusions

This paper shows that the main causes of the failure of KAMAZ vehicle side step frame made of PDCPD are environmental stress failure, thermal degradation, quality of raw materials, as well as failure to comply with the production process.

It shows the heterogeneity of the physical-mechanical properties throughout the product. Thus, the flexural strength can differ by 12-15% in one part.

The study of the IR spectra of PDCPD samples showed that the failed part (unlike the standard samples) featured a more intensive peak at around 1745 cm^{-1}, which corresponded to the vibrations of carbonyl groups –C=O, which was indicative of the formation of the oxidized structures. The probability of formation of these structures can be a result of the thermal oxidation of the end product due to violation of the production process, operation at increased temperatures, and UV exposure, as well as low-quality raw materials.

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