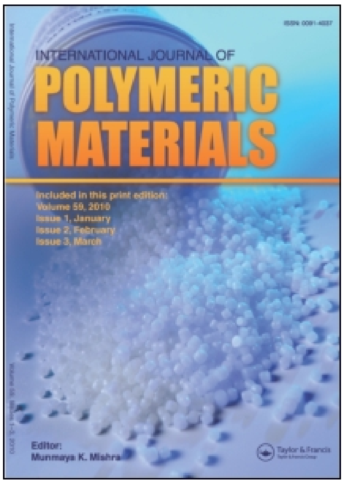

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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Paul Stratton[a]
[a] Linde Gas, Rother Valley Way, Holbrook, Sheffield, United Kingdom

To cite this Article Stratton, Paul(2009) 'Deep Cold Treatment of Polymeric Materials', International Journal of Polymeric Materials, 58: 11, 581 — 587

To link to this Article: DOI: 10.1080/00914030903081455

URL: http://dx.doi.org/10.1080/00914030903081455

International Journal of Polymeric Materials, 58:581–587, 2009
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ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030903081455

Deep Cold Treatment of Polymeric Materials

Paul Stratton
Linde Gas, Rother Valley Way, Holbrook, Sheffield,
United Kingdom

There is much anecdotal evidence to suggest that deep cold improves some properties of polymers; those most often quoted are strength, wear resistance and clarity of transparent polymers. However, little scientific evidence has been published to support these claims. To find out if there was in fact any improvement in properties, two common polymers were selected for testing. Samples were deep cold treated and tested for improvements in properties that were known to be weak. Some of the tests showed no significant change. However, the wear of acetal was almost half that of untreated material although the environmental stress resistance of polycarbonate deteriorated.

Keywords: cryogenics, wear

INTRODUCTION

Since the first systematic investigations of deep cold treatment, notably by Barron [1], there have been reports that the treatment typically used for metals (soaking for 24 h at −196°C) can improve the properties of polymers. Some of the reports are apocryphal, like improved wear in nuns' habits and ladies' nylon stockings, but others have been taken somewhat more seriously [2–4]. However, there is still little scientific evidence for the claimed effects.

In order to investigate the possibility that deep cold treatment could improve the properties of some polymers, two common polymers with

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Received 27 April 2009; in final form 3 May 2009.

The author wishes to acknowledge the work of Smithers Rapra, particularly Joy Harrison, in preparing the samples, carrying out the tests and reporting the results. The author would also like to thank Michael Graf of Linde Gas, Germany for carrying out the deep cold treatments.

Address correspondence to Paul Stratton, Linde Gas, Rother Valley Way, Holbrook, Sheffield S20 3RP, U.K. E-mail: Paul.Stratton@linde.com

known shortcomings were selected for study. Polycarbonate is known to suffer from poor tensile fatigue properties at a high level of strain [5] and from environmental stress cracking [6,7]. Acetal (polyoxymethylene) has poor notched impact [7] and its good wear resistance needs further improvement for some applications [8]. Tests were proposed to measure the effect of deep cold treatment on these properties. In addition, as it has been claimed that deep cold treatment improved the clarity of polycarbonate [4], this property was to be assessed visually.

This paper reports the results of these experiments and discusses whether the process could be used to improve these properties in typical applications.

EXPERIMENTAL PROCEDURE

The polycarbonate tested was Makrolon 2405. This is a free-flowing grade offering easier molding of thin-walled moldings and large moldings with long flow lengths. The acetal was Ticona general purpose grade C9021. The selected acetal and polycarbonate materials were molded into the form of bars 4 × 10 × 180 mm at Smithers Rapra, Shawbury, UK.

The deep cold treatments were undertaken at the Linde Laboratories in Unterschleissheim, Germany, using a CRYOFLEX^{TM} cold treatment chamber. All the test pieces were subjected to the same deep cold temperature and time (−196°C for 24 h), which is known to be effective for treating metals. However, as polymers generally have a lower thermal conductivity than metals, the samples were cooled slowly prior to immersion in the liquid nitrogen and slowly rewarmed to room temperature to avoid thermal stress that might result in cracking in the brittle polymers at low temperatures. Because these polymers can absorb water that might affect their properties, they were inerted in dry nitrogen throughout the cycle. The samples were warmed to room temperature (20°C) before removal from the treatment chamber to prevent any condensation on the cold parts.

Photographs were taken of the test pieces before and after treatment to try and check the claim that deep cold treatment improved the clarity of some polymers by removing defects. The test bars were then returned to Smithers Rapra for their properties to be retested.

Polycarbonate Environmental Stress Cracking (ESC)

The flexural test pieces were placed in three-point bend test jigs (Figure 1). Metal cylinders of various diameters are inserted into the jig to give different levels of strain. In order to produce calibration data,

FIGURE 1 3-point bend test jig.

several bending strains between 0.25 and 0.77% were used. The thickness of the test specimen was measured at three points within the gauge length of the specimen. All samples were found to be 3.99 mm thick.

Specimens were slid into place in the constant strain jig, with the required strain collar in place. The test environment was applied to the center of the specimen (point of maximum strain), at a predetermined time after the specimen was put into the jig, usually between 5 and 10 sec. To ensure reproducibility, a single jig was used and each sample was tested in turn. The same collars were used for the treated and untreated samples. The specimens under test were observed continuously for the first 10 min after application of the ESC test environment during which time all the samples failed. The time from the application of the strain to crack initiation was recorded.

Polycarbonate Fatigue

Three-point flexural fatigue was undertaken using the following parameters:

- Distance between supports = 65 mm
- Deflection = 3 mm and 5 mm
- Frequency = 2 Hz

Each molding was cut in two to produce two test pieces for each deflection condition, which were then tested simultaneously. Testing was undertaken on a servo-hydraulic test machine using a 5 kN load cell.

Acetal Notched Izod Impact

Ten Type ISO 180/A specimens were tested for each material in general accordance with BS EN ISO 180: 2001, which requires the specimen size to be 63.5 ± 2 mm in length and 10 ± 0.2 mm in width, with a 0.25 mm radius notch machined in one edge of the specimen. After notching, the specimens were conditioned for a minimum of 16 h at 23 ± 2°C and 50 ± 10% relative humidity, and then tested at 23 ± 2°C.

Each specimen was placed in turn into the test apparatus and impacted with a 1.08 J hammer in order to break the specimen. The impact strength (kJ/m^2) of each specimen was then calculated and the type of break was also noted. Ambient temperature was maintained at 23°C ± 2°C and all equipment used was calibrated to the accuracy required in the appropriate standard.

Acetal Taber Abrasion

A single test sample was prepared from the strips supplied of each of the test materials. The initial mass of each sample was measured before they were subjected to 2000 taber cycles, using H18 type wheels, and a 500 g test load per wheel. The samples were weighed before they were subjected to a further 3000 cycles, then weighed for a third time. The test wheels were refaced both before use and after each 2000 cycles had been completed. All testing was performed in accordance with the principles of ISO 9352:1995. Ambient temperature was maintained at 23°C ± 2°C and all equipment was calibrated to the accuracy required in the appropriate standard.

RESULTS

It is always difficult to judge such things from photographs (Figure 2), but there was a significant improvement in clarity of the polycarbonate samples after cryogenic treatment.

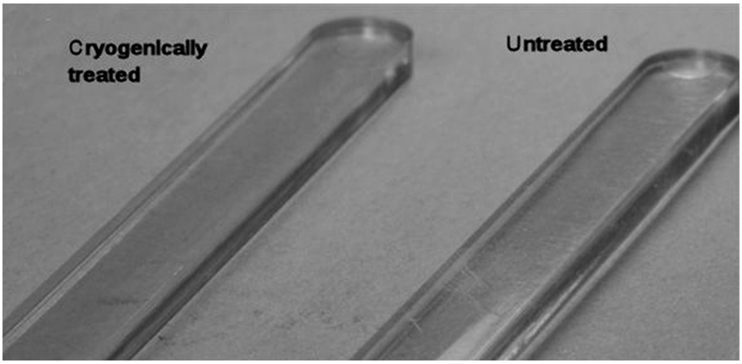

FIGURE 2 Improved clarity of polycarbonate after cryogenic processing.

TABLE 1 Environmental Stress Cracking Times at Various Strains

	Time to crack (s)	
Strain (%)	Annealed	Annealed and deep cold treated
0.77	~1	~1
0.67	4.5	3.6
0.46	11.45	3.5
0.36	11.5	32
0.24	117	9.3
0.24	352	10.4

Polycarbonate Environmental Stress Cracking

The results are shown in Table 1. The environmental stress cracking resistance was noticeably poorer for the treated material.

Polycarbonate Fatigue

The fatigue results for the polycarbonate samples are shown in Table 2. At 3 mm deflection, the deep cold treated samples had a poorer fatigue life than the untreated samples. When a larger deflection was applied, however, the difference was eroded, and the performance was considered to be the same.

Acetal Notched Izod Impact

There was a small improvement in the deep cold treated samples from an average of 8.0 kJ/m^2 to 8.4. However, this modest 5% increase should be treated with caution given that impact testing is prone to scatter. This result cannot be considered significant.

TABLE 2 Polycarbonate Fatigue Results for Annealed and Deep Cold Treated Samples

Condition	Cycles to failure at 3 mm deflection	Cycles to failure at 5 mm deflection
Annealed	7500	1800
	10500	2000
Annealed and deep cold treated	5500	1700
	6000	2000

TABLE 3 Polyacetal Taber Abrasion Results for Annealed and Deep Cold Treated Samples

	Mass lost after 2000 cycles (g)	Mass lost after 5000 cycles (g)
Annealed	0.20	0.57
Annealed and deep cold treated	0.17	0.3

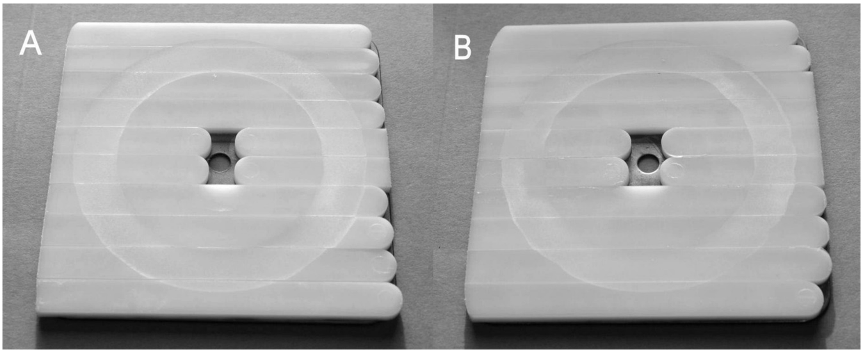

FIGURE 3 The wear tracks from the Taber abrasion test for (A) as annealed and (B) as annealed and deep cold treated.

Acetal Taber Abrasion

The results from the Taber abrasion testing of the acetal are shown in Table 3. It is clear that after 5000 cycles the wear rate of the deep cold treated samples is almost half that of the untreated ones.

The wear tracks are compared in Figure 3.

DISCUSSION

It has been suggested that when a plastic part is made, the molten material solidifies and traps molecules in a random pattern. The deep cryogenic process realigns them and creates a denser, more uniform pattern to the structure of the plastic. This more uniform spacing reduces the voids inside the matrixes, resulting in better wear life [2]. Another similar theory suggests that the deep cold treatment aligns the molecules better, increasing properties such as clarity [4].

Even if these theories are causally incorrect, the experimental evidence seems to support them. There is a visual improvement in the clarity of polycarbonate, although this is not confirmed by measurement in this study. The environmental stress cracking of polycarbonate deteriorates, But there is little effect on the fatigue properties of polycarbonate, confirming previous evidence [3], and a negligible improvement in the impact performance of acetal. The greatest gain is in the wear performance of acetal.

This improvement in wear also confirms previous anecdotal evidence. As acetal is used for the manufacture of lightweight industrial wheels, conveyor components, gears, cams, and bearings, all of which suffer from wear, it must be seen as industrially important.

CONCLUSIONS

- Deep cold treatment almost halves the abrasive wear of acetal.
- Deep cold treatment appears to improve the clarity of polycarbonate.
- Deep cold treatment has a deleterious effect on the environmental stress cracking resistance of polycarbonate.
- Deep cold treatment has no significant effect on either the fatigue performance of polycarbonate or the impact strength of acetal.

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