Tribology International 77 (2014) 32–42

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Observation and evaluation of scratch characteristics of injection-molded poly(methyl methacrylate) toughened by acrylic rubbers

Jihun An [a], Byung-Hyun Kang [a], Byoung-Ho Choi [a,*], Hyoung-Jun Kim [b]

[a] School of Mechanical Engineering, Graduate School of Korea University, 1 5-ga Anam-Dong, Seongbuk-Gu, Seoul 136-701, Republic of Korea
[b] Media Instrument Development Gr., Digital Media Instrument Development Dept., LG Electronics Inc., 19-1, Cheongho-ri, Jinwi-myeon, Pyeongtaek-si, Gyeonggi-do 451-713, Republic of Korea

ARTICLE INFO

Article history:
Received 19 January 2014
Received in revised form
19 March 2014
Accepted 13 April 2014
Available online 24 April 2014

Keywords:
Scratch
Acrylic rubbers
Poly(methyl methacrylate)
Damage mechanism

ABSTRACT

Poly(methyl methacrylate) (PMMA) is frequently toughened by blending with elastomers such as acrylic rubbers to improve its toughness, but the addition of acrylic rubbers to PMMA deteriorates its scratch properties. In this study, the scratch properties of PMMA toughened by the addition of acrylic rubbers were investigated by performing static and progressive scratch tests. Three scratch damage modes, namely, mar/plowing, whitening, and cutting modes, were identified by observing the scratch damage using various microscopy techniques. In addition, two critical loads for defining the variation of scratch damage mechanisms were recorded to evaluate the scratch resistance of rubber-toughened PMMA samples.

1. Introduction

The demand for enhanced polymeric materials for use in electronic goods and automobile components has increased [1,2]. Injection molding is a popular method for preparing such polymeric materials; however, under incorrect conditions can cause polymeric materials to have poor mechanical properties and poor scratch properties. Scratch properties have been one of the most important factors to be considered while selecting engineering polymeric materials for consumer products, especially electronic and automobile ones [3–6]. However, it is difficult to predict the appropriateness of a polymer for a consumer product at the design stage unless the fundamental understanding of the correlation between injection molding and scratch characteristics of the polymer is fully gained. Scratch properties of engineering polymers have become a key factor in their selection, especially in the case of poly(methyl methacrylate) (PMMA), because these polymers are used as an exterior for consumer electronic products [1,7]. PMMA is transparent and has good injection molding characteristics, chemical resistance, and mechanical properties. However, PMMA does not have good impact toughness in comparison to other competitive materials. Therefore, PMMA is often blended with elastomers to improve its impact toughness [8,9].

However, the scratch properties of PMMA are deteriorated upon the addition of elastomers. Moreover, it is difficult to control the scratch properties of PMMA at various temperatures. Unexpected scratch formation due to temperature change can deteriorate the aesthetics and reliability of electronic products. Therefore, the addition of a suitable concentration of acrylic rubber to PMMA at proper temperature is required in order to improve both the impact toughness and scratch properties of PMMA. Three distinctive scratch damage mechanism modes have been identified for PMMA containing rubber particles, namely, mar/plowing [10], whitening, and cutting modes [1]. Further, two critical points have been observed during progressive scratch tests; the first one is between mar/plowing and whitening modes, and the second one is between whitening and cutting modes [1]. These critical points have been investigated in many studies on the scratch properties of PMMA because they may be a key to analyzing the scratch properties of PMMA [4,5,11–13]. However, critical points are not enough to explain all the scratch properties because scratch behavior is characterized by many physical factors such as scratch width, scratch depth, and shoulder height [5,14]. In addition, many polymeric materials do not show a clear scratch transition under standardized test conditions [6]. Therefore, in recent times, studies on scratch visibility determined using image-J software are gaining popularity [6,8,15,16]. Nevertheless, it is still difficult to define proper parameters that can be used to evaluate the scratch behavior. On the other hand, the scratch behavior of brittle materials such as PMMA shows relatively clear transition between

---

[*] Corresponding author. Tel.: +82 2 3290 3378; fax: +82 2 926 9290.
E-mail addresses: bhchoi@korea.ac.kr, cqbiho@gmail.com (B.-H. Choi).

http://dx.doi.org/10.1016/j.triboint.2014.04.011
0301-679X/© 2014 Elsevier Ltd. All rights reserved.

scratch damage modes. Jardret et al. [17] studied the characteristic strain on PMMA during scratch tests at various temperatures; further, Kim et al. [1] evaluated the scratch characteristics on PMMA as a function of the concentration of an added slip agent. However, the effect of soft phases on scratch properties at various temperatures is not understood well; therefore, quantitative evaluation and detailed analysis of the scratch characteristics of PMMA toughened with acrylic rubbers are required. Additionally, the scratch behavior of rubber-toughened PMMA can be influenced by morphology changes due to the addition of rubber particles during the injection molding process. Zhou et al. [18] reported that the yield strength and fatigue strength of a talc-filled polypropylene specimen were improved when its mechanical properties were tested in the flow direction, and the holding pressure influenced the skin-core morphology of the specimen that affected the orientation of talc particles in the skin and at the core of the injection-molded specimen. Thus, it can be understood that the particle orientation and holding pressure are important factors in determining the scratch behavior of a polymer.

In this study, rubber-toughened PMMA plates were prepared by injection molding, and were then subjected to static and progressive scratch tests. The samples were prepared under various injection molding conditions, and two orientations (machine direction and transverse direction) of the injection-molded plates were considered in the scratch tests. In addition, the quantitative scratch properties of rubber-toughened PMMA were investigated under various temperatures. Scratch damage characteristics of the samples were examined by various microscopy techniques such as optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and optical profilometry. Further, the scratch damage modes of the samples were classified as mar/plowing, whitening, and cutting mode, and critical loads were defined by microstructural observation of the scratch morphology of the samples. Furthermore, the fracture mechanism of each damage mode was also investigated in detail.

Table 1
Physical properties of base PMMA material.

Material	Density (g/cm^3)	Melt flow (g/10 min)	VICAT softening point (°C)	Reflective index (nd)	Mold shrinkage (%)
PMMA	1.18	12.3	99.9	1.49	0.5

Table 2
Material codes for rubber toughened PMMA.

Material code	PMMA (wt%)	Acrylic rubber (wt%)
MMA-r00	100	0
MMA-r10	90	10
MMA-r20	80	20
MMA-r40	60	40

2. Experimental

2.1. Materials

PMMA used in this study was of high flowability grade provided by LG MMA Corporation, and is commonly used for thin wall parts with complicated profiles. The key physical properties of base PMMA are listed in Table 1. Methacrylate-butadiene-styrene (MBS) and acrylic rubbers are commonly used as an impact modifier of PMMA, but, in this study, acrylic rubbers are selected to improve the toughness of rigid PMMA. The samples are labeled as MMA-r00, MMA-r10, MMA-r20, MMA-r40 according to their rubber content (0, 10, 20, and 40 wt% of acrylic rubber, respectively), as listed in Table 2. Test specimens were prepared by injection molding at three holding pressures, i.e., 50, 65, and 80 bar, with the injection molding speed and cooling time being 32 mm/s and 20 s, respectively. The barrel temperatures were 245 °C/250 °C/230 °C/230 °C, and the mold temperatures were 90 °C/50 °C. Additionally, two square plates (140 × 100 mm^2) were prepared by injection molding in a different flow direction at a time, as shown in Fig. 1.

2.2. Scratch tests and observation of scratch damage

Scratch tests were performed on a custom-built scratch test device that could be used for performing both the ISO 19252 [13] and ASTM D7027-05 [14] standard test methods. In this study, the base test case followed ASTM D7027-05, but the heating plate was used for other test cases to evaluate the effects of test temperature on the scratch properties of the samples. Both a linearly progressive load in 2–50 N and a constant load in 30 N were used with the constant scratch speed at 100 mm/s. During scratch tests, a hemispherical scratch tip 1 mm in diameter was employed. The scratch specimens had an area of 140 mm × 120 mm and a thickness of 3 mm. Other scratch tests for evaluating the injection molding of samples were not performed because the object of this study was only to investigate the concentration of rubber. In addition, a heated plate with two thermocouples was designed to monitor the temperature of the test samples in order to maintain a constant temperature during high-temperature scratch tests. Critical loads are measured by observing the change of scratch damage modes, and the definition of critical loads and proposed scratch damage modes for PMMA is shown in Fig. 2. There are some key scratch properties, e.g. critical loads, the onset of visibility, scratch width, scratch depth as well as scratch modes

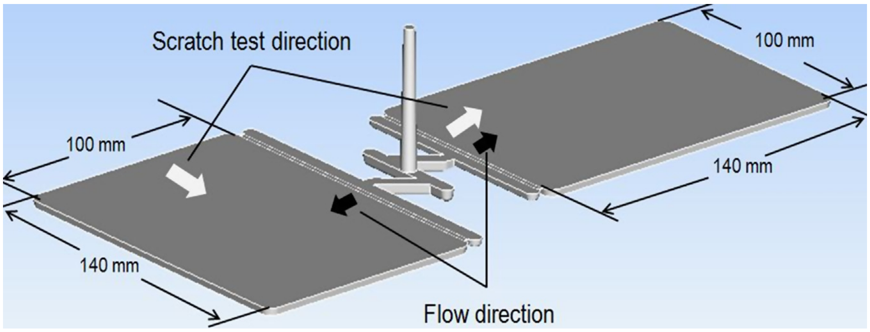

Fig. 1. Preparation of injection-molded specimens for scratch tests in two flow directions.