

Utilization of poly(methyl methacrylate) rejection blended with acrylonitrile butadiene styrene resins and the effect on product properties

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ABSTRACT

PMMA is one of the main raw materials for the injection molding process in the lens industries. Since this process requires extremely careful techniques to obtain lens with the best quality, it leads to a high rate of product rejection. These rejected products do not only pose an issue for the industrial environment and require storage space, their price also falls significantly. Among the solutions to this problem is to reuse the rejected products as substitute materials for the manufacture of another product's part such as lamp holders. This process reuses rejected PMMA-containing products in the ABS base polymer industries so as to generate PMMA-containing products with better physical properties. In this experiment, 10 to 40 % (w/w) of rejected PMMA was blended with ABS resins. The monomer content in the ABS resins was analyzed by NMR. Moreover, the mechanical, thermal, and morphological properties of the blended products were also examined. The NMR analysis showed that the resin contained 21.6 % butadiene monomer, in which its value was higher than the value required for materials with high-impact class application. The blend of resins and rejected PMMA (10-30% w/w) could increase the tensile strength value and decrease Izod impact strength and elongation percentage. The morphological analysis showed that this increased PMMA content may also result in widespread brittle areas. Since the blend was designed without compatibilizers, the DSC analysis indicated that the resulting blend in any ratios was not completely miscible. It was revealed that ABS resins containing 10% PMMA was the best blend for the polymer engineering application and this blend still had adequate properties and elastomer content required.

Keywords: ABS, blending, properties, PMMA regrind.

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is an important homopolymer in acrylic groups which has a high glass transition that can be used as raw materials for producing lens (Tsui *et al.*, 2012; Sankar, *et al.*, 2004). In motorcycle lamp manufacturing, the lamp structure consists of two parts, namely the lens and the lamp holder. The lamp holder surface will be applied with silver paste to be a reflector of the lamp. Based on the Indonesian National Standard No.7398:2008 concerning light reflectors for motor vehicles adapted from the UN-ECE (United Nations-Economic Commission for Europe) Vehicle Regulations No. 3 on uniform provisions concerning the approval of retro-reflecting devices for power-driven vehicles and their trailers, the raw materials for lamp holder

(reflector) must have an adequate impact and heat resistance (SNI 7398, 2008).

PMMA is required for producing the lens section, while the lamp holder is made from acrylonitrile butadiene styrene (Kuo *et al.*, 2016; Oepen & Gottschalk, 2011). The injection molding process to prepare lens materials requires extremely careful techniques so that the resulting product is free from bubbles, weld-lines, scratches, silver streaks and cracks (Kenplas, 2016). This requirement leads to a high rate of rejected lens products, whereas the need of PMMA on these products is 50% of the total raw materials. These rejected products do not only pose an issue for the industrial environment and require storage space, their price also falls significantly.

Among the solutions to this problem is to reuse

the rejected products as substitute materials for the manufacture of another product's part such as lamp holders. Since the rejected products consist of lens, their size needs to be reduced into smaller pieces using a grinder. Therefore, these materials are usually called the PMMA regrind. Although the concept of blending polymer has long existed, if the blended product reaches particular physical properties, it will be economically favourable (Alhydary *et al.*, 2012). This blending process takes place physically in the form of contact surfaces so that there will be an interaction between the polymer molecules. The solubility parameter of polymers to be mixed and the polarity level of polymers are crucial factors in this process (Li *et al.*, 2009). It is known that both ABS and PMMA are materials with polar areas and an adjacent melting point, thus allowing them to form a compact mix (Buthainadan & Kadum, 2010; Alper *et al.*, 2006). The mechanical and thermal properties of products with different weight ratios of both polymers shall be observed (Gaur *et al.*, 2008; Polli *et al.*, 2009).

MATERIALS AND METHODS

Materials

The raw materials of the polymers used were ABS LG HI 121 produced by LG Chem. (ρ : 1.04 g/cm³; Tm: 220-25 °C; MFR: 21.4 g/10 min), while the PMMA regrind was the by-product made from PMMA, i.e. 80 N Delpit Asahi Kasei (ρ : 1.19 g/cm³; r: 230-245°C; MFR: 2.0 g/10min).

Methods

The process of blending ABS materials and the PMMA regrind was carried out using a twin screw extruder. There were different concentrations of PMMA regrind added to the ABS, namely 10%, 20%, 30%, and 40% (W/W). The characterization equipment consisted of Rheomix Haake 3000; Hydraulic Hot Press 150 kg/cm Toyoseiki; Stereograph P-I Toyoseiki; Izod Impact Toyoseiki

40 kg.cm; SEM (Scanning Electron Microscopy) JEOL Scanning Microscope (JSM) 5310LV; and dog bone specimens which were prepared using the compression molding machine to comply with the standards of ASTM D638 and ASTM D256. The polymer structure prediction was identified using ¹H NMR supported by the software ChemDraw Ultra 10.

RESULTS AND DISCUSSION

The Analysis of Monomer Composition in ABS Using NMR

Fig. 1 presents the spectrum measurement result of ABS using NMR and Table 1 presents the content of each monomer in ABS calculated based on the peak area.

Table 1 shows that the ABS LG Chem. 121 contains styrene, butadiene, and acrylonitrile monomers with a ratio of 76%, 22%, and 2%, respectively. The percentage of each monomer in the ABS is specific for each polymer because the polymer manufacturer had it adjusted to the percentage of applications to be used. According to Oepen & Gottschalk (2011), ABS with butadiene monomers at a percentage of greater than 18%

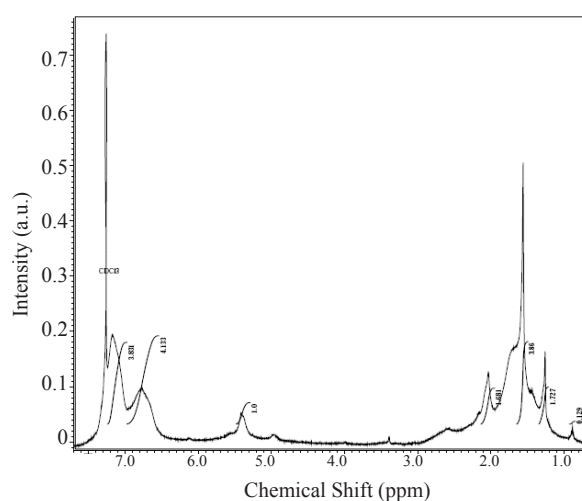


Fig 1. NMR spectrum output.

Table 1. Determination of the monomer content in ABS using the ¹H NMR instrument.

Monomer	ChemDraw Ultra Prediction (ppm)	Peak Area	Percentage (%)
Acrylonitrile	2.45	0.427	2.05
Butadiene	2.33-2.29	2.211	21.61
	5.48	2.298	
Styrene	7.27-7.40	15.929	76.34

belongs to engineering polymers with a high-impact class that is used for applications that require frequent impact and stress on the environment. Therefore, it can be calculated for the engineering polymer that the highest ratio between the PMMA and ABS resins is (2:9) or 18.2% PMMA in ABS resins.

Mechanical Properties of the ABS-PMMA Re-grind Blend: The Effect of the PMMA Content

Fig. 2 describes the effect of the PMMA re-grind content on the mechanical strength of the ABS-PMMA blend. The effect of the PMMA re-

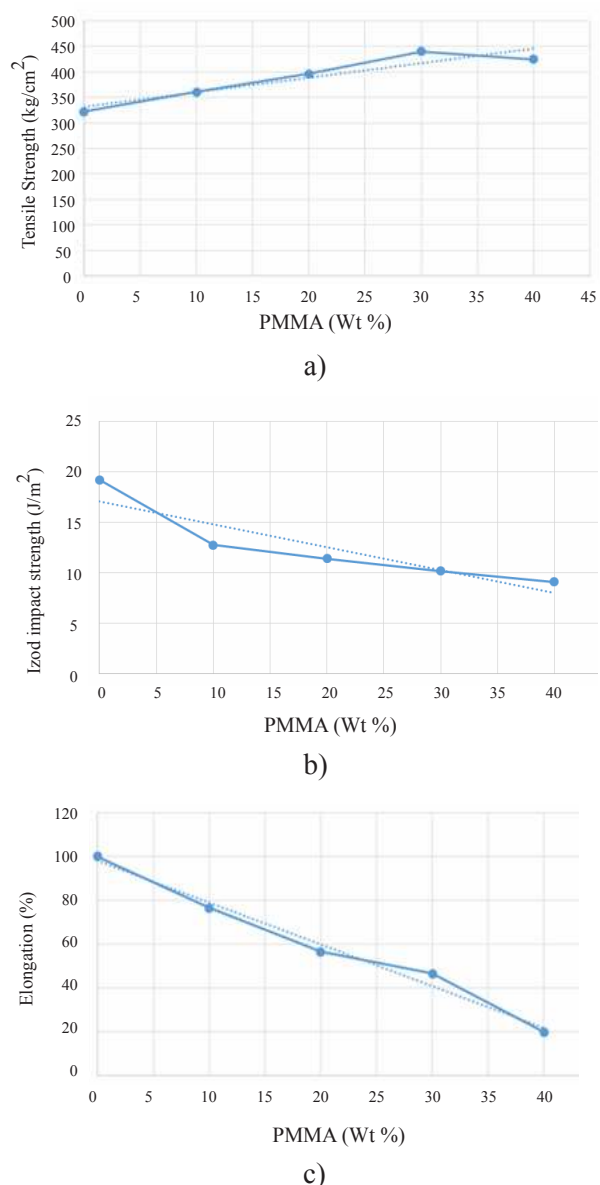


Fig 2. The effect of the PMMA re-grind content on the mechanical strength of the ABS PMMA blend a) Tensile strength; b) Izod impact strength, and c) Elongation.

grind content on the tensile strength (Fig. 2A); the Izod impact strength (Fig. 2B); and the elongation percentage (Fig. 2C).

Fig. 2 shows that the increased PMMA re-grind content will increase the tensile strength and decrease the Izod impact strength and the elongation percentage compared to those in ABS resins. Fig. 2a shows that the tensile strength of the ABS-PMMA blend increases almost linearly as the percentage of the PMMA re-grind is increased. This indicates that the ABS-PMMA blend is harder than pure ABS polymers. At the 30% PMMA content, the blended product obtains the strongest tensile strength, which is 37% stronger than the strength of ABS polymers without PMMA addition. From this graph, it can also be said that the addition of the 10% PMMA content (w/w) to the resins results in an increased strength by 7.7%. Fig. 2b shows the Izod impact strength of the ABS-PMMA blend decreases when the PMMA re-grind content is increased. This indicates that the ABS-PMMA blend is less brittle than pure ABS polymers. At the 30% PMMA content, the Izod impact strength is 50% lower than that of pure ABS polymers, whereas, at the 10% PMMA content, it was decreasing to 35% lower than that of pure ABS polymers.

Morphology of the Blended Product

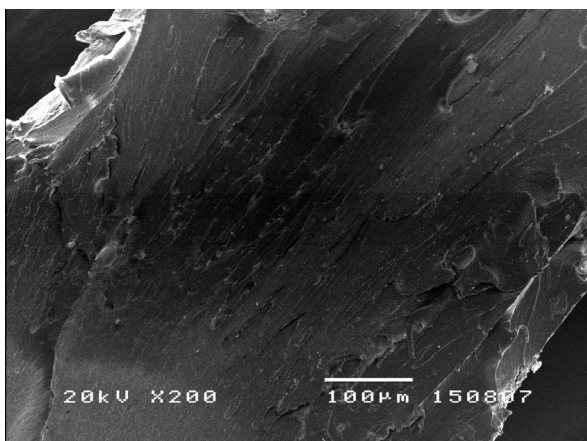
Fig. 3 shows the microstructure of the ABS-PMMA blend sample containing different PMMA re-grind content. The observation into the polymer morphology was performed using the Scanning Electron Microscopy (SEM) on the cross-section specimen on the break side while testing the tensile strength in order to determine the results of the interaction between ABS and PMMA. Fig. 3 presents the measurement result with a magnification of 200 X.

From Fig. 3, it can be seen easily that the blend of ABS resins with PMMA at a percentage of 10% did not result in fibril formation, and when the PMMA content was increased to 30%, cavities existed which were assumed to be resulting from fibril formation. This brittle area expanded since the beginning of the fracture formation. This data confirmed that the blend containing 10% PMMA still has the properties such as high impact materials and suitability for engineering polymers.

Determination of the Thermal Properties of the Blended Product

The Differential Scanning Calorimeter curves

a) ABS:PMMA regrinds (90:10)



b) ABS:PMMA regrinds (70:30)

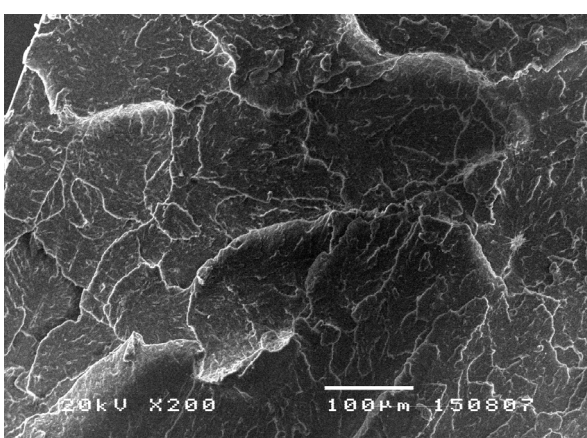


Fig. 3. SEM images of the PMMA-ABS blend containing a) 10% and b) 30% PMMA regrind.

of the pure ABS and the ABS-PMMA blend containing 10% PMMA are shown in Fig. 4.

From Fig. 4(a), it can be seen that the DSC profile for pure ABS had a single glass transition temperature (Tg) of approximately 178.02°C and

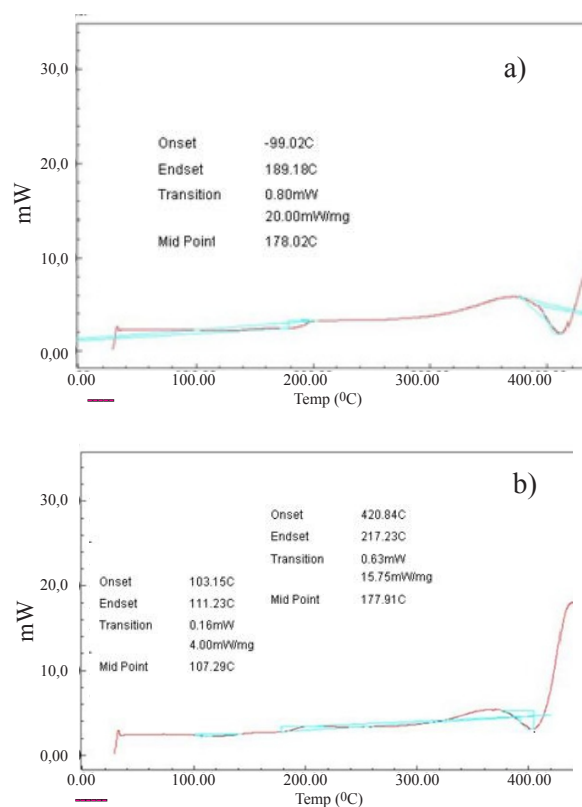


Fig. 4. The DCS of a) ABS: PMMA (100: 0) and b)ABS: PMMA (90:10).

its melting point (Tm-blend) was 410.36 °C, while in Fig. 4(b) the ratio of ABS to PMMA regrind by 90:10 of the sample had two Tg values, namely 107.29 °C and 177.91 °C, and a single melting point by 404 °C. Two glass transition temperatures in the DSC profile were predicted as the Tg of PMMA and ABS respectively. The differential between the Tg values (ΔT_g) was calculated by subtracting the value of Tg-ABS from that of Tg-PMMA. The values of the resulting Tg-ABS, Tg-PMMA regrind, ΔT_g , and melting point of the

Table 2. The Tm-blend and the ΔT_g based on the PMMA content.

ABS:PMMA ratio (w/w)	Tg-ABS	Tg-PMMA	ΔT_g	Tm-blend
100:0	-	178.02		410.36
90:10	107.29	177.91	70.62	404.00
80:20	111.54	171.69	60.15	390.13
70:30	107.34	173.41	66.07	390.43
60:40	105.33	175.55	70.22	389.51

Note:

ΔT_g : Differential between Tg PMMA and Tg ABS at certain ratios

Tm-blend : Melting point

blend are presented in Table 2.

Table 2 shows that the presence of a ΔT_g value which is not equal to zero indicated that ABS and PMMA are not fully miscible with each other, and to generate a ΔT_g value which is equal to zero, the blend needs a compatibilizer (Zhou *et al.*, 2014). On the other hand, each blend had a single melting point ranging from 390 to 410°C, suggesting that the sample was fully melted during the preparation process. An increased PMMA amount resulted in a decreased melting temperature of the blend.

CONCLUSIONS

PMMA products which are rejected can be reused as substitute materials for ABS resins in the production of high-abuse applications, such as lamp holders. The NMR analysis showed that the resins contained 21.6% butadiene monomer, which was greater than the required value for materials with high-impact class application. The blend of resins and rejected PMMA (10-30% w/w) could increase the tensile strength value and decrease Izod impact strength and elongation percentage. The morphological analysis showed that this increased PMMA content may also result in widespread brittle areas. Since the blend was designed without compatibilizers, the DSC analysis indicated that the resulting blend in any ratios was not completely miscible. It is revealed that ABS resins containing 10% PMMA was the best blend for the polymer engineering application and this blend still had adequate properties and the elastomer content required.

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