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Viscoelastic and adhesive properties of PMMA-b-PtBA with tackifier

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ABSTRACT

The study of adhesive behavior of poly(methyl methacrylate)-b-poly(t-butyl acrylate) (PMMA-b-PtBA) diblock copolymers is rare in literature. In this study, we prepared a PMMA-b-PtBA diblock copolymer (B-16) by the anionic polymerization technique and compounded it with various amounts of tackifier (Staybelite Ester 3 synthetic resin of Hercules Inc., a triethylene glycol ester of partially hydrogenated wood rosin). The B-16 contained 10 parts of tackifier per hundred parts of polymer (phr), which has a better storage modulus (*G*') at 120 °C and 0.1 rad/s than counterpart homopolymer PMMAs of different average molecular weights, containing the same phr of tackifier. Increasing the molecular weight of homopolymer PMMA samples (containing 10 phr of tackifier), the *G*' value at 120 °C increases toward the optimum region. The peel performance relates rather well to the viscoelastic property.

1. Introduction

The performance of pressure sensitive adhesives (PSAs) of block copolymers compounding with other ingredients (such as tackifier) has been reported in [1], where rubber–resin compatibility was studied and block copolymers used included styrene–isoprene–styrene (SIS), styrene–butadiene–styrene (SBS) and styrene–ethylene–butadiene–styrene (SEBS). The compatibility of resin with either the midblock or the endblock imparts different viscoelastic properties.

The resins increase the T_g of the midblock, or the endblock, depending on the compatibility of resins with either block. Midblock compatible resins decrease the plateau modulus values, and therefore, generate tack. The resins that are compatible with both blocks of the copolymer increase the T_g of the midblock and decrease the T_g of the endblock, depending on the molecular weight and T_g of the resins [1].

As the rheological conditions for PSAs are concerned, the PSAs should have a low G' (i.e., the real part of modulus) value at low frequencies and a high G' value at high frequencies, since the bonding process usually undergoes a low rate and the peeling (or detaching) process undergoes a high rate [1]. Also, it is stressed that PSAs with $2\times10^4\ \mathrm{N/m^2} < G'\ (\omega=0.1\ \mathrm{rad./s}) < 4\times10^4\ \mathrm{N/m^2}$ and $5 < [G'\ (\omega=100)/G'\ (\omega=0.1)] < 300$ have good peel, tack, and shear properties [1].

Considerable studies of the PSAs containing block copolymers have been reported on. The reports have included topics such as the following: the effect of substrate and tackifier on peel strength of SIS-based hot-melt (HM) pressure sensitive adhesives (PSAs) [2] and the effect of SIS-based PSAs blending with certain kinds of tackifiers (hydrogenated dicyclopentadiene, H-DCPD) [3]. There are also some articles on the study of ethylene-vinyl acetate (EVA) copolymer HMPSAs [4,5]. The Review article on hot-melt adhesives can be referred to in Ref. [6].

PMMA-b-PtBA is another type of block copolymer that is hardly encountered in the PSA study. It can be prepared by using the anionic polymerization and sequential addition technique [7,8], and was carried out in this study. Furthermore, viscoelastic properties were then investigated by using dynamic mechanical analysis, and the adhesive properties were determined by using the mechanical test methods.

2. Material and methods

2.1. Materials

Monomers methyl methacrylate (MMA, from Acros organics, 99%) and t-butyl acrylate (t-BA, from Acros organics, 99%) were purified by distillation under reduced pressure, then dried over CaH_2, and stored at −20 °C Solvent tetrahydrofuran (THF, 99% purity, from TEDIA company, Inc.) was dried over molecular sieve overnight before being used. Lithium chloride (LiCl) (used as ligand, from ICN Biomedicals Inc.) was dried at 130 °C (in an oven) for 24 h prior to use. Other compounds were used as received, such as *n*-butyllithium (*n*-BuLi) (anionic initiator, 1.6 M solution in hexane, from Aldrich Chemical Co. Inc.), 1,1-diphenylethylene (DPE) (giving high stereo hindrance and showing a deep red color when attached to anion, from Alfa Aesar,

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USA), and “Staybelite Ester 3” synthetic resin (the triethylene glycol ester of partially hydrogenated wood rosin, used as a tackifier, from Hercules Inc. with M_n of 385 and M_w of 400). Other compounds for using in emulsion polymerization, were used as received, such as potassium persulfate ($K_2S_2O_8$, KPS, as initiator, from Wako Laboratory Chemicals, Japan, 99%), sodium dodecyl sulfate (SDS, as surfactant, from Sigma Company, 99%), 1-hexadecanol (or cetyl alcohol, CA, as a cosurfactant, from Aldrich Chemical Co. Inc., 99%), 4-methoxyphenol (MEHQ, Tokyo Chemical Industry Co. Ltd., 99%) and *n*-dodecyl mercaptan (as a chain transfer agent, from Acros, 98%). Water was purified through a Reverse Osmosis System (Ultra-pure Water System, Model DI-S3, Kintech Co.) with a conductivity of 2 μmho.

2.2. Preparation procedure of PMMA and PMMA-b-PtBA by anionic polymerization

Anionic polymerization of MMA was performed in THF at −68 °C , under a nitrogen atmosphere, using *n*-BuLi as the initiator, and in the presence of LiCl and DPE. Recipes for the preparation are shown in Table 1. LiCl (0.53 g) was dissolved in THF (80 mL) in a 250 mL flask first. DPE (1.5 g) was injected to the flask, and the *n*-BuLi solution was titrated to the reaction mixture in the flask until the mixture turned blood-red to eliminate possible moisture content, then a suitable amount of *n*-BuLi solution (20 mL) was injected to the flask, and the flask was cooled to −68 °C, then monomer MMA (20 mL) was added to run the polymerization. The temperature rose 10 °C in 5 min, and went back to −68 °C in 10 min. In 30 min, the reaction mixture turned colorless. Aliquot of the reaction mixture was withdrawn for characterization and the polymerization was stopped. The reaction mixture was precipitated by adding a mixture of methanol and water (80/20, V/V), filtrating with suction, and then dried. The characterizations include the determination of % conversion by a gravimetrical method and the determination of molecular weight and distribution of PMMA by a gel-permeation chromatographic (GPC) technique. Several batches of sample products with closer molecular weights were mixed together to make mixed batches (A-61 and A-62).

The preparation of PMMA-b-PtBA by anionic polymerization was conducted by adding t-BA slowly to the living PMMA anions, avoiding a temperature-rise of over 5 °C. The recipe is shown in Table 2. Aliquot of the reaction mixture was withdrawn for characterization. The determinations of % conversion, molecular weight and molecular weight distribution, and the collection of PMMA-b-PtBA followed those mentioned in the previous paragraph for PMMA.

2.3. Preparation of PMMA by emulsion polymerization

To prepare PMMA (A-63) with a molecular weight of around 3.0 to 4.0×10^4, an emulsion polymerization of MMA was performed at 60 °C, in a 250 cm^3, four-necked, round-bottom flask in a constant temperature bath, with a mechanical stirring rate of 150 rpm. Surfactants (2.5 g of SDS and 1.0 g of CA) and initiator (1.5 g of KPS) were dissolved in 400 cm^3 of water in the flask at 40 °C first. The chain transfer agent (1.0 g of dodecyl mercaptan) was added and stirred continuously for 10 min, then the bath temperature was raised to 60 °C. Next, the monomer MMA (100 g) was added into the flask to start the polymerization. The MMA emulsion polymerization recipe for the preparation of A-63 is shown in Table 3. The procedure is similar to those reported elsewhere [9]. During the polymerization, samples for monomer conversion were withdrawn using a hypodermic needle and a syringe. The conversion of monomer to polymer was determined gravimetrically; i.e., using MEHQ as a shortstop and methanol as a coagulation agent.

Table 1
Recipes for the preparation of PMMA by anionic polymerization.

Batch	A-61	A-62
LiCl	0.53 g	0.48 g
DPE	1.5 mL	0.20 mL
n-BuLi (1.6 M solution in Hexane)[a]	20 mL	0.71 mL
MMA	20 mL	12 mL
THF	80 mL	50 mL

[a] Before each aliquot of *n*-BuLi (1.6 M solution) was added, 7.0 mL and 3.7 mL of *n*-BuLi (1.6 M solution) were added to A-61 and A-62, respectively, for eliminating moisture content.

Table 2
Recipe for the preparation of PMMA-b-PtBA (B-16) by anionic polymerization.

LiCl	0.48 g
DPE	0.20 mL
n-BuLi (1.6 M solution in Hexane)[a]	0.71 mL
MMA	24 mL
tBA	25 mL
THF	150 mL

[a] Before the aliquot of n-BuLi (1.6 M solution) was added, 12.1 mL of *n*-BuLi (1.6 M solution) was added to the mixture for eliminating moisture content.

Table 3
Recipe for the preparation of PMMA (A-63) by radical emulsion polymerization.

SDS	2.5 g
CA	1.0 g
Potassium persulfate	1.5 g
MMA	100 g
Dodecyl mercaptan	1.0 g
H_2O	400 g

2.4. GPC determination of molecular weight and molecular weight distribution

The number-average and weight-average molecular weights (M_n and M_w) of PMMA and PMMA-b-PtBA were determined with a gel-permeation chromatograph (GPC) (Jasco, PU-980 pump with Phenolgel columns (pore sizes of 10^3, 10^4, $10^5$and 10^6 Å, respectively) and refractive index detector (Jasco, RI-930)), where the oven temperature was set at 40 °C, and the flow rate of THF was 0.8 mL/min. The molecular weight was calibrated using monodisperse polystyrene as the standard.

2.5. Mechanical tests

The peel test was performed according to ASTM [10]. Formulas for preparing PSAs with a certain phr of tackifier are shown in Table 4. PET films with a surface area of 152.4 mm × 25.4 mm and a thickness of 0.05 mm were coated with a toluene solution of PSA formula, and the thickness, after drying, of the coated adhesive was 0.050 mm. The coated tape was preheated at 180 °C for 5 min, then pressed onto a stainless steel plate ($L=7$ in., $W=2$ in. and thickness of 2 mm, pretreated with ethyl alcohol and led dry) with a 2 kg roller at once. The sample was left at room temperature for 1 h before the test began. 1 in. of separation was preset. Then the procedure was to progressively separate one piece from the other over the adhered surfaces at a separation