Original Research Paper

J. Jpn. Soc. Colour Mater., 80 [5], 199–204 (2007)

Mechanical Properties of the Polymer Blend Film Consisted of Epoxy Resin and Acrylic Polymers

Masahide KAWARAYA, Yoshinori HARA * and Shinichi OGINO **

(Received December 25, 2006 ; Accepted April 18, 2007)

Abstract

Mechanical properties of polymer films containing a domain structure were investigated. Blend films were made from various solutions of acrylics and epoxy by crosslinking with an amine. In the system, the domain sizes of the films were controlled according to the acrylic polymer's molecular weight, the functionality in the acrylics, stirring temperature and presence or absence of a compatibilizer. The domain size was estimated under a phase microscope and digital processing of images. Mechanical properties of those blend films were evaluated using a tensile test and a relaxation test. Results clarified that films containing smaller domain particles have larger elongation properties and a shorter relaxation time than films containing larger domain particles.

Key-words : Epoxy resin, Acrylic resin, Thermosetting, Domain structure, Mechanical property

1. Introduction

Now, at the beginning of the twenty-first century, the importance of environmental preservation on a global scale is increasing. People around the world must consider their contribution to the creation of a stable environment in fields of new energy sources, recycling systems, and product endurance¹⁾. Coatings are closely linked to the environmental issues, not only toxic chemical compounds but also product durability, impacting industrial circles. In other words, coatings are an indispensable means to protect buildings, automobiles and all objects that are especially used outdoors from degradation²⁾. Therefore, coatings themselves must require toughness during exposure to natural weathering, which includes sunlight, heat, moisture, and pollutants. To maintain mechanically sound coating films even after prolonged exposure under harsh circumstances, various techniques must be employed to strengthen films³⁾. Furthermore, it is

necessary to improve mechanical properties of initial coating films before exposure.

The concept of impact absorption by rubbery particles in plastic materials was first advanced by Merz *et al.*⁴⁾ for the system of butadiene-styrene rubber in polystyrene. In accordance with that concept, many studies rationalized the energy in polymer materials to rupture in tensile tests. Consequently, the rubber particles are subjected to combined stresses under which they are sufficiently strong to withstand the dilatational forces involved in tensile strain. Alternatively, the rubber particles can serve to prevent premature catastrophic crack propagation of polymer films under tensile strain⁵⁾.

All of these developments rely upon toughening polymers using thermoplastics. On the other hand, many investigations have been undertaken in the last several decades to explore toughening of thermoset polymers with phase separation system^{6,7)}. In addition, in some cases a system, which is applied with functional groups on the surface between the matrix and the domains, has been advanced^{8,9)}.

In this report, using that polymer blend system^{10,11)}, we study mechanical properties of thermoset coating films, amine-cured epoxy matrix, and acrylic polymers

* Analysis Center, Kansai Paint Co., Ltd.

** AT Laboratory, Kansai Paint Co., Ltd.

4-17-1 Higashi Yawata, Hiratsuka-shi, Kanagawa
254-8562, Japan

as domain structures. Various sizes of the domain were made using materials of different molecular weights, addition of functional groups, and so on. Results clarified that the domain structure has an influence on the physical, and especially mechanical, properties of the coating films.

2. Experimental

2.1 Materials

The following five acrylic polymers were synthesized using a drop-solution polymerization method at 80 °C over 5 h with azobis-isobutyro-nitrile (AIBN) as a polymerization catalyst in methylethylketone (MEK).

- 1) poly n-Butylmethacrylate homopolymer ($M_w = 7000, 50000$)
- 2) poly n-Butylmethacrylate-methacrylicacid copolymer (94/6 wt. ratio) ($M_w = 30000$)
- 3) poly n-Butylmethacrylate-methacrylicacid copolymer (88/12) ($M_w = 40000, 60000$)

Solid contents of the acrylic solutions were all 30 wt %. The weight-average molecular (M_w) of the polymers were measured using gel-permeation chromatography (HLC-8020 ; Tosoh Corp.).

30 wt % epoxy ($M_w = 3800$, Epikote 1009 ; Japan Epoxy Resins Co., Ltd.) solution in MEK was prepared with sufficient agitation. Meta-xylylenediamine (MXDA) as a cross-linker for epoxy polymer was used for all samples. Tetraethyl ammonium bromide (TEAB) was used for some samples as a catalytic

agent for reaction of glycidyl groups of the epoxy resin and carboxyl groups of the acrylic polymers. Two kinds of TEAB solution, 50 wt % in MEK and dimethylformamide (DMF), were prepared to elucidate effects of those solvents on film morphology and properties.

2.2 Mixing procedure

Mixture ratios of the acrylics in the epoxy polymer were set as 10 and 20 wt % to study effects of the amount of the acrylic polymer on the films' morphology and mechanical properties. The acrylic polymer solution was blended into the epoxy solution in a 200 ml Erlenmeyer flask at 20, 50, and 70 °C for 60 min with a magnetic stirrer and a magnetic tip (5 × 20 mm) at a constant agitation speed of 200 rpm.

The MXDA was mixed into the epoxy-acryl blended solution upon blending, to achieve chemical equivalence of amine volume to epoxy volume ; 1 wt % TEAB was added to polymer solid. Simultaneously, MXDA and TEAB were put into the epoxy-acrylic mixture solution in the flask and stirred with the magnetic stirrer for 10 min at room temperature.

2.3 Film preparation

Sample films were obtained as follows : 1) coating the blended solutions onto a tin plate with a blade applicator to form a ca. 100 μm dry film eventually ; 2) baking the coated plates at 170 °C for 60 min in a hot-air oven after flashing off the solvent at 25 °C, 50 rh % for 30 min ; and 3) releasing the sample films from the tin plates using amalgam.

Fig. 1 Scheme of the procedure of blending the solutions and to make the sample films.

Fig. 2 A differential interference photomicroscope image of the sample film (a) ; a digitally processed image from the photomicroscope image (b) .

Schematically, Fig. 1 shows the procedure of blending solutions and producing the sample films.

2.4 Characterization

Aspects, sizes, and dispersion of the acrylic domains in the sample films were assessed using a differential interference photomicroscope. An image digital processing (Luzex-500) linked photomicroscope was used to investigate domain sizes quantitatively (Fig. 2) .

The tensile test, the dynamic viscoelasticity spectroscopy (DVS) and stress relaxation apparatus were used to investigate mechanical properties of the sample films. Rectangular specimens for those mechanical tests were 5×20 mm with ca. 100 μm thickness.

In tensile tests, elongation and Young's moduli of the samples were measured using an automatic tensile test machine, Tensilon (UTM-II ; Toyo Measuring Instruments) at 2 mm/min strain rate at 20 $^{\circ}\text{C}$, 50 rh %. Miscibility of the sample films was evaluated using loss tangent behavior ($\tan \delta = E''/E'$) of the DVS (FT rheospectoler DV4 (UBM Co.)) in the temperature dependence test at 0 ~ 150 $^{\circ}\text{C}$ at 10 Hz. The viscoelastic relaxation characteristics of the sample were examined from the static relaxation time using an Autograph AGS-20kNG (Shimadzu Corp.), giving a strain of 1 % of the sample length, 0.2 mm, holding the strain, and

Fig. 3 Schematic of the curve of changing stress during relaxation.

measuring the time to $1/e$ of the initial stress (σ_0), σ_s . The relaxation time is denoted as t_s . Fig. 3 shows the behavior of relaxing the stress.

Gelation fractions of the sample films were determined as follows : (1) weighing the sample films ; (2) extracting uncured components of the films in acetone for 6 h at 80 $^{\circ}\text{C}$ using Soxhlet method ; (3) drying the remaining films at 120 $^{\circ}\text{C}$ for 30 min ; and (4) estimating the rate of changed weight of the films as the result of extraction.

3. Results and Discussion

Results of domain sizes, mechanical properties, and gelation fractions of all 16 sample films are shown in Table 1. In Table 1, the acrylic contents of Nos. 10, 11, 13, and 16 were 20 wt %. Bar symbols in the column of the domain sizes mean that the domains were indistinct because of the irregularly shaped particles. Samples with TEAB in MEK are denoted in the "TEAB column" with a circle sign, TEAB in DMF were used in Nos. 9 and 15.

Particles tend to be smaller according to the following : lower MW of the acrylic polymers (comparing No. 12 with No. 14 ; No. 13 with No. 16), lower amount of the acrylic polymers (No. 6 with No. 10 ; No. 7 with No. 11 ; No. 12 with No. 13), existence of MAA of the acrylic polymer (No. 3 with No. 5), addition of TEAB (No. 5 and No. 7), and use of the DMF solvent rather than MEK to solute TEAB (No. 7 with No. 9 ; No. 14 with No. 15). Results demonstrated that some methods, according to general principles (5) are available to change the domain sizes of the acrylic phase in the epoxy matrix without special techniques.

The relation between domain sizes, elongation at breaking, and Young's moduli of the sample films are

Table 1 Details of acrylic polymers contained in the sample films, stirring temperatures, acrylic domain sizes, and mechanical properties of the films.

No.	Acrylic	Mw	Content (%)	TEAB	Stirr. Temp. (°C)	Domain size (μm)	Young's Modu. (GPa)	Elongation (%)	Relax. Time (sec)	Gel. fraction (%)
1	None	—		—	20	None	2.27	7.21	0.1	72.4
2	n-BMA	50000	10	—	50	—	1.73	3.83	24.8	62.6
3	↑	7000	10	—	50	503	1.68	2.89	19.1	59.1
4	n-BMA/MAA (94/6)	30000	10	—	20	—	1.76	1.03	20.3	58.3
5	↑	↑	10	—	50	322	1.8	1.72	8.9	59.7
6	↑	↑	10	○	20	237	1.71	2.41	7.3	65.8
7	↑	↑	10	○	50	78	2.04	4.2	1.6	65.7
8	↑	↑	10	○	70	1	1.91	12.6	0.2	67.8
9	↑	↑	10	DMF	50	2	1.88	10.55	0.1	68.1
10	↑	↑	20	○	20	562	1.03	1.17	2.7	61.3
11	↑	↑	20	○	50	265	1.45	3.25	0.3	63.8
12	n-BMA/MAA (88/12)	40000	10	○	50	18	2.01	4.71	2.6	66.7
13	↑	↑	20	○	50	206	2.08	3.23	1.2	67.1
14	↑	60000	10	○	50	43	1.99	4.43	1.8	63.0
15	↑	↑	10	DMF	50	1	2.07	10.43	0.6	70.6
16	↑	↑	20	○	50	84	2.06	4.7	0.7	66.9

Fig. 4 Relation between domain size of the sample films and elongation at break ; ● 10 wt % of acrylic polymer, ○ 20 wt %. The arrow sign indicates the value of the film without domains, non-acrylic polymer. **Fig. 5** Relation between domain size of the sample films and Young's modulus : ◆ 10 wt % of acrylic polymer, ◇ 20 wt %. The arrow sign indicates the value of the film without domains, non-acrylic polymer.

shown in Fig. 4 and Fig. 5. In those Figures, the arrows indicate the values of sample film No. 1, the criterion sample, to which was added no acrylic polymer. Fig. 4 shows that the films with the smaller acrylic domains around 1 μm extend more : they show about 10 % more elongation than the criterion sample. It can be readily inferred that the larger acrylic domains decrease the elongation or shorten the breaking time

(Fig. 6 (a)). The smaller domains prolong the time at breakage (Fig. 6 (b)) or have an arresting effect on the progression of breaking by rubbery domains though lack of crosslinking (Fig. 6 (c)). In Fig. 5, all sample films have a lower Young's modulus than the criterion sample. It can be accepted that the non-crosslinking components and acrylic "brittle" domains influence the films weakening, and lowered Young's modulus.

Fig. 6 Schematic diagram of films under breaking : (a) with larger domain, (b) and (c) with smaller domain.

Fig. 7 Relation between the domain sizes and the relaxation time of the sample films, $\blacktriangle$: 10 wt % acrylics ratio, $\triangle$: 20 wt % acrylic ratio. The arrow sign indicates the value of the film without domains, non-acrylic polymer.

Fig. 7 displays the relation between domain sizes and relaxation times of the films. The points of the arrows show values of the criterion film, No. 1. Although the relaxation times of all sample films with the acrylic polymer are longer than those of the films without acrylics, the relaxation times of the films reduce as the domain size is getting smaller. It is noteworthy that the relaxation times of the films with 20 wt % acrylic contents tend to be shorter than those of films with 10 wt % content. This result contradicts the inference that addition of acrylic polymer lengthens the films' relaxation time, whereas the number of the same size domains influences on the relaxation time. It might be argued that the morphology in such an island structure more emphasizes the relaxation characteristic than the amount of polymer in the composition.

A $\tan \delta$ curve pertains in the dynamic mechanical

Fig. 8 Loss tangent δ of the sample No. 1 ($\circ$) and No. 2 ($\bullet$) in the dynamic mechanical spectroscopy.

Fig. 9 Loss tangent δ of the sample No. 5 ($\bullet$), No. 7 ($\bullet$) and No. 8 ($\circ$) in the dynamic mechanical spectroscopy.

spectroscopy of samples No. 1 and No. 2 in Fig. 8 ; Nos. 5, 7 and 8 are shown in Fig. 9. The glass-transition temperature (T_g) of n-BMA from the general data is around 20 °C. A peak is apparent around 40 °C, which is derived from n-BMA components in the $\tan \delta$ (Fig. 8). Fig. 9 shows that the peak disappears through the combination of the two factors : addition of TBAB ; increased mixing temperature, thereby giving the two polymers good miscibility and shrinking their respective domains.

They might have affected the acrylic domains themselves, especially with MAA, and cured inside the domains with the epoxy polymer. This prospect comes from the values of the gel fraction in sample Nos. 5, 7 and 8. Detailed study of these results is necessary, perhaps using infrared microscopic observation or other means.

Conclusion

Results of this study suggest the following conclusions.

- i) Domain sizes in this system tend to be smaller based on : lower MW of the acrylic polymers, higher stirring temperature, MAA copolymerization to the acrylic polymer, and addition of TEAB (DMF solvent rather than MEK).
- ii) Correlation between the domain sizes and the mechanical properties was clarified ; the films with smaller domains of less than a few micrometers show greater elongation and shorter relaxation time.

References

- 1) H. Komiyama : "Chikyuu jizoku no gijutsu", Iwanamishinsho (1999).
- 2) Z. W. Wicks, Jr., F. N. Jones and S. P. Pappas : "Organic Coatings : Science and Technology", John Wiley & Sons, Inc. (1992).
- 3) K. Satou : "Toryou Bussei Kogaku", Rikkou Shuppansha (1979).
- 4) E. H. Merz, G. C. Claver and M. Baer : "Studies on Heterogeneous Polymeric Systems", *J. Polym. Sci.*, **22**, 325-341 (1956).
- 5) S. Newmann and S. Stella : *J. Appl. Polym. Sci.*, **9**, 2297-2302 (1965).
- 6) H. M. Buettner and L. T. Manzione : Soc. Plast. Eng. Annu. Tech. Conf., 40th, 140-142 (1982).
- 7) I. Frischinger, S. Dirlikov and P. Muturi : *Adv. Coat. Technol.*, 193-204 (1993).
- 8) R. Thomas, J. Abraham and S. Thomas : *J. Polym. Sci. Part B*, **42**, 2531-2544 (2004).
- 9) B. Francis, R. Ramaswamy and V. Lakshmana : *Polymer*, **46**, 12372-12385 (2005).
- 10) D. R. Paul and S. Newmann : "Polymer Blends", Academic Press (1978).
- 11) S. Akiyama, T. Nishi and T. Inoue : "Porimah Brendo", CMC shuppan (1984).

アクリルポリマーをブレンドしたエポキシ硬化フィルムのドメインサイズと力学的特性の関連性

瓦家正英・原 義則*・荻野晋一**

*関西ペイント株式会社 分析センター 神奈川県平塚市東八幡4-17-1 (〒254-8562)

**関西ペイント株式会社 AT研究所 神奈川県平塚市東八幡4-17-1 (〒254-8562)

(2006年12月25日受付；2007年4月18日審査終了)

要 旨

ドメイン構造を有するフィルムの力学的特性を調べた。アミン硬化エポキシフィルムのドメインサイズを添加するアクリルポリマーの分子量、官能基、攪拌温度、相溶化剤の有無によりコントロールした。ドメインサイズは位相差顕微鏡観察した画像のデジタル処理画面から評価し、フィルムの引張り特性、応力緩和特性との関連性を調べた。ドメインサイズが小さくなるほど破断のび率が増加し、応力緩和時間が短くなることがわかった。