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Properties

Surface Active Properties of Silicone Containing Polymers

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Summary

The efficiency and durability of surface modification of poly(methyl methacrylate) [PMMA] by silicone containing graft and random copolymers were studied by contact angle measurement of water droplet. The efficiency principally depended on the content of the siloxane; however, the durability of surface modification to hexane extraction differed according to the type of the silicone polymer and the siloxane content.

Introduction

The importance of surface properties of polymer film has been recognized in a variety of applications, and many physicochemical methods have been employed for the surface modification of polymer film (1). Among these, the use of graft copolymers for the purpose of surface modification of other polymers merits special attention because these can be made-to-order for a specific need (2-4). We have already reported the synthesis and study of surface properties of silicone containing graft copolymers (4). In this communication, we would like to report on the comparative study of surface properties of silicone-containing polymers.

Experimental

Silicone containing graft graft copolymers with MMA (GM-211, 213 411 and 413) were synthesized as reported earlier (4). 3-Methacryloyloxypropyltris(trimethylsiloxy)silane (MTS) was prepared in 70% yield by known method (5). B.p. 115°/0.2mmHg. Random copolymers of MTS with MMA (namely, MTS-25 and MTS-45), and its homopolymer (PMTS) were synthesized by the usual free-radical polymerization technique using toluene as solvent. Commercial poly(dimethylsiloxane) (PDMS) was used as received. The characteristics of all the silicone polymers are shown in Table-1.

Contact angle Studies

Film of binary blends containing the silicone polymers (0.1-10% by wt) with commercial PMMA ($\overline{M}_n$=67,000; $\overline{M}_w/\overline{M}_n$=2.2) were prepared from 6-8% THF solutions by casting technique.

Table 1. Characteristics of silicone polymers

Polymer code	Siloxane content(wt%)[a)] in feed	found[b)]	$\overline{M}_n$ [c)]	$\overline{M}_w/\overline{M}_n$ [c)]	Number of grafts
GM-211	50	42	42,300	1.84	4.0
GM-213	25	23	31,000	1.96	1.5
GM-411	50	43	57,700	1.46	2.7
GM-413	25	23	32,100	1.73	0.7
PMTS[d)]	(70)[e)]		125,000	2.20	-
MTS-25[f)]	25	24	102,000	1.36	-
MTS-45[g)]	45	44	123,000	1.41	-
PMTS[h)]	(100)		40,000	-	-

a) Assumed to be same as macromer content (wt.%).

b) By ^{1}H-NMR($CDCl_3$) analysis.

c) Determined from GPC. Molecular weights $\overline{M}_n$ are calibrated to standard polystyrene.

d) Polymerization was carried out at 60°C for 60h using AIBN (1 mol%) as the initiator.

e) Taken to be same as that of MTS's siloxane content.

f) Polymerization condition: MTS (1.0g), MMA (1.8g), AIBN (1 mol% based on MMA) and toluene (14.2g); time, 20h; temperature, 60°C.

g) Feed: MTS (1.8g), MMA (1.0g), AIBN (1 mol% based on MMA), and toluene (14.2g). Polymerization condition was same as in (f).

h) A viscous liquid.

The films were dried under vacuum for at least 48h. To study the effect of treatment with n-hexane, the films were placed in stirring n-hexane for 6h, removed and dried in vacuum. Contact angles of water droplet at 20°C were measured by the conventional telescopic goniometer technique (CA-A model; Kyowa Scientific Industries Co., Ltd; Tokyo, Japan)

Results and Discussion

Contact angle measurements indicated that 0.5-1.0% by wt of the silicone or random copolymers were enough to make the PMMA film surface completely hydrophobic on the air-surface side (Fig. 1). On the glass-side surface, the contact angle variation, though observed, was not significant. The extent of surface modification on the air-side seems to be dependent on the percent siloxane content in the blends, e.g. GM-211 and GM-411 (both having similar siloxane content of 42% by wt.) are better than GM-213 and GM-413 (both having similar siloxane

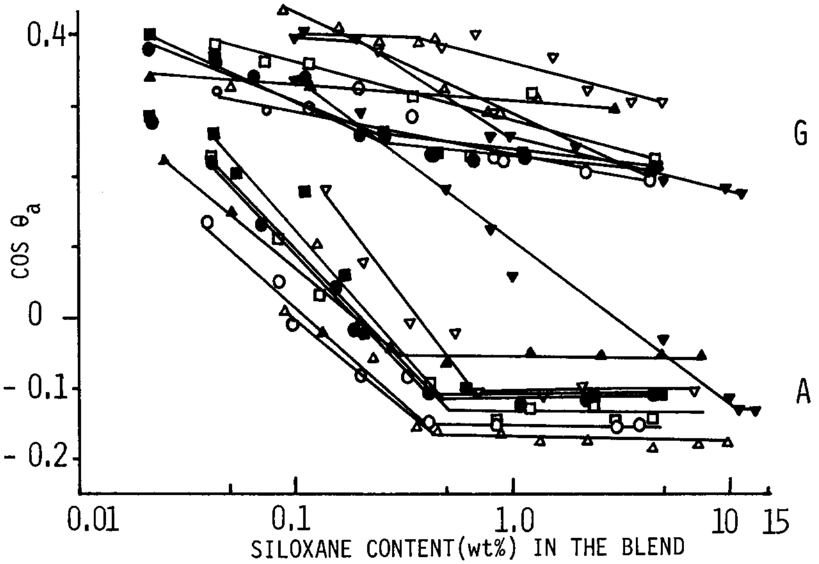

Fig.1. Contact angle of water droplet at 20 °C for various silicone polymer-PMMA binary blends (A: air side surface; G: glass side surface). The symbols represent following silicone polymers: ○:GM-211, ●:GM-213, □:GM-411, ■:GM-413, ▼:PDMS, ▽:PMTS, ▲:MTS-45, and △:MTS-25

content of 22% by wt.). The same phenomenon was observed in case of MTS-45 and MTS-25. However, this may not be the only factor responsible since the two silicone homopolymers(PDMS and PMTS) having the siloxane contents far higher than any graft or random copolymer are relatively inefficient. Particular mention must be made of the very large quantities of PDMS, namely, 10-13% by wt., required for complete surface modification of the PMMA blend film. It is to be noted that PDMS is a viscous liquid with the result that globules of PDMS accumulated as a separate liquid layer on the blend film surface. The measurement of contact angle on such physically heterogeneous surfaces is quite difficult and prone to be nonreproducible. Such a phenomenon was unforeseen nad undesirable, too, because of the chances of loss of the surface-modifying silicone component from the surface under certain conditions. This possibility was realized by the following treatment with n-hexane. The results are shown in Fig. 2.

n-Hexane was selected because it is a good solvent for silicone polymers. As can be seen from Fig. 2, the PDMS polymer was completely washed away due to its solubility in n-hexane, and consequently, the blend film was deprived of any surface hydrophobic modification. Similarly, and most surprisingly, observed was the complete removal of PMTS and

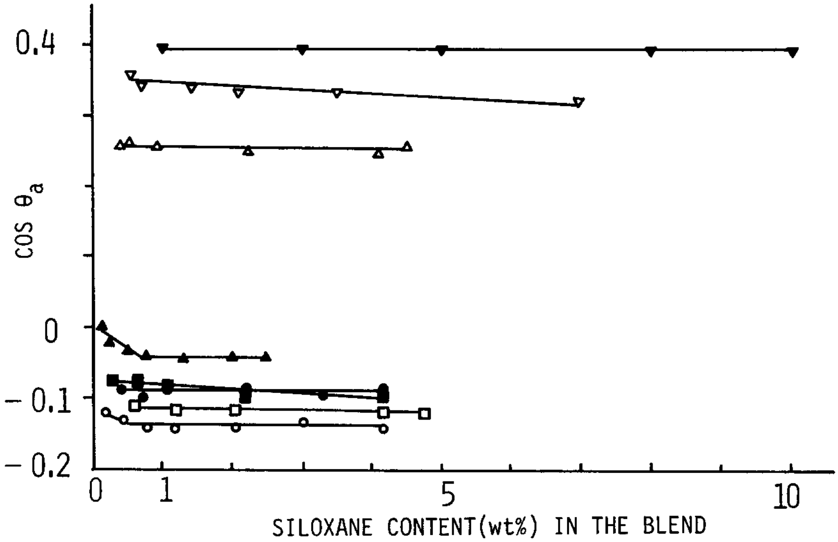

Fig.2. Contact angle of water droplet at 20°C on air side surface of various silicone polymer-PMMA blend films after treatment with n-hexane. (For an explanation of symbols, and for contact angle values before n-hexane treatment, see the Fig.1.)

MTS-45 also from the surface of the blend films, and this also, it was found, was due to their solubility in n-hexane. The silicone graft copolymers, and MTS-25, on the other hand, were resistant to solvent extraction from the blend film surface as these polymers were insoluble in n-hexane. It is interesting to note that the graft copolymers GM-211, and GM-411, both having siloxane contents similar to MTS-45, were not extracted from the blend film surface by n-hexane treatment. This phenomenon is significant to imply the behaviors of silicone polymers on the surface. The surface active properties of the silicone graft copolymers, and their resistance to hexane-extraction may indicate that they are accumulated on the surface with the backbone PMMA chain remaining in bulk PMMA as anchor segment. The easy removal of silicone random copolymer MTS-45, despite its high siloxane content, from the PMMA surface seems to indicate the inefficiency of backbone PMMA chain as anchor segment. Furthermore, this seems to indicate that in the silicone random copolymers tested in this study, the resistance to solvent extraction depends on the MMA content unlike that in the graft copolymers.

A comparison of the silicone graft copolymers with random copolymers makes the former more attractive not only because of the possibility of synthesizing such made-to-order graft copolymers by the use of easily accessible silicone macromers (6), but also because of the durability of surface modification characteristics imparted by them.

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