GRAFT POLYMER EFFECT FOR VISCOELASTICITY OF CORE-SHELL ACRYLIC RUBBER BLENDED PMMA

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Abstract We investigated the dynamic viscoelastic behavior of core-shell acrylic rubber(CSR) blended PMMA(CSRP) which has been used for various application because of its high toughness and enhanced ductility. Various types of CSR prepared by emulsion polymerization were used for the linear viscoelastic measurements in the molten state. G' and G'' of CSRP were influenced by content, degree of cross linking and copolymer content(shell) of CSR. CSRP which had high contents of rubber, or high degree of cross linking of rubber showed high G' and G''. Especially in high graft polymer ratio, CSRP showed high G'. We concluded that it is due to development of entanglement between graft-graft polymer chain by estimating for radius of gyration Rg and C*.

Keywords: PMMA, core-shell acrylic rubber, graft polymer, dynamic viscoelasticity, radius of gyration

Introduction

Polymethylmethacrylate (PMMA) is widely used in many fields such as automobile, construction and FPD areas due to the excellent transparency, high resistance for weathering and image of high-class. Although PMMA has such high usefulness, lack of toughness often gives rise to serious problems of processability and reliability as a final product. To improve toughness of PMMA, blending core-shell acrylic rubber were developed recently as reported for ABS to enhance to toughness of AN.[1)] Core is consisted of crosslinked polybutylacrylate(PBA) based rubber and shell is PMMA based polymer to give compatibility with PMMA. However, blending core-shell acrylic rubber to PMMA leads to change of rheological behavior and it also affect processability. To control rheological behavior of CSRP accurately is extremely important, but it has not been reported.

Therefore, in this paper we focused on the effect of CSRP structures (contents of rubber, degree of cross linking of rubber and copolymer content(shell) grafted on rubber) by measuring dynamic viscoelasiticity.

Experimental

-Materials-

Core-shell acrylic rubbers (CSR);

We used Butylacrylate(BA)/MMA(80/20) as monomer of core, and hydroperoxide as initiator in emulsion. In addition, as a crosslinking agent, we used Allylmethacrylate of 0.5, 1, and 3 wt% against core. For shell(graft polymer) parts, we used MMA(100) monomer of 35-150 wt% to change graft ratio .

Core-shell acrylic rubber blended PMMA (CSRP);

CSR of 5, 10, 20, and 30 wt% was blended with PMMA(HR-S, Claray Co., LTD, Japan/ Mw135,000) by twin-screw mixer(Laboprastmill, Toyo Seiki Seisaku-sho., Co, LTD) at 260℃. Test speciments for dynamic viscoelasticity were molded by a hot press at 260 ℃.

-Analysis-

Dynamic viscoelasticity measurement were performed by rotational rheometer at a constant temperature of 260℃(ARES, TA instrument) and constant strain with in linear viscoelasticity.

Results and Discussion

Fig.1 shows storage modulus(G') of CSR which weight percentage against core of crosslinking agent (CLA) are 0.5, 1, and 3. As increasing CLA, G' showed high value and weak flequency dependence. Supposing that the plateu G' at low flequencies resulted from the network structure, this increase of G' means molecular weight between cross linking points Mx became shorter. Using G' at 10^{-2}rads^{-1} as Ge, Mx of CSRP with CLA with 0.5 and 3 wt% was estimated as 101,000 and 21,000, respectively.

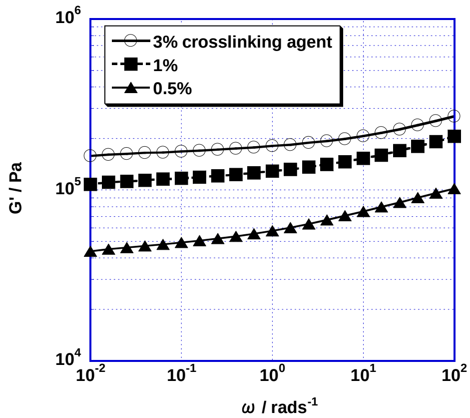

Fig.1 Strage modulus of core with crosslinking agent of 0.5, 1, 3% at 260℃

Fig.2 shows G' of CSRP which weight percentage against core of copolymer contens(graft shell) are 35, 80, and 100. Each core content(30wt%) and CLA weight percentage(0.5wt%) are constant values. As increasing of graft polymer ratio, G' at low flequencies increased and leveled off. In graft ratio of 100%, this tendency was most obvious. We considered that it was due to the effect of entanglement of graft polymer. Weight-average molecular weight Mw of graft polymer which graft ratio was 100% was 56,900. It is enough to entangle with matrix PMMA chain because entanglement molecular weight Me of PMMA is 10,000. Mw of graft polymer which 35% graft ratio is 12,000, therefore it is difficult to cause entanglements of graft polymer.

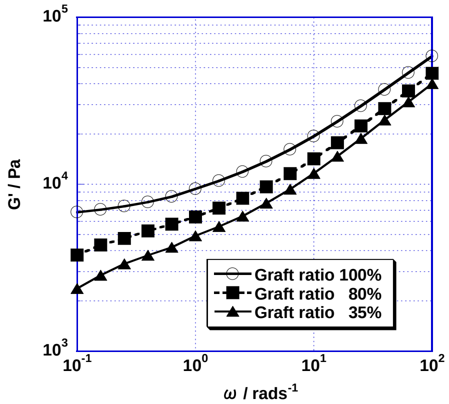

Fig.2 Strage modulus of CSRP with graft ratio of 35, 80, 100% at 260℃

Fig.3 and 4 show G' of CSRP which weight percentage against core of CSR(core-shell rubber) are 5, 10, 20 and 30 at each graft polymer ratio(80 and 150%). At CSRP with graft ratio of 80%,as increasing CSR contents, G' increased monotonically. On the other hand, at CSRP (graft ratio 150%), G' increased notably and showed weak flequency dependence in particular for 30wt% CSR content.We consider that this difference resulted from the length of shell chain. Mw of graft polymer which 150% graft ratio CSR was 92,500, and it is enough to entangle.

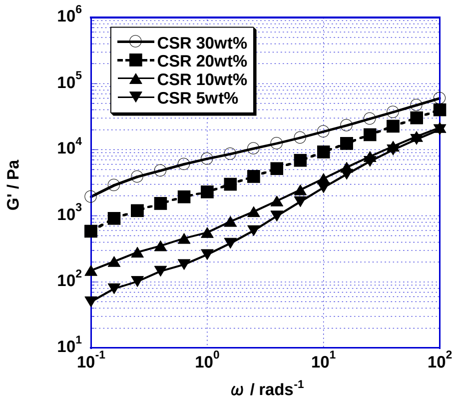

Fig.3 Strage modulus of CSRP with core rubber content of 5, 10, 20,30 wt%. The weight ratio of shell polymer (graft polymer) to core rubber is 80/100.

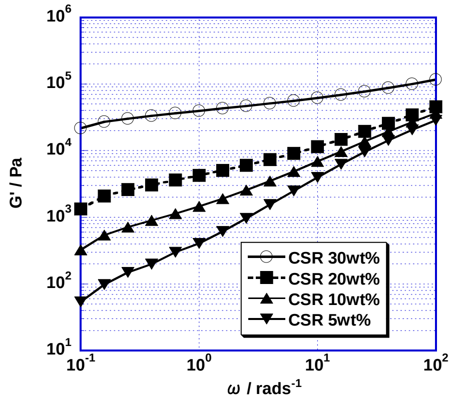

Fig.4 Strage modulus of CSRP with core rubber of 5, 10, 20,30 wt%. The weight ratio of shell polymer (graft polymer) to core rubber is 150/100.

This suggests the development of entanglement not only between graft polymer chain-matrix but also between graft-graft polymer chain. Fig.5 shows G' at 0.1rads^{-1} of CSRP of each contents of CSR. Defference of critical concentration C^* which estimated by radius of gyration Rg of PMMA[2)] and excluded volume of core rubber was confirmed. C^* of 150% graft ratio CSRP is lower(33%) compared to C^* of 80% graft ratio CSRP(72%).

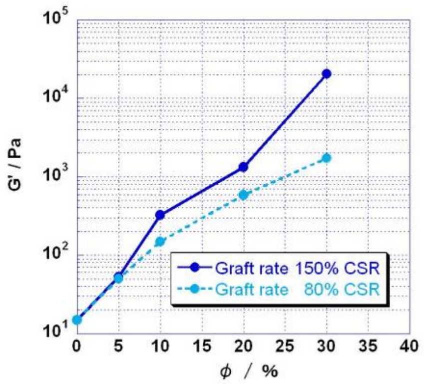

Fig.5 Strage modulus of CSRP with CSR of 5, 10, 20, 30wt% at 0.1rads^{-1} (260℃)

Conclusions

CSRPs were measured in the molten state of their linear viscoelastic properties. G', G''were increased and showed low flequency dependence by contents of rubber, degree of cross linking of rubber and copolymer content grafted on rubber. Because of development of entanglement between graft-graft polymer chain by estimating for radius of gyration *Rg* and the *C**, in high graft polymer ratio(150%), these tendency was more conspicuous.

References

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