

Rheology Modification of PVC Plastisols with Poly(butylene terephthalate)-*b*-Poly(tetramethylene glycol)

XIA WANG, YUNZHAO YU

PCLCC, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*

Received 3 January 1997; accepted 17 April 1997

ABSTRACT: A few percent of poly(butylene)-*b*-poly(tetramethylene glycol) was able to turn a liquid plasticizer into a gel, and thus imparted yield stresses to the fluid. When the plasticizer contained as little as 2.5 wt % of the block copolymer, sag free plastisols were obtained. A reduction in tensile strength was found for the modified plastisols, while the elongation was not affected. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 749–753, 1997

Key words: PVC plastisol; rheology modifier; gel; dioctyl phthalate; poly(butylene terephthalate)-*b*-poly(tetramethylene glycol)

INTRODUCTION

Poly(vinyl chloride) (PVC) plastisols are extensively used as sealant in automobile assembly. They should be formulated to be easily pumpable while nonsagging during curing. Fillers such as calcium carbonate are frequently included in the formulation to reduce cost and to impart yield stresses and thixotropy. However, they tend to negatively affect such properties as tensile strength, elongation, and tear resistance.

Fumed silica is a typical thixotropic modifier for PVC plastisols. It provides yield stresses and thixotropy at low concentrations through particle aggregation. However, the transient network based on hydrogen bonding between hydroxyl groups on the surface silicon atoms of silica particles can be resolved through wetting by liquid components in the composition. Consequently, the sag resistance loses gradually on storage, and rheological properties change irreversibly by the action of shearing.

This research project is to explore an alternative approach of rheology modification of plastisols, i.e., to use polymer as a rheology modifier. Polymers influence fluid rheology powerfully by virtue of their great hydrodynamic volume, which is determined by polymer structure parameters and polymer–solvent interactions, as well as polymer associations and repulsion.¹

It is known that, in many cases, semicrystalline polymers form physical networks in solution and thus turn a liquid into a gel.^{2–7} In our previous articles,^{8,9} reversible gels of poly(butylene terephthalate) (PBT) and poly(butylene terephthalate)-*b*-poly(tetramethylene glycol) (PBT-*b*-PTMG) in epoxy resins were studied with respect to rheological and mechanical properties. Yield stresses were imparted to the resin by incorporation of a few percent of modifier to prevent sag during curing. The same strategy was applied to the rheology modification of PVC plastisols. PBT-*b*-PTMG, which has been used for making polymer alloys with PVC,¹⁰ was studied for rheology modification in this article.

EXPERIMENTAL

Materials

PVC powder of Type III was produced by Gehua Industry Group Company, Wuhan, China. Dibutyltin dilaurate was produced by Wuxi Chemical Industry Group Company, Wuxi, China.

Correspondence to: Yunzhao Yu.

* PCLCC is the Polymer Chemistry Laboratory, Chinese Academy of Sciences and China Petro-Chemical Corporation.

Journal of Applied Polymer Science, Vol. 66, 749–753 (1997)

© 1997 John Wiley & Sons, Inc.

CCC 0021-8995/97/040749-05

Table I The Copolymer PBT-*b*-PTMG

PBT : PTMG weight ratio	40 : 60
M_n of PTMG segment	1000
$[\eta]$ (dL g) ^a	1.2
Tensile strength (MPa)	21
Ultimate elongation (%)	500
mp (°C)	178

^a In m-cresol; 30°C.

tyl phthalate (DBP) and dioctyl phthalate (DOP) were chemical reagents from Beijing Chemicals Factory. Dibutyltin dilaurate was a chemical reagent from Beijing Elf Atochem Polystab Co.

PBT-*b*-PTMG was prepared by melting polycondensation, starting with dimethyl terephthalate, butylene glycol, and poly(tetramethylene glycol) of a molecular weight of 1000. The copolymer with a PBT : PTMG weight ratio of 40 : 60, given in Table I, is a good thermoplastic elastomer. The structural parameter and properties of this copolymer are given in Table I.

Preparation

PBT-*b*-PTMG was dissolved in DOP by heating at 165°C with stirring, and the solution was cooled to the room temperature to get a gel. For the preparation of the model plastisol, 100 g PVC powder was mixed with 80 g DOP. For the preparation of modified plastisols, the gel of PBT-*b*-PTMG in DOP was mixed with PVC powder. For the preparation of cured material, the plastisol was deaerated *in vacua*, compress molded, and cured at 150°C for 30 min.

Measurement

A Bohlin rheometer, CS-50, was used for steady and dynamic rheological measurements, using a parallel plate geometry with a radius of 25 mm and a gap at 1 mm. Rheometric mechanical spectra was studied using a rheometric mechanical spectrometer, RMS 650. Mechanical properties of cured plastisols were determined according to ASTM D412, using compact dumbbell specimens of 10 mm gauge length and 2 mm thickness.

RESULTS AND DISCUSSION

Gel Formation in Plasticizers

PVC plastisols are stable dispersion of fine PVC particles in the plasticizer, which makes the com-

position fluid. On heating, the plasticizer is absorbed into the particles, and the material is cured.

Dioctyl phthalate (DOP) and dibutyl phthalate (DBP) are the primary plasticizers for plastisol formulation. In order to prevent sag of plastisols, readily available polymers were screened for gel formation in these plasticizers. It was found that PBT can dissolve in DBP by heating at a temperature near the melting point of the polymer, and the solution gelled on cooling. However, PBT did not form stable gel in DOP because the solubility parameters are too far away from each other.

In order to improve the compatibility, PTMG segments were introduced to the polymer molecules. The block copolymer PBT-*b*-PTMG can form stable gels both in DBP and in DOP. It was therefore used in the following studies.

Flow Behavior of DOP Modified with PBT-*b*-PTMG

Flow behavior of the plasticizer changed dramatically by incorporation of PBT-*b*-PTMG. A few percent of the block copolymer was enough to turn the liquid into a gel.

Dynamic mechanical measurement in the linear viscoelastic regime was carried out because the dynamic modulus is sensitive to structure. Gel is characterized by an elastic modulus at zero frequency. Figure 1 shows the frequency dependence of the storage modulus G' and the loss modulus G'' for a DOP gel containing 5 wt % of PBT-*b*-PTMG. It is seen that G' was one order of magnitude higher than G'' in the whole range of frequency.

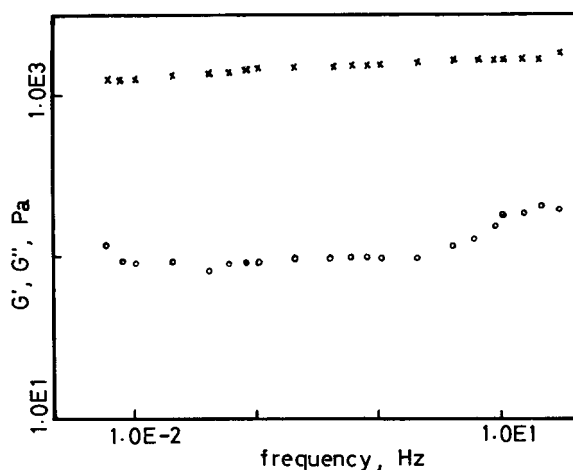


Figure 1 G' (\times) and G'' (\circ) versus frequency at 25°C for the DOP gel containing 5% PBT-*b*-PTMG.

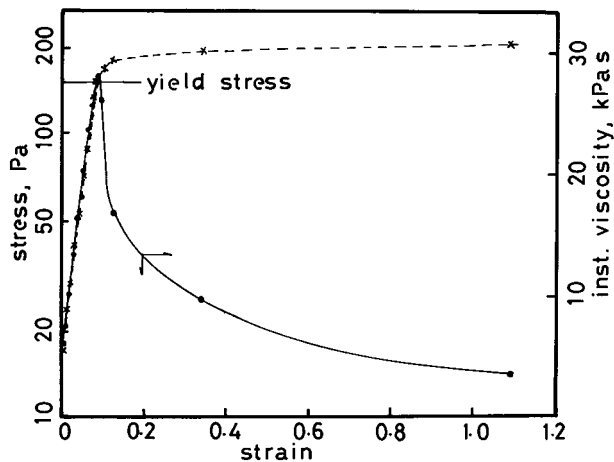


Figure 2 Determination of yield stress for the DOP gel containing 5% PBT-*b*-PTMG.

The elasticity at zero frequency is closely related to the yield stress. Figure 2 shows a diagram for yield stress determination using a controlled stress rheometer, in which shear stress was increased from 0 to 1000 Pa in 100 s in 100 steps, the strain was measured, and the apparent viscosity calculated by the computer. The stress, under which the viscosity began to fall off, was taken as the yield stress.

The yield stress of DOP gels increased rapidly with the content of the block copolymer, as shown in Figure 3. Therefore, it is convenient to control the level of yield stress of plastisols by regulating the concentration of the modifier.

The gels of PBT-*b*-PTMG in DOP were thermo-reversible. The change of G' and G'' with tempera-

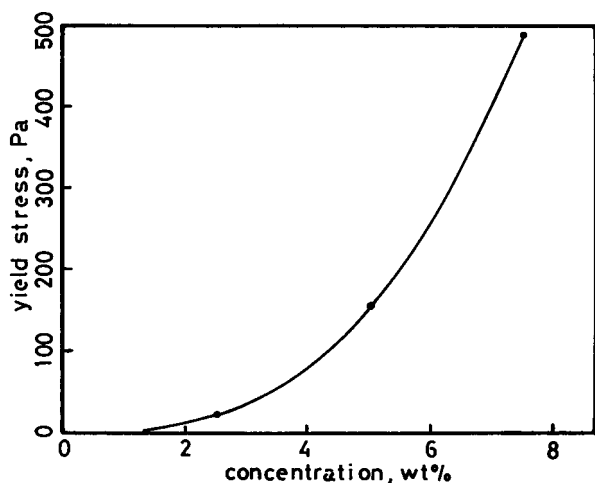


Figure 3 Yield stress of DOP gels vs. PBT-*b*-PTMG concentration at 25°C.

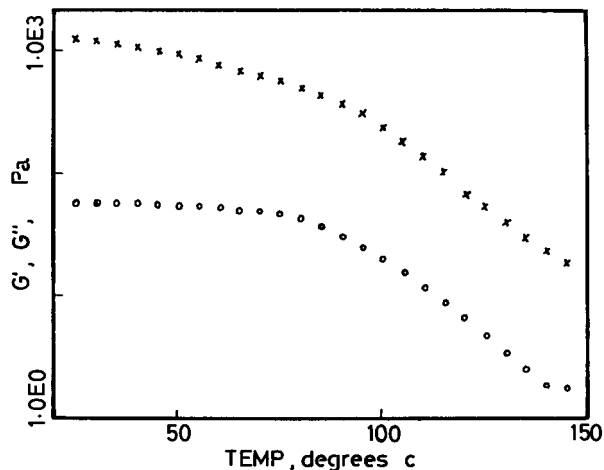


Figure 4 G' (x) and G'' (o) at 0.1 Hz versus temperature for the DOP gel containing 5% PBT-*b*-PTMG.

ture is shown in Figure 4. The steep change of properties around 90°C was attributed to the dissolution of PBT-*b*-PTMG spherulites, which formed a network in the plasticizer on cooling.

Rheological Behavior of Modified Plastisols

A model plastisol was made up of 100 parts (wt) of PVC powder and 80 parts of DOP. At this concentration, the dispersion was easily flowable. In the dynamic mechanical measurement, elastic stresses in-phase with the strain relaxed, and out-of-phase stresses dominated. Therefore, G'' was higher than G' (Fig. 5).

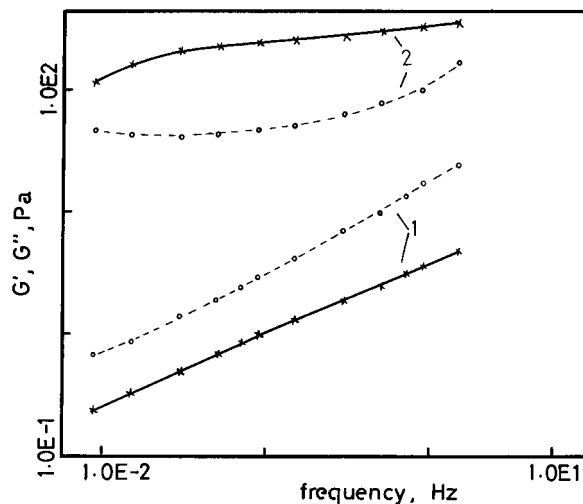


Figure 5 G' (x) and G'' (o) versus frequency at 25°C for the model plastisol (1) and the modified plastisol (2).

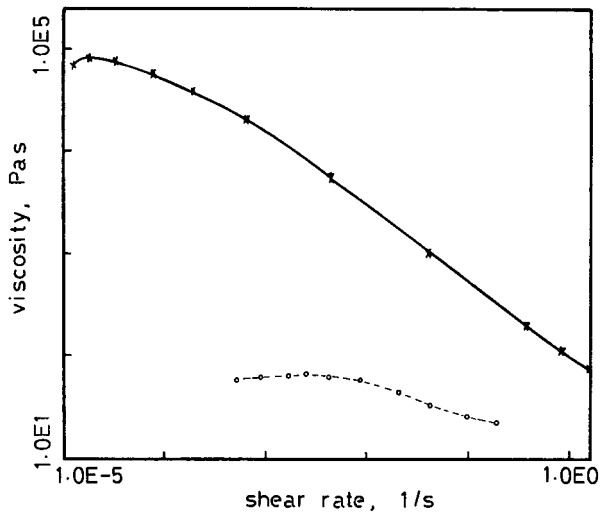


Figure 6 Viscosity at 25°C versus shear rate for the model plastisol (○) and the modified plastisol (×).

When the plasticizer containing 2.5 wt % of PBT-*b*-PTMG was used for the preparation, the modified plastisol showed rheological behavior of a gel, i.e., elastic stresses dominated in the dynamic mechanical measurement, and G' was higher than G'' .

In steady shear measurement, the model plastisol showed slight shear thinning, Figure 6. In comparison, the viscosity of the modified plastisol decreased much more rapidly at higher shear rates. At the low shear rate end, the viscosity was enhanced for three orders of magnitude in the presence of the modifier.

It has been found that 2.5 wt % of the block copolymer in the plasticizer was able to prevent sag during the curing. In the test, a steel plate with a bead of $1 \times 10 \times 100$ mm of the plastisol was placed vertically in an oven and was heated at 150°C for 30 min to effect the cure. In this way, a sag of 28 mm was found for the model plastisol, while the plastisol with 2.5 wt % of PBT-*b*-PTMG was sag free.

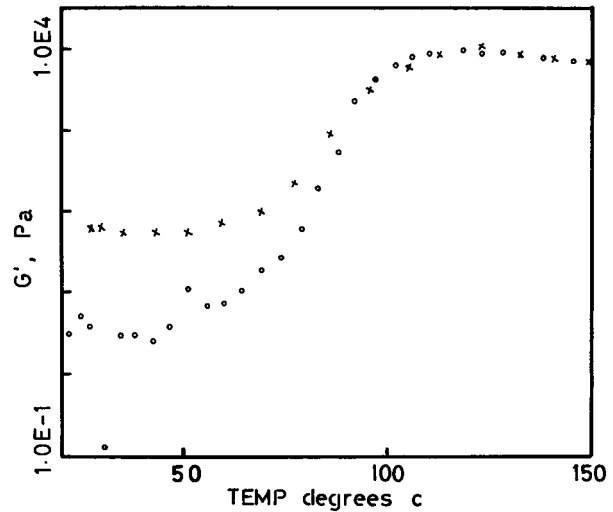


Figure 7 G' at 0.1 Hz vs. temperature for the model plastisol (○) and the modified plastisol (×).

The sag resistance of the modified plastisol was expected upon studying the temperature dependence of the storage modulus. A plot of G' versus temperature is given in Figure 7. It is seen that for the modified plastisol G' did not fall off in the range of 30–70°C. As the temperature increased further, fusion of the PVC particles became evident. As a result, G' was enhanced with the temperature.

Mechanical Properties of PVC Plastisols Modified with PBT-*b*-PTMG

It is important to know the influence of the rheology modifier on mechanical properties of the plastisol. In Table II, a set of experiment results is given. It is seen that the plastisol became softer, and a remarkable reduction in tensile strength was caused by replacing a part of PVC with PBT-*b*-PTMG while the break elongation was not affected. Therefore, the use of the rheology modifier should be restricted at low concentrations.

Table II Mechanical Properties of PVC Plastisols Modified with PBT-*b*-PTMG

Composition (by wt)				Tensile Strength (MPa)	Elongation at Break (%)
PVC Powder	DOP	PBT- <i>b</i> -PTMG	Dibutyltin Dilaurate		
100	80	0	2	7.8	351
95.8	80	4.2	2	6.9	358
93.5	80	6.5	2	6.5	344

The authors wish to thank the Ford-China Research and Development Fund for support of this work under Grant No. 9415311.

REFERENCES

1. J. E. Glass, D. N. Schulz, and C. F. Zukoski, in *Polymers as Rheology Modifiers*, D. N. Schulz and J. E. Glass, Eds., ACS Symposium Series 642, American Chemical Society, Washington, DC, 1991, Chap. 1.
2. P. S. Russo, in *Reversible Polymeric Gels and Related Systems*, P. S. Russo, Ed., ACS Symposium Series 350, American Chemical Society, Washington, DC, 1987, Chap. 1.
3. W. Burchard and S. B. Ross-Murphy, in *Physical Networks—Polymers and Gels*, W. Burchard and S. B. Ross-Murphy, Eds., Elsevier Applied Science, London, 1990, Chap. 1.
4. S. J. Guerrero and A. J. Keller, *J. Macromol. Sci., Phys.*, **B20**, 167 (1981).
5. J. M. Guenet, B. Lotz, and J. C. Wittmann, *Macromolecules*, **18**, 420 (1985).
6. T. Tenigami, K. En, K. Yamaura and S. Matzushima, *Polym. J.*, **18**, 31 (1986).
7. M. E. Nichols and R. E. Robertson, *J. Polym. Sci., Polym. Phys.*, **B32**, 1607 (1994).
8. X. Wang, Y. Li, and Y. Yu, *J. Mat. Sci. Tech.*, **32**, 111 (1997).
9. X. Wang, B. Zhao, Zh. Li, and Y. Yu, *Chin. J. Polym. Sci.*, **15** 84 (1997).
10. R. S. Brookman, in *Handbook of PVC Formulation*, E. J. Wickson, Ed., Wiley, New York, 1993, Ch. 24.