

The Effect of Citrate Esters as Plasticizers on the Thermal and Mechanical Properties of Poly(Methyl Methacrylate)

Mario H. Gutierrez-Villarreal, Jesús Rodríguez-Velazquez

Centro de Investigación en Química Aplicada. Blvd. Enrique Reyna 140, Saltillo Coahuila, 25253, Mexico

Received 15 June 2006; accepted 11 September 2006

DOI 10.1002/app.25482

Published online 8 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Plasticizers play a key role in the formulation of polymers and in determining their physical properties and processability. This study examines the effects of citrate esters, triethylcitrate, and triacetine as plasticizers on the thermal and mechanical properties of poly(methyl methacrylate). The samples were characterized by differential scanning calorimetry, dynamical mechanical analysis, and mechanical testing under different plasticizer contents. Both citrate esters proved to be effective as plasticizers, DSC data for the triacetine additive fits with Fox equation. Microstructure and relaxation properties were studied by dynamic mechanical analysis where loss modulus shows clearly that absorbed plasticizer shifts the α -transition to lower temperature and β -relaxations associated to ester side groups are unchanged even up

to 30 wt % plasticizer. Mechanical properties were evaluated with an Instron testing machine. Both additives produced (1) an initial plasticization, with a decrease in tensile strength and modulus; (2) an antiplasticization, reflected as an increase in tensile strength; and modulus and (3) a final plasticization, with a notable decrease in tensile strength and modulus and an increase in elongation where a 35 wt % of triethylcitrate added to the poly(methyl methacrylate) increased in 200% its elongation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2370–2375, 2007

Key words: poly(methyl methacrylate); dynamic mechanical analysis; plasticizer; mechanical properties; glass transition

INTRODUCTION

Polyacrylates and poly(methyl methacrylate) (PMMA) belong to the family of biocompatible nonbiodegradable materials that have been used in different fields such as industrial and medical.^{1–3} The PMMA has been chosen as a minor phase to improve some properties of biodegradable matrices like polycaprolactone, poly-*l*-lactic acid, polyhydroxybutyrate, etc. Here plasticizers play an important roll to improve and promote a better interfacial adhesion between these polymers.⁴ PMMA is also used in the orthodontic market, for instance in the manufacture of dentures, teeth, denture bases, and as fissure-resin sealant which is painted over teeth to act as a barrier to tooth decay; PMMA is also suitable for the construction of custom appliances because of its high structural stiffness and glassy nature, its easy and accurate moldability, formability, structuring gluing, and polishing.⁵

Respecting citrate plasticizers, these are nontoxic additives, derived from natural citric acid that have been used on many applications, such as additives

for personal care products, foods, and medical plastics.⁶ Cellulose acetates and polylactic acid have been plasticized with citrate esters to improve their processability, although accelerated degradation rates have been observed as compared with those of unplasticized materials.^{7,8}

According with the theory⁹ when a solid polymer interacts with a solvent, a slow, and often remarkable, dissolution process can occur. The process is usually divided into two stages. First, solvent molecules slowly diffuse into the polymer structure to produce a swollen gel; this happens if the polymer–polymer intermolecular forces are large compared with the self-affinity of the solvent. If these forces are overcome by the introduction of a strong polymer–solvent interaction, the second stage of the solution process can take place. Here, the gel gradually dissolves to form a solution. For the case of plasticizers, the penetration of a solvent plasticizer through the polymer matrix causes a partial relaxation of the polymer chains by reducing the intermolecular forces of attraction, hence producing a greater freedom of movement among the polymeric macromolecules. The result is a change in the material properties, for instance: a greater flexibility and plasticity, a decrease in the tensile strength and the lowering of the glass transition temperature. In a polymeric system, the penetration rate of a plasticizer depends upon the relaxation rates of the polymeric

Correspondence to: M. H. Gutierrez-Villarreal (mariogtz@ciqua.mx).

molecules and the structural constitution. Sometimes when additives are mixed with polymers, an increase in modulus, tensile strength, and a decrease in elongation are observed. Such antiplasticization effect is present when small amounts of plasticizer are used, and this phenomenon occurs with many polymers and with different types of plasticizer. The most general explanation for this phenomenon is that small amounts of plasticizer, below a certain "threshold level," provide enough additional free volume to the system to permit limited polymer chain mobility and realignment. This apparently results in a greater degree of polymer-polymer interaction and development of small increases in localized molecular order. Jackson and Caldwell¹⁰ also reported on their work that antiplasticization is manifested when a plasticizer has both a high polarity and a relatively bulky or rigid structure.

EXPERIMENTAL

Materials

The PMMA under investigation in this work was supplied by Arkema/Atoglas, USA, with a trade name of Plexiglas V045. Triacetone (TA) 99% and triethylcitrate (TEC) 99% were provided by Aldrich. Resins, chemicals, and solvents were used as received.

Gas chromatography analysis

The determination of molecular weight of PMMA was obtained with an Alliance GPC system (Model 2695), operating with chloroform and using three different columns of Styragel HR 5E 7.8 × 30 mm, and a Waters 2414 refractive index detector. A series of 10 PS standards were used for calibration. The number- and weight-average molecular weight thus obtained were 59,000 and 132,000 g/mol, and a polydispersity of 2.23. The glass transition temperature by DSC was 105°C. The melt flow index has a value of 2.3 g/10 min and the density of the pellets is equal to 1.19 g/cm³.

The polymer was dried during 4 h at 40°C under vacuum (Shell Lab vacuum oven Model 1410) and then stored in a desiccator at room temperature.

Blending

Blending experiments were performed in a Brabender Plastograph with counter-rotating screws at 190°C for 15 min at 32 rpm. The composition for each blend was 5, 10, 15, 20, 25, and 35 wt % of plasticizer and these mixtures were allowed to stand overnight before film preparation.

Film preparation

Films were prepared from the blends by pressing at 200°C. Small samples of the blends were placed in a template frame, to ensure a constant film thickness and covered with Teflon sheets to prevent sticking to the press plates. This assembly was then placed between the press plates for 3.5 min, without applying pressure, until the material was properly melted, and then pressed for 30 s at a pressure of 440 Pa; samples were removed from the press plates and cooled in air until they reached ambient temperature. The specimens were then stored in sealed plastic bags in air, awaiting for analysis.

Neat PMMA was also subjected to an identical two processing cycles to ensure the same thermal histories.

CHARACTERIZATION METHODS

Differential scanning calorimetry (DSC)

DSC analysis was performed by means of a TA Instruments differential scanning calorimeter (Model 2920). The samples were sealed in aluminum pans (~10 mg) and heated from -40 to 200°C at a rate of 20°C/min. They were cooled back to -40°C at a rate of 50°C/min. The glass transition temperature, T_g , was measured at the midpoint of the stepwise deviation in the heat-flow curves during the second heating of the samples.

Dynamic mechanical analysis

Investigation of the α -relaxational process associated with the glass transition and the β -transition were performed by dynamic mechanical analysis (DMA) on a DMA 983 from TA Instruments (New Castle, Delaware). Test rectangular bars were cut from the pressed plates (dimensions 5 cm × 1 cm × 1 mm) and mounted. The runs were conducted at a heating rate of 2°C/min between -70 and 150°C. Flexure mode was used under isochronal conditions at a frequency of 0.1 Hz. The aim of these runs was to locate the glass transition region for each sample and see the effect of plasticizer content on the β -transition of the polymer.

The viscoelastic properties were characterized versus temperature, namely, the storage modulus, E' , the loss modulus, E'' , and the mechanical loss factor $\tan \delta = E''/E'$.

Mechanical tensile test

An Instron Universal Testing Machine (model 4301) was used for measuring the tensile properties, such as elongation at break, stress at yield, and stress at break. The ASTM D638-03 method was followed.

TABLE I
Main Properties of Raw Materials

Name	Molecular weight (M_w)	Density (g/mL)	Glass transition (T_g) °C	Solubility parameter (J/cm^3) ^{1/2}
Triethyl-citrate	276.29	1.14	-71 ^a	19.7 ^b
Triacetine	218.21	1.15	-68 ^a	19.1 ^b
PMMA	132,000	1.19	105	18.6 ^c

^a Values obtained in this work by DSC.

^b Ref. 12.

^c Ref. 11.

The testing was performed using a gauge length of 0.5 cm and sample width of 1.0 cm, with a crosshead speed of 2 cm/min, using a cell of 500N. All tests were carried out at room temperature. The data reported were averages of at least five measurements and the standard deviation was found to be within 1.5% for tensile strength and 7.0% for elongation at break.

RESULTS AND DISCUSSION

Differential scanning calorimetry

All of the scans were conducted at a heating rate of 20°C/min between -40 to 200°C under a nitrogen atmosphere at a flow rate of 20 cc/min using approximately 10 mg of sample. T_g s were measured from the second run. The cooling process was performed after annealing the sample for 1 min at 220°C. Glass transition temperature of TEC and TA were measured by DSC from -150 to 50°C at 20°C/min, and their values are shown in Table I.

The corresponding values of T_g was also calculated for the system, applying Fox equation: $1/T_g = W_1/T_{g1} + W_2/T_{g2}$, where W_1 and T_{g1} correspond to weight and glass transition temperature of PMMA and W_2 and T_{g2} the weight and glass transition of plasticizer (Table II).

TABLE II
 T_g Values as Measured by DSC at Different wt % of Plasticizer

	wt % content	T_g (°C)	T_g (°C) Fox Eq.
Neat PMMA	-	105	-
Neat Triethylcitrate	-	-71	-
Triethylcitrate	10	64	75
Triethylcitrate	20	49	49
Triethylcitrate	25	41	37
Triethylcitrate	30	40	27
Neat Triacetine	-	-68	-
Triacetine	10	67	76
Triacetine	20	47	50
Triacetine	25	40	39
Triacetine	30	30	29

Theoretical and experimental values for each plasticizer are shown in Figures 1 and 2. Triacetine fits Fox equation, but TEC shows scattering points that deviates from it; this behavior can be explained in terms of the solubility parameter difference between plasticizers and PMMA. This polymer has a solubility parameter value of 18.2 (J/cm^3)^{1/2},¹¹ TA 19.1 (J/cm^3)^{1/2}, and TEC 19.6 (J/cm^3)^{1/2}.¹² Triacetine solubility parameter is closer to the PMMA value than that of TEC, thus suggesting that it should be a better plasticizer owing to its higher compatibility; as a result, TA has a better ability to weaken polymeric intermolecular attractions allowing the polymeric molecules to move more easily.

Dynamic mechanical analysis

Loss modulus E'' , versus temperature, for plasticized PMMA samples are shown in Figures 3 and 4. The loss modulus E'' for the plain PMMA and plasticized samples show two peaks, one is associated with the α -transition, in correspondence with the glass transition at 104°C, and the other a broad secondary β -transition centered at 1°C. Plasticized samples show a shift to lower temperatures for the glass transition temperature at different level of plasticizer. These shifts are associated with the esters that

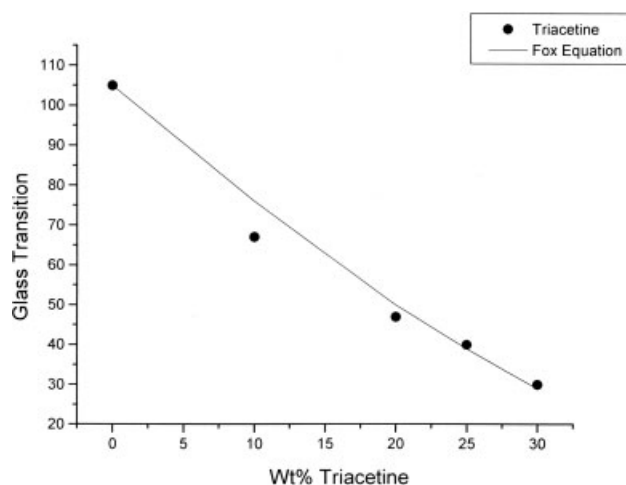


Figure 1 Influence of triacetine on T_g of PMMA.

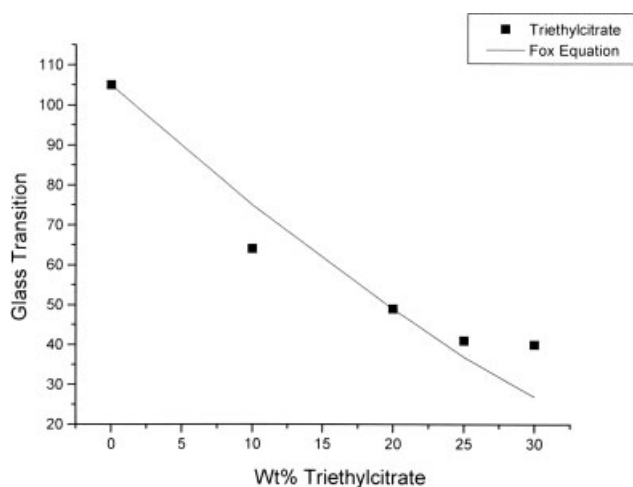


Figure 2 Influence of triethylcitrate on T_g of PMMA.

may interact with the polymer molecules, and are able to fill the free volume in the polymer matrix, increasing chain mobility of PMMA and allowing the long-range motions. T_g values obtained by DMA are usually different from those obtained by DSC; this is because DMA measurements are sensitive to the structural change on a microlevel, where DSC is not as much sensitive at these ranges. The peaks at lower temperatures in loss modulus correspond to β -relaxation of side groups and/or chain segments,¹³ T_g values obtained by DMA are not exactly the same as those given by DSC, such differences have been published and discussed by many authors for different polymeric systems.¹⁴

β -relaxations, shown in Table III, have little shifts from the maximum temperature value, apparently unaffected by the presence of plasticizer even up to 25 wt % level if they are compared with the change experimented by the α -transition. These observations are in line with dielectric studies made by Mikhailov

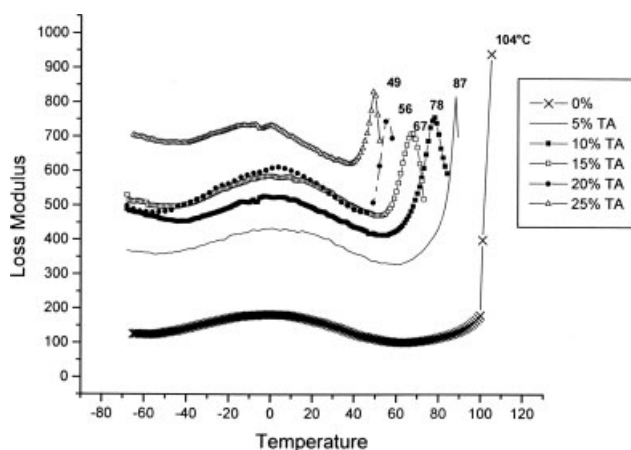


Figure 3 Loss modulus from DMA runs comparing blends of PMMA with different wt (%) of triacetate.

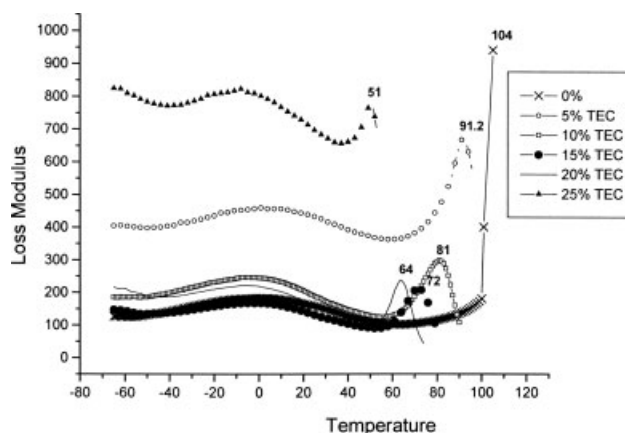


Figure 4 Loss modulus from DMA runs comparing blends of PMMA with different wt (%) of triethylcitrate.

et al. on PMMA containing up to 25 wt % dibutylphthalate.¹⁵ Also in a study of mechanical properties, Heijboer concluded that plasticizing PMMA with dibutylphthalate does not change the location of the β -relaxation.¹⁶ It is generally believed that this maximum is due to the hindered rotation of the $-\text{COOCH}_3$ group, in the C—C bond linking it to the main chain.¹⁷ The hindrance to this rotation mainly arises from interaction with the main-chain methyl groups of the adjacent units.

Tensile properties

Tensile strength at break and tensile strength at yield as a function of wt % of plasticizers are shown in Figures 5 and 6. Both plasticizers produced on the polymer an initial plasticization with a decrease in tensile strength, showing a maximum at about 5 wt %; an antiplasticization, which is reflected by an increase in tensile strength with a maximum

TABLE III
Effect of Absorbed Plasticizer on the Temperatures of Relaxation Measured at 0.1 Hz

Wt % additive	T_g (°C) at E'' max	Temp. of β -relaxation (°C) at E'' max
0% Triacetate	104	1.0
5% Triacetate	88	2.3
10% Triacetate	78	0.2
15% Triacetate	67	1.0
20% Triacetate	56	2.5
25% Triacetate	49	-0.3
0% Triethylcitrate	104	1.3
5% Triethylcitrate	91	2.7
10% Triethylcitrate	81	-3.2
15% Triethylcitrate	72	-1.9
20% Triethylcitrate	64	-4.1
25% Triethylcitrate	51	-8.0

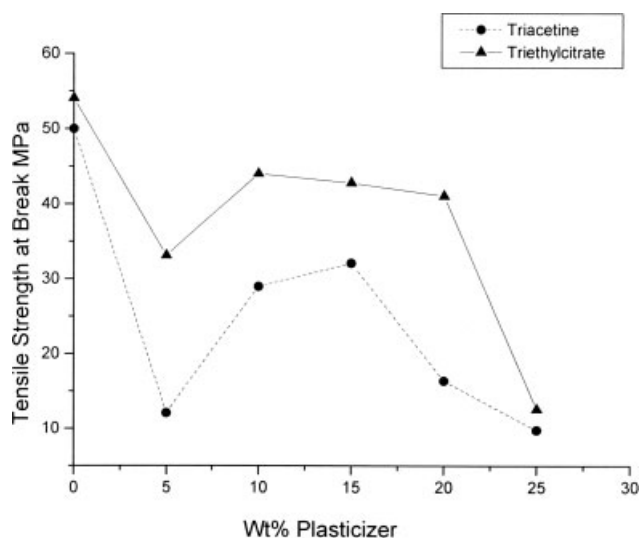


Figure 5 Tensile strength at break versus wt (%) of plasticizer.

at ~ 13 wt % of TEC or TA, and a final plasticization at higher contents of additives. With respect to PMMA modulus, results are like those of tensile strength, where antiplasticization is present at ~ 13 wt %. Figure 7 shows this behavior. Similar results were observed previously by Olayemi et al.¹⁸ when PMMA was plasticized with dimethyl and dibutyl phthalate and polyvinylacetate. Antiplasticization is explained by the formation of secondary bonds like hydrogen bonds and van der Waals interactions between the additive and the PMMA molecules. Initial plasticization can be explained in terms of penetration of a plasticizer through the polymer matrix, which causes a partial relaxation of the polymer chains by reducing the intermolecular forces of attraction, hence producing a greater freedom of movements among

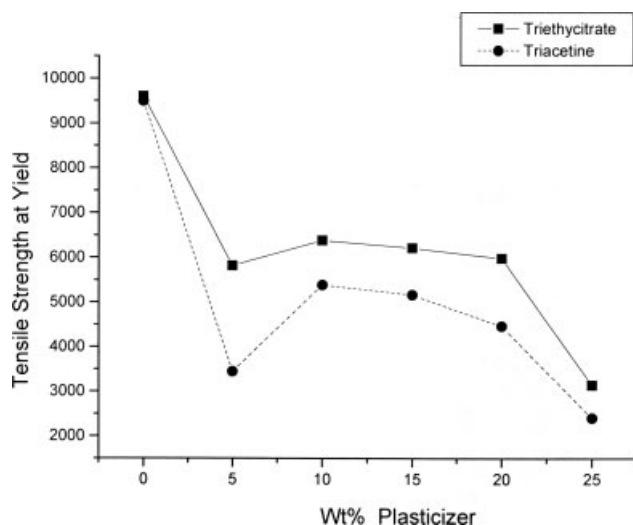


Figure 6 Tensile strength at yield versus wt (%) of plasticizer.

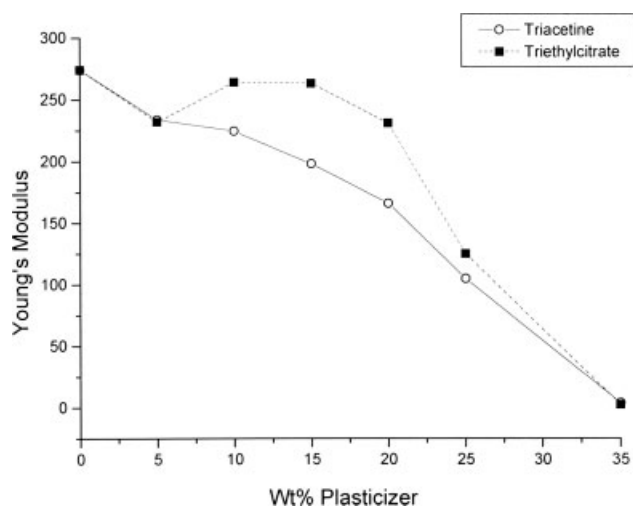


Figure 7 Young's modulus versus wt (%) of plasticizer.

the polymeric chains, and the final plasticization with a marked decrease in tensile strength and considerable increase of elongation as a result of less interaction between the molecules of PMMA. Figure 8 shows that below 20 wt % of plasticizer, PMMA has low elongation values; however, at level of 35 wt % TEC, it reaches a value of 200% elongation; for the TA sample, a value of 100% elongation is reached at 35 wt %. These high values are a result of cooperative motion between PMMA molecules and the plasticizer which increase the amount of free volume.

CONCLUSIONS

Both citrate esters studied on this work proved to be good plasticizers for PMMA. Glass transition tem-

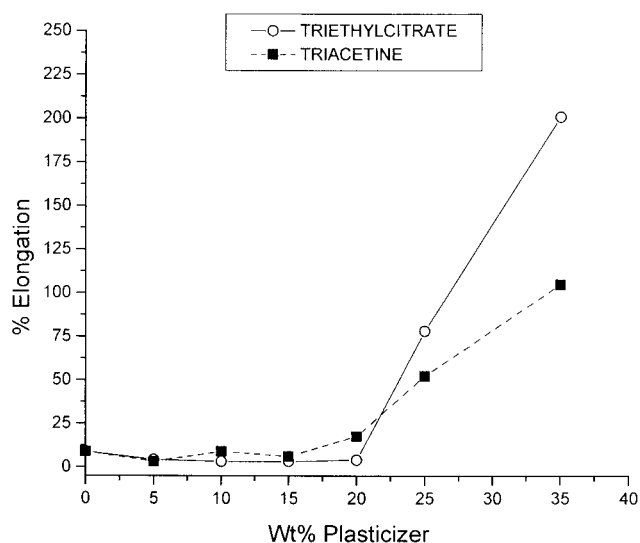


Figure 8 Elongation at break versus wt (%) of plasticizer.

perature measured by DSC decreased as plasticizer content increased. Experimental values for the TA additive fit theoretical Fox equation with deviations for the case of TEC.

Regarding DMA analysis, plasticizers cause the glass transition to shift to markedly lower temperatures, the typical effect of plasticizers; however, the temperatures and peak heights of the β -relaxation, which involves noncooperative motions of the ester groups, are unchanged even up to 25 wt % additive. This behavior was similar in both plasticizers. Regarding mechanical properties, both additives interact with the polymer showing three steps: at low concentration act as plasticizers decreasing the tensile strength and modulus of PMMA polymer; then, an antiplasticization effect was observed with a maximum at ~ 13 wt % of additives causing an increase in both, tensile strength and elastic modulus at this concentration. Finally, after this maximum, a plasticization effect was observed when the wt % of additives was increased. Elongation at break does not show a significant change at lower concentration level, however, a dramatically increase is reached at higher concentration. A maximum value of 200% at 35 wt % of TEC was observed. This increase in elongation and significant decreases in tensile strength and modulus of PMMA that follow after antiplasticization is due to the large volume of plasticizer present which has the effect of reducing even the attractive forces between the polymer chains.

References

1. Goldberg, E. P.; Nakagima, A., Eds. *Biomedical Polymers*; Academic Press: New York, 1980.
2. Kopecek, J.; Sprine, L. *Polim Med* 1971, 4, 109.
3. Sevcik, S.; Stanburg, J.; Schmid, P. *J Polym Sci Part C* 1967, 16, 821.
4. Jenkis, A. D., Ed. In *Polymer Science Library 10; Advanced Routes for Polymer Toughening*; Martuscelli, E.; Musto, P.; Ragosta, G., Eds.; Elsevier: Amsterdam, 1996.
5. Muhtarogullari, I. Y.; Dogan, A.; Muhtarogullari, M.; Usanmaz, A. *J App Polym Sci* 1999, 74, 2971.
6. Morflex Technical Bull 101, Morflex, Inc., N.C. 1993.
7. Ghiya, V. P.; Dave, V.; Gross, R. A.; McCarthy, S. P. *Pure Appl Chem* 1996, A33, 627.
8. Labrecque, L. V.; Kumar, R. A.; Davé, V.; Gross, R. A.; McCarthy, S. P. *J Appl Polym Sci* 1997, 66, 1507.
9. Heijboer, J. In *Molecular Basis of Transitions and Relaxations*; Meier, D. J., Ed.; Gordon and Breach: New York, 1978.
10. Jackson, W. J.; Caldwell, J. R. In *Plasticization and Plasticizer Process*; ACS Adv in Chemistry Series 48, Gould, R. F., Ed.; American Chemical Society: Washington, D.C., 1965; Chapter 17.
11. Zhang, G.; Zhang, J.; Wang, S.; Shen, D. *J. Polym Sci Polym Phys Ed* 2003, 41, 23.
12. Ljunberg, N.; Wesslén, B. *J App Polym Sci* 2002, 86, 1227.
13. McCrum, N. G.; Buckley, C. P.; Bucknal, C. B. *Principles of Polymer Engineering*, 2nd ed.; Oxford University Press: Oxford, UK, 1997; p 136.
14. Avérous, L.; Moro, L.; Dole, P.; Fringant C. *Polymer* 2000, 39, 3857.
15. Mikhailov, G. P.; Borisova, T. I.; Dmitrochenko, D. A.; *Sov Phys Tech Phys (Engl Transl)* 1956, 1, 1857.
16. Heijboer, J. J. *Kolloid Z* 1956, 134, 149.
17. McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymer Solids*; Wiley: London, 1967.
18. Olayemi, J. Y.; Oniyangi, N. A. *J App Polym Sci* 1981, 26, 4059.