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Miscibility Studies of Coextruded Polycarbonate/Polymethyl Methacrylate Composites

by Alex J. Hsieh
and Alex W. Gutierrez

ARL-TR-1714 July 1998

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Alex J. Hsieh, Alex W. Gutierrez
Weapons and Materials Research Directorate, ARL

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Abstract

Miscibility and molecular relaxation measurements have been carried out using dynamic mechanical analysis (DMA) on the coextruded polycarbonate (PC)/polymethyl methacrylate (PMMA) multilayers with various compositions. Three distinct transitions are observed; two of these are corresponding to the glass transition of the PC-rich phase and PMMA-rich phase. The glass transition temperatures, T_g, of both phases shift slightly toward each other, compared to the T_g of pure PC and pure PMMA, indicating limited miscibility. A third relaxation, which was not observed with differential scanning calorimetry (DSC), is present at a temperature between the T_g of PC-rich and PMMA-rich phases. The transition temperature of this intermediate relaxation increases as the PC composition increases, and it also shifts to a higher temperature with an increase in the molecular weight of PMMA. The origin of the intermediate transition is attributed to the molecular relaxation response of an interphase resulted from interdiffusion between the PC and PMMA. In addition, this intermediate relaxation is more sensitive to the change in frequency compared to the response of glass transition of either pure component. As a result, the apparent activation energy values determined for the corresponding third relaxation are consistently smaller than those measured for the glass transition of pure PC and pure PMMA. The former values, however, remain relatively constant with respect to the variation in composition and molecular weight for all the PC/PMMA multilayers.

Acknowledgments

The authors would like to thank Ms. Julia A Kerns of Case Western Reserve University for the preparation of multilayered polycarbonate/polymethyl methacrylate composites. In addition, Dr. Gume Rodriguez at the Polymers Research Branch, Weapons and Materials Research Directorate, U.S. Army Research Laboratory, is also thanked for his careful review of this manuscript.

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1. Introduction

An innovative coextrusion process has demonstrated the potentials for allowing the design of polymer-polymer multilayers with multifunctional properties [1, 2, 3]. The goal of this research is to develop transparent multilayered composites by incorporating a ductile polycarbonate (PC) with a brittle polymethyl methacrylate (PMMA). PC has excellent high-speed impact strength; however, it has very poor resistance to many organic solvents and can also scratch easily. PMMA, on the other hand, has high yield strength and better barrier properties; however, it is brittle upon impact. The technical challenges reside upon the ability to enhance the overall barrier properties without the expense of impact strength of polycarbonate. In addition, adhesion between the individual layers, which strongly depends upon the miscibility or compatibility between the PC and PMMA, is critical in determining the durability of these interphase-dominated laminates.

There have been many reports addressing the miscibility and the equilibrium phase behavior of PC/PMMA blends [4–9], and it is generally recognized that the phase morphology of the blends strongly depends upon the method of preparation. Single-phase morphology was observed in the PC/PMMA blends prepared by rapid solvent casting with tetrahydrofuran (THF); however, these mixtures became phase separated upon heating to just above the glass transition temperature [4–8]. In most PC/PMMA blends that were prepared by melt processing, heterogeneous phases were obtained. Despite the incomplete miscibility between the PC and PMMA, a weak intermolecular interaction between the phenyl rings of PC and the carbonyl groups of PMMA has been reported by Gardlund and Wendorff [10, 11].

The motivation for this work stems from our earlier study on a 388-layer PC/PMMA composite, in which we reported that a third relaxation was observed with DMA at a temperature between the T_g's of PC-rich and PMMA-rich phases [12]. This intermediate relaxation, however, was not observed with DSC. In order to verify the presence of this additional relaxation, we have extended our studies using a series of PC/PMMA multilayers with various compositions. DSC data reveal that only two distinct glass transitions are present in all the

PC/PMMA composites. This work further examines the molecular relaxation of these multilayers with the DMA measurements, which include the effects of composition and molecular weight on the intermediate relaxation.

2. Experimental

Coextruded PC/PMMA multilayers with volume percentages of 20%, 35%, 50%, 65%, and 80% of PMMA have been fabricated. A commercial grade of PC from Dow Chemical Company, Caliber 200-10 with molecular weight (Mw) of 29,500 was used along with two different types of PMMA (VM-100 [Mw = 95,000] and V826-100 [Mw = 135,000]). PMMA's were made by the Rohm and Haas Company.

Test specimens of PC/PMMA composites used in this work for thermal characterization were typically of 64 layers; however, a multilayer of 4 layers with 50 volume-percent of PMMA was also selected for comparison.

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-7. The temperature was calibrated with both indium and zinc standards. Samples of 5–10 mg were prepared in an aluminum pan and scanned in a nitrogen atmosphere. Thermal properties were determined typically at a heating rate of 20° C/min.

Dynamic mechanical measurements were performed with a dynamic mechanical analyzer DuPont 983 DMA. Microlayered PC/PMMA specimens 30 mm long and 13 mm wide were mounted with serrated vertical clamps at a clamping distance of 8 mm. The samples were analyzed in a fixed frequency mode at 1 Hz with a peak-to-peak amplitude of oscillation of 0.3 mm and typically at a heating rate of 3° C/min. Multifrequency scans were also performed using the frequency values of 0.05, 0.1, 0.2, 0.5, and 1 Hz for the determination of apparent activation energy values.

3. Results and Discussion

Figure 1 displays the DSC heating curves of pure PC, pure PMMA, and PC/PMMA multilayers with various compositions. Two distinct glass transitions are shown in all the PC-PMMA multilayers; however, T_g's are shifted slightly toward each other, compared to that of either pure components, indicating limited miscibility.

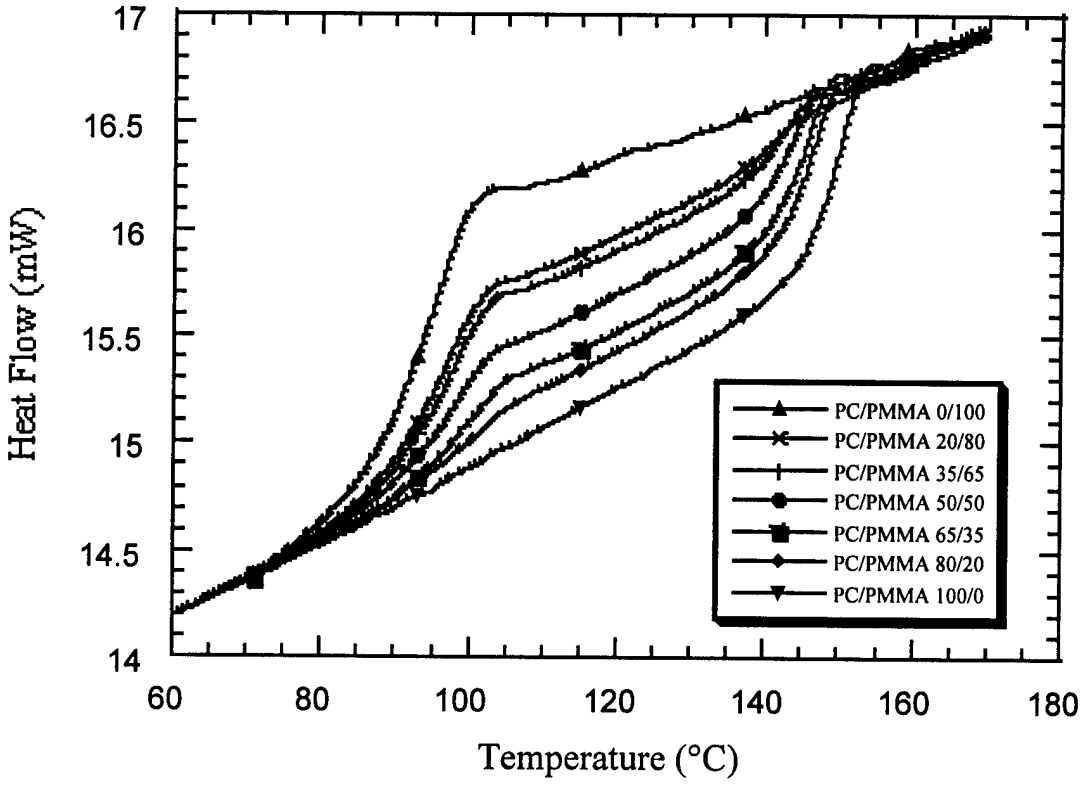

Figure 1. DSC scans obtained at a heating rate of 20° C/min for pure PC, pure PMMA (Mw = 95,000), and PC/PMMA multilayers with volume-percents of PMMA (Mw = 95,000) being 20%, 35%, 50%, 65%, and 80%.

DMA measurements of the loss modulus, E", vs. temperature for the aforementioned multilayers and pure components are shown in Figure 2. An additional relaxation is clearly seen in all the PC/PMMA multilayers in addition to the glass transition of the corresponding PC-rich and PMMA-rich phases. These results are consistent with data reported in our previous studies

on a similar PC-PMMA multilayer [12]. Figure 2 also reveals that the magnitude of the intermediate loss peak increases as the composition of PC increases, as does the maximum temperature of the corresponding loss peak.

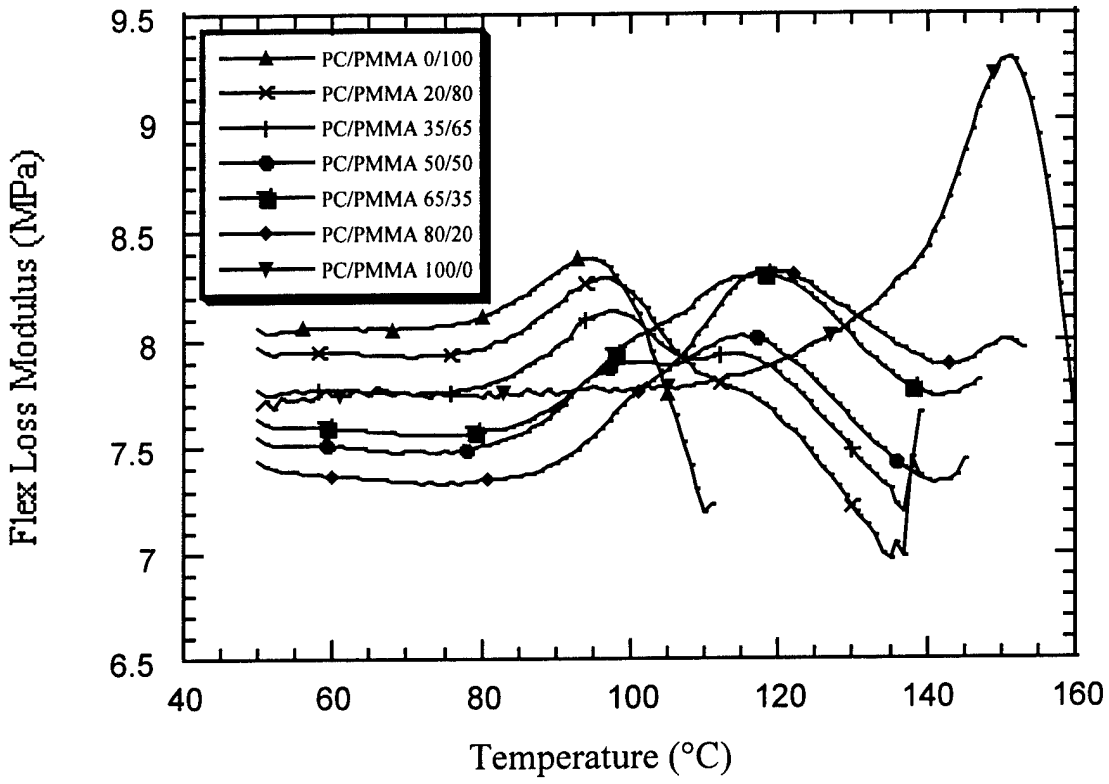

Figure 2. Plots of loss modulus, E", vs. temperature at 1 Hz for pure PC, pure PMMA (Mw = 95,000), and PC/PMMA multilayers with volume-percents of PMMA (Mw = 95,000) being 20%, 35%, 50%, 65%, and 80%.

A multiplexing frequency analysis was performed to further probe the response of these relaxation peaks to a shift in frequency. Figures 3a and 3b display the E" vs. temperature curves obtained with the heating rate of 3° C/min and frequencies at 0.05, 0.1, 0.2, 0.5, and 1.0 Hz for the pure PC and PMMA, respectively. Only the loss peaks associated with glass transition are seen for either pure components, indicating that the presence of a third relaxation is characteristic of PC/PMMA multilayers.

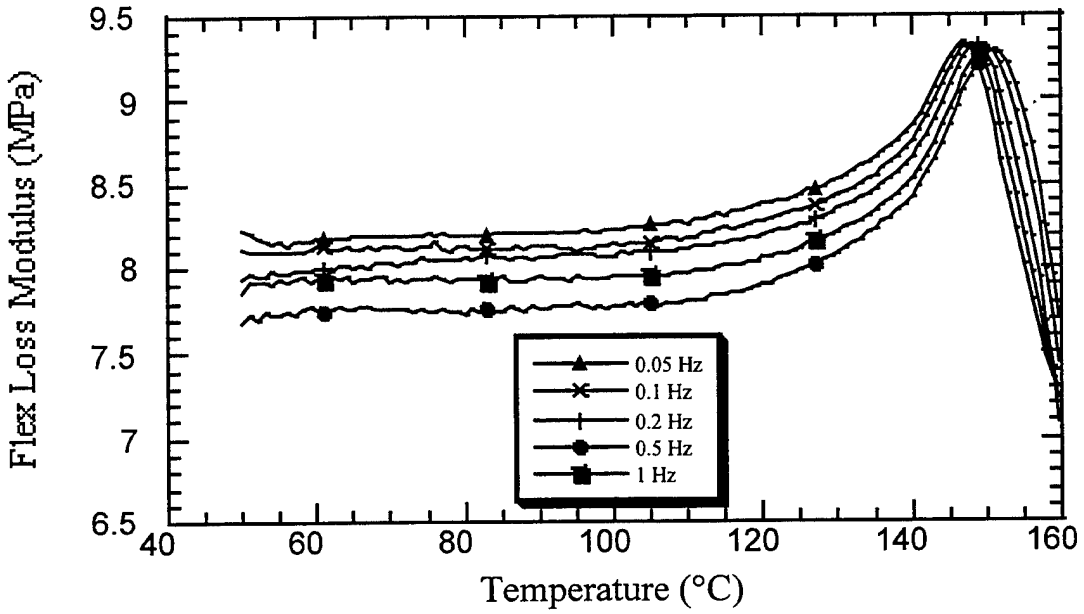

Figure 3a. Plots of E" vs. temperature obtained with DMA for pure PC by using multifrequency measurements at 0.05, 0.1, 0.2, 0.5, and 1.0 Hz.

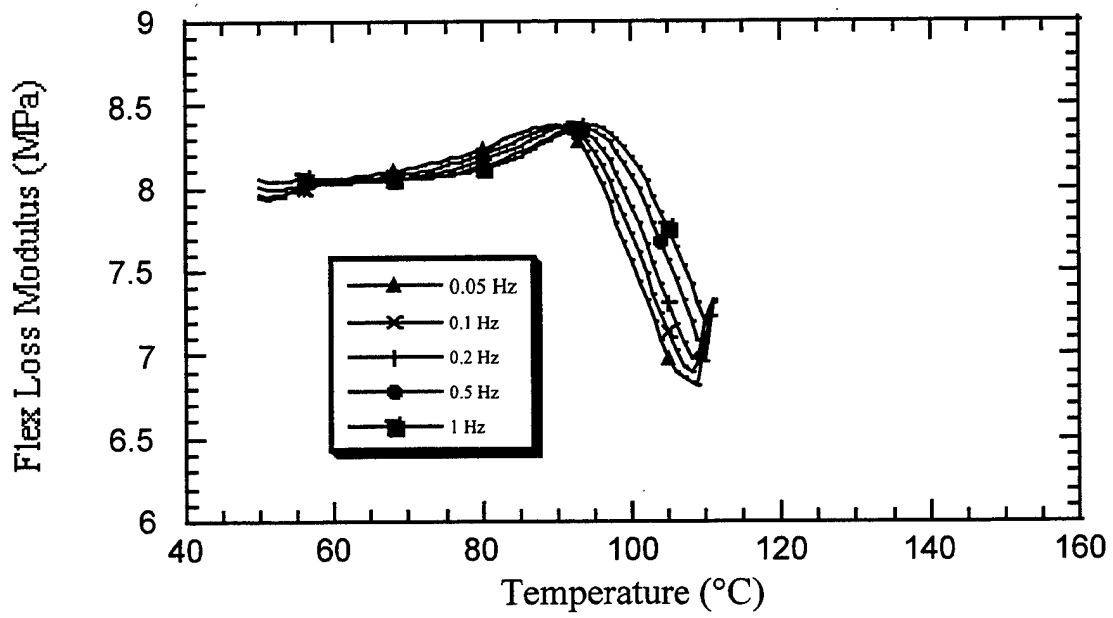

Figure 3b. Plots of E" vs. temperature obtained with DMA for pure PMMA (Mw = 95,000) by using multifrequency measurements at 0.05, 0.1, 0.2, 0.5, and 1.0 Hz.

Figures 4a and 4b are the typical multifrequency scans showing the loss modulus E" vs. temperature curves for the multilayers with 35 volume-percent and 50 volume-percent of PMMA, respectively.

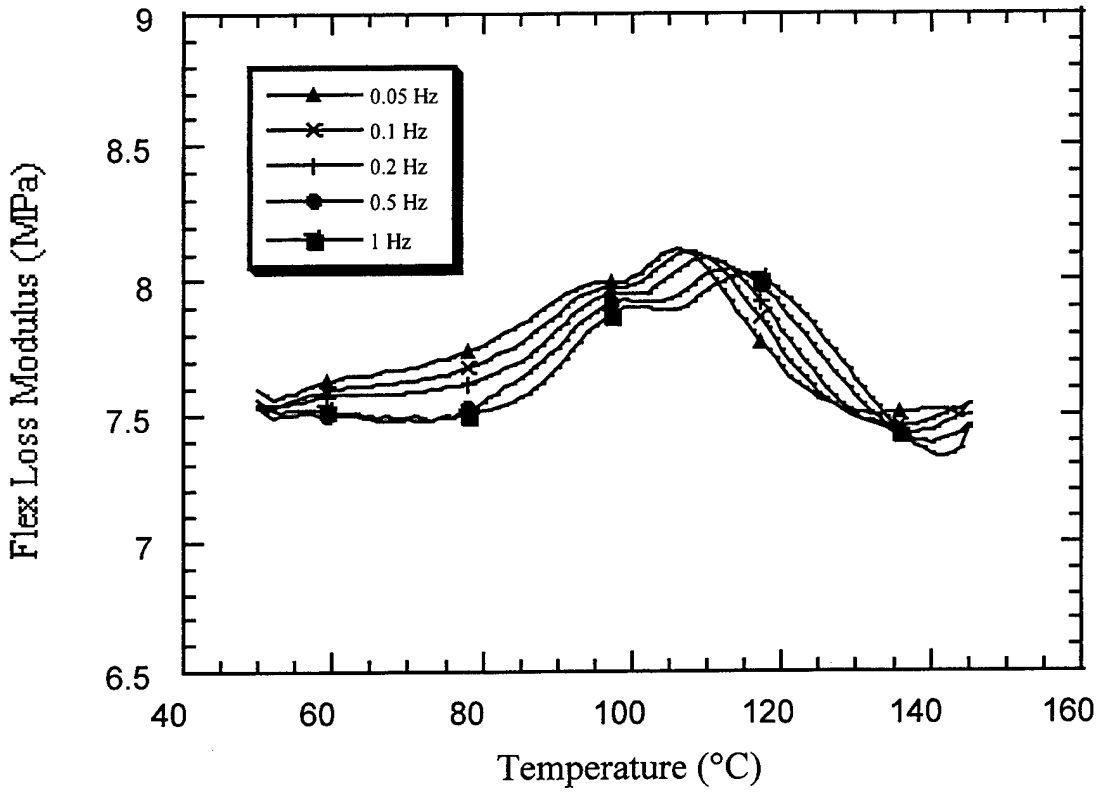

Figure 4a. Plots of E" vs. temperature obtained from multifrequency measurements at 0.05, 0.1, 0.2, 0.5, and 1.0 Hz for PC/PMMA multilayers with 35 volume-percent of PMMA (Mw = 95,000).

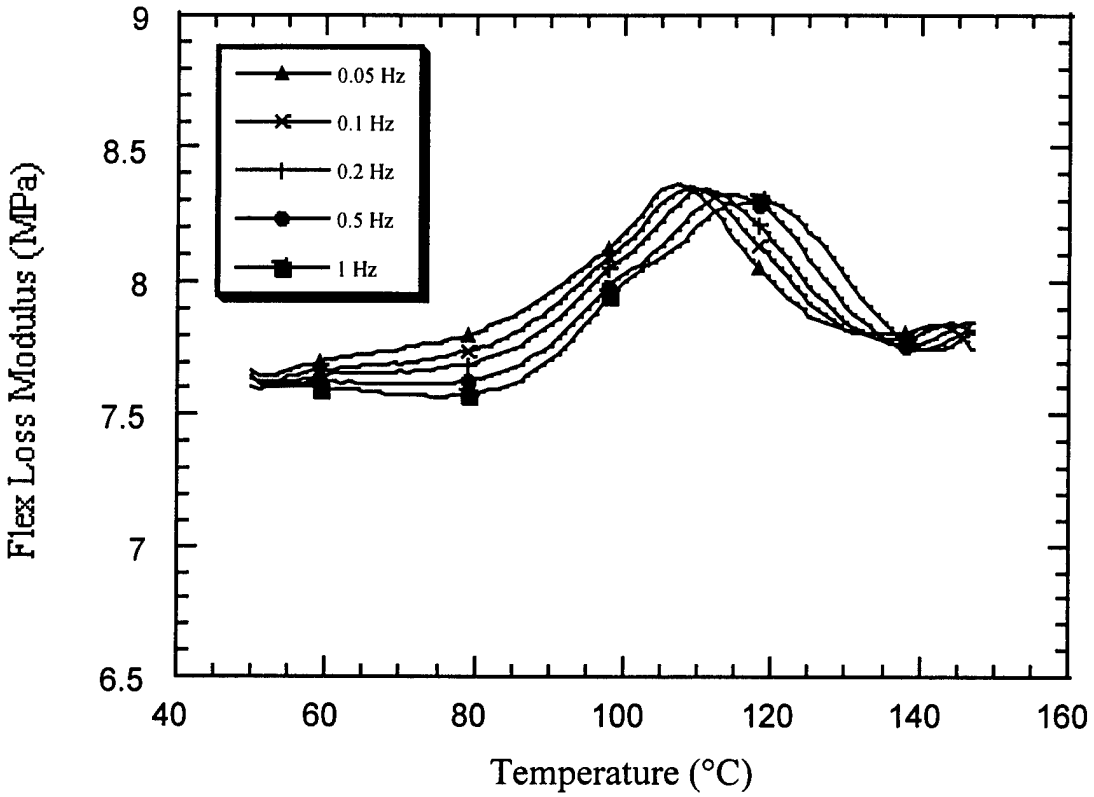

Figure 4b. Plots of E" vs. temperature obtained from multifrequency measurements at 0.05, 0.1, 0.2, 0.5, and 1.0 Hz for PC/PMMA multilayers with 50 volume-percent of PMMA (Mw = 95,000).

The intermediate relaxations are clearly seen, and their transition temperatures increase with an increase in frequency; a similar effect on the T_g is also present in both PC-rich phase and PMMA-rich phase. The dependence of the peak maximum temperature upon the shift in frequency appears to be more significant for the intermediate relaxation than that for the glass transition of either PC-rich or PMMA-rich phase. This is true for all the multilayers with various compositions.

Our earlier work on a 388-layer PC/PMMA composite also indicated that the apparent activation energy value determined for the intermediate relaxation is smaller than those measured for the PC-rich and PMMA-rich phases. Following the same approach by assuming that all the relaxation processes can be modeled by an Arrhenius temperature dependence, we have

determined the apparent activation energy (ΔE) values for all the relaxations including the glass transition of pure PC and pure PMMA. Plots of the logarithm of the frequency vs. the reciprocal of peak maximum temperature are shown in Figure 5 for the intermediate relaxation, pure PMMA and pure PC. Each data set in Figure 5 was fit to a straight line, and its slope was further reduced for the determination of the corresponding apparent activation energy. Figure 6 compares the ΔE values associated with the intermediate relaxations of the multilayers to those of both pure components. The ΔE values obtained for the multilayers with various compositions appear to be relatively constant, averaging 163 ±10% kJ/mol, which are much smaller than those determined for pure PC (480 kJ/mol) and pure PMMA (318 kJ/mol).

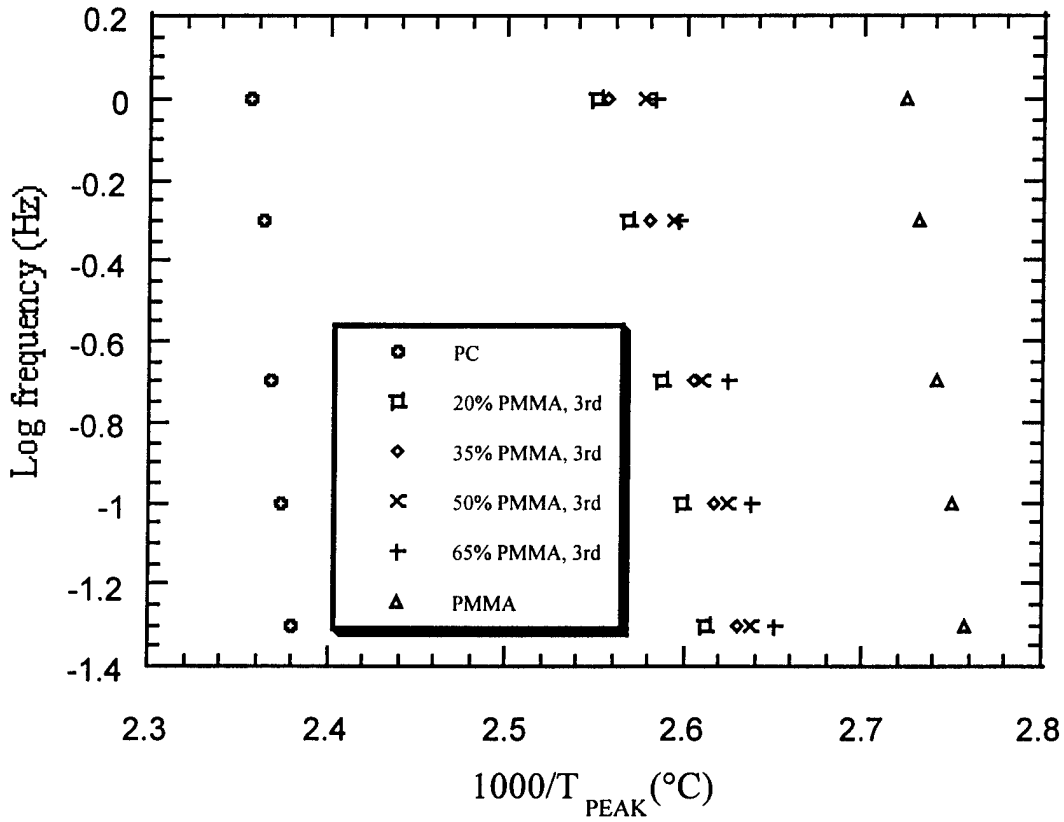

Figure 5. Plots of log (frequency) vs. reciprocal peak temperature data obtained for pure PMMA (Mw = 95,000), pure PC, and the intermediate (3rd) transition of PC/PMMA multilayers with 20, 35, 50, and 65 volume-percents of PMMA (Mw = 95,000).

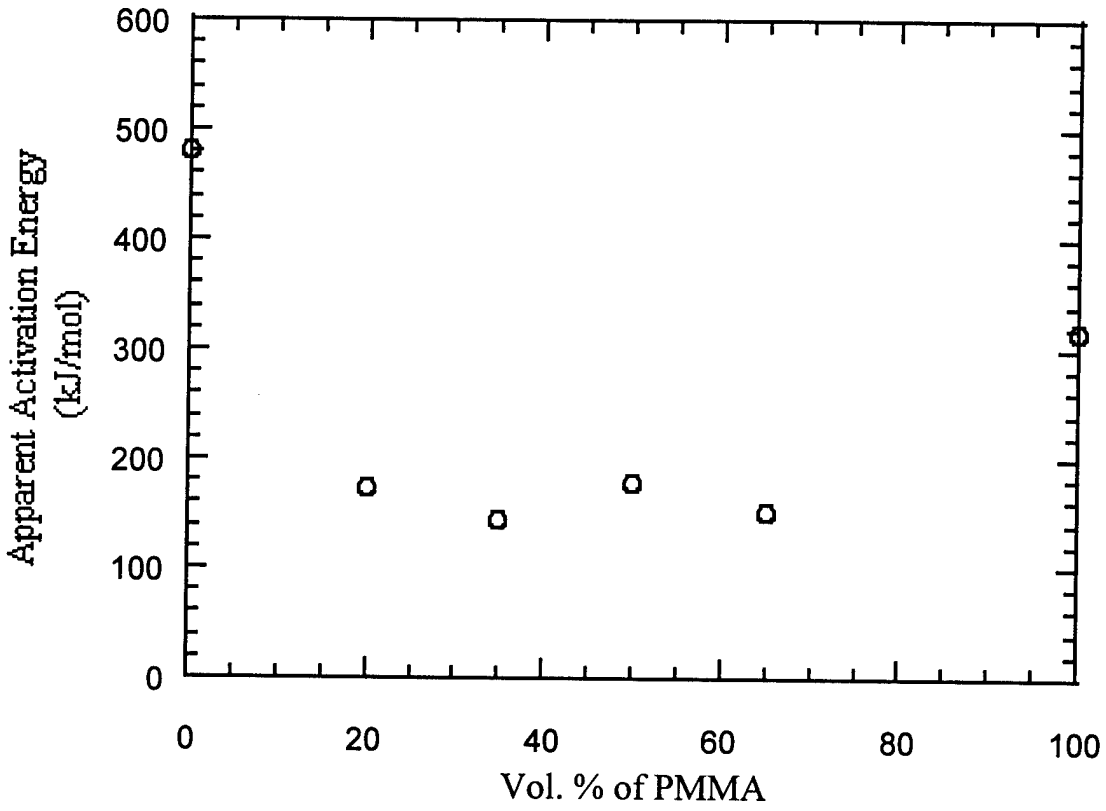

Figure 6. The determined apparent activation energy values for pure PC, pure PMMA (Mw = 95,000), and the intermediate transition of PC/PMMA multilayers with 20, 35, 50, and 65 volume-percents of PMMA (Mw = 95,000).

A linear dependence of log (frequency) vs. the reciprocal of peak maximum temperature is also seen in Figure 7a and 7b for the PMMA-rich phase and PC-rich phase, respectively. The slope of each data set in Figure 7a remains relatively the same with respect to the variation in composition for the PMMA-rich phase; however, the slope appears to be much more sensitive to the addition of PMMA into the PC-rich phase as shown in Figure 7b. The ΔE values determined for these PC-rich and PMMA-rich phases are shown in Figure 8, in which the ΔE values obtained for the intermediate transition of the corresponding multilayers are also included for comparison.

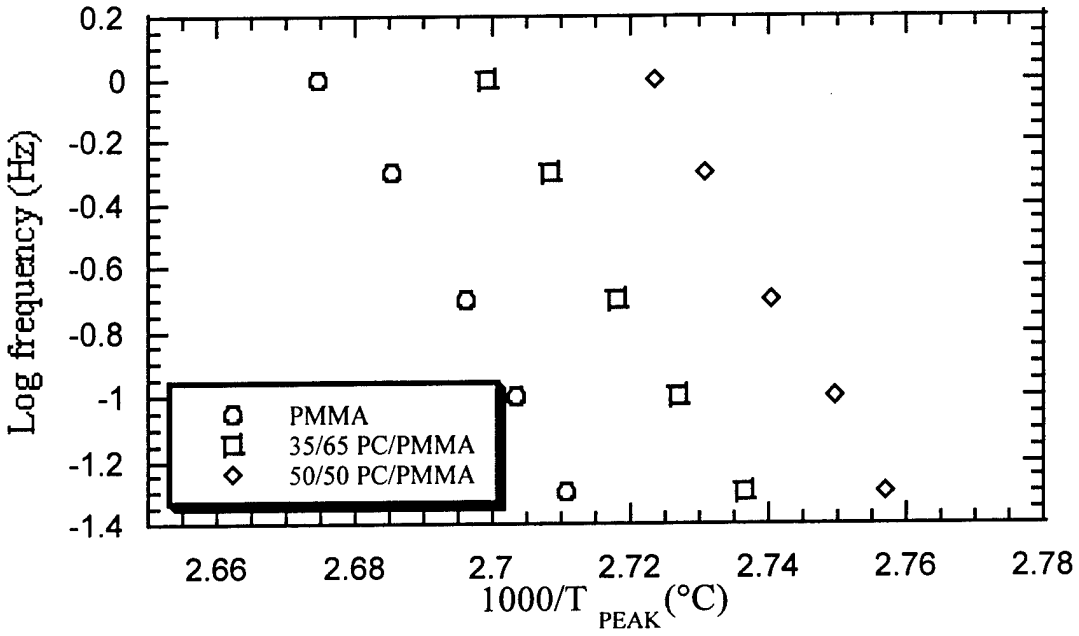

Figure 7a. Plots of log (frequency) vs. reciprocal peak temperature data obtained for pure PMMA (Mw = 95,000), and the PMMA-rich phase of PC/PMMA multilayers with 50 and 65 volume-percents of PMMA (Mw = 95,000).

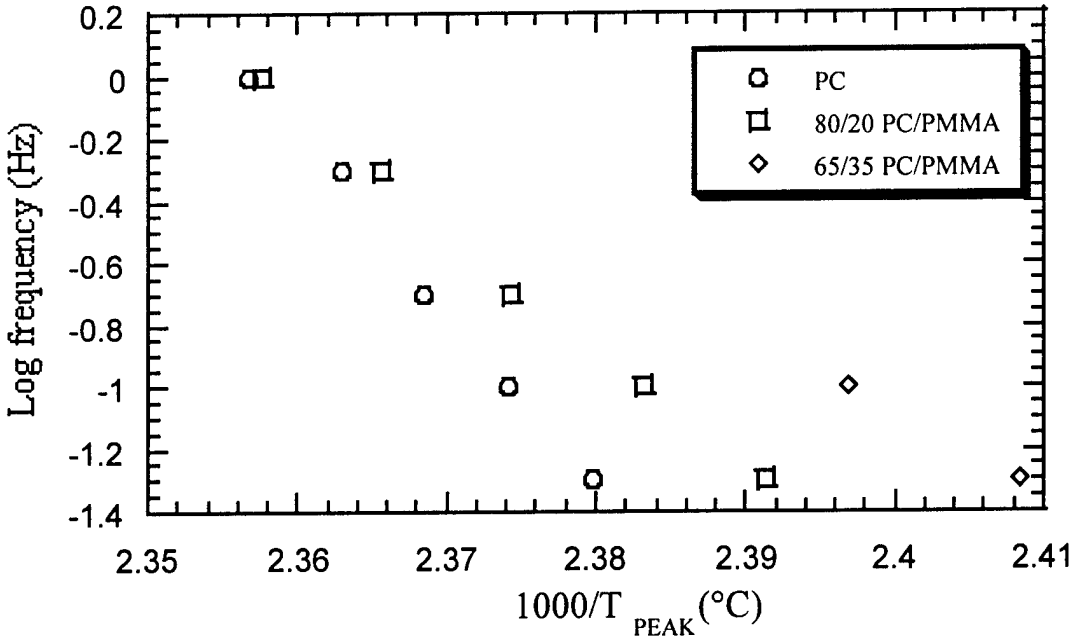

Figure 7b. Plots of log (frequency) vs. reciprocal peak temperature data obtained for the PC-rich phase of PC/PMMA multilayers with 65 and 80 volume-percents of PC.

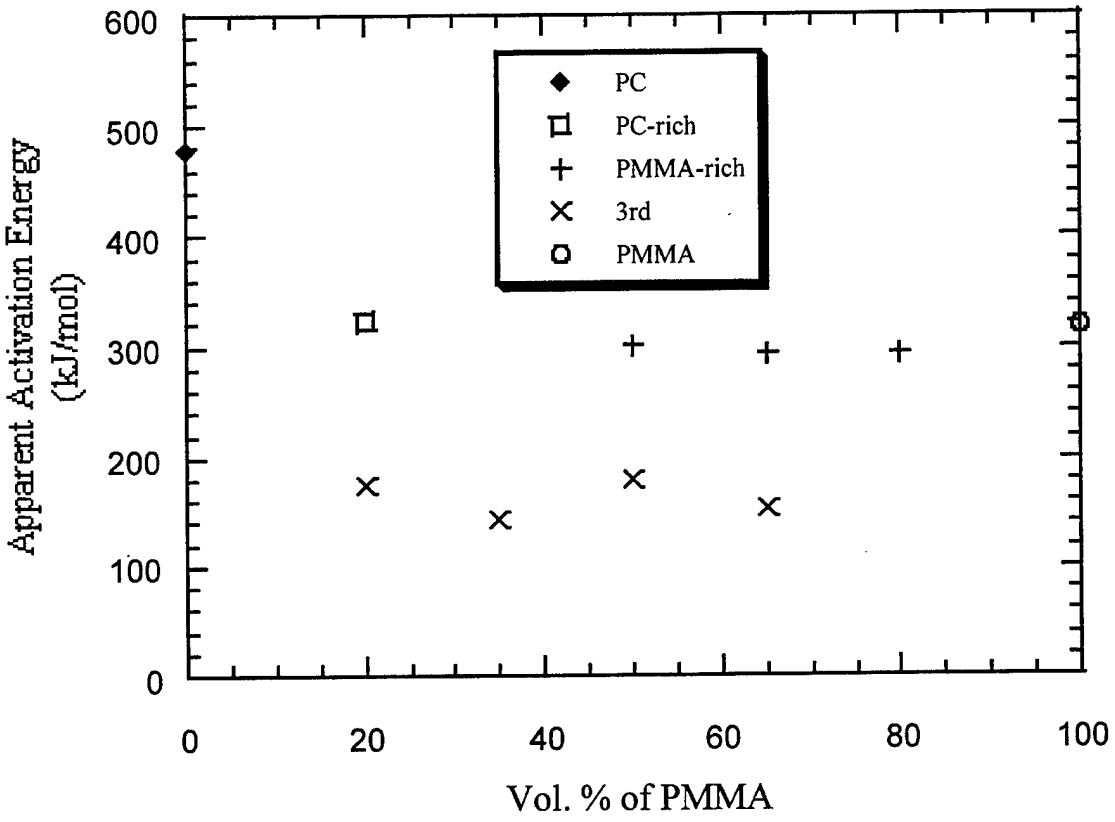

Figure 8. ΔE values obtained for the relaxations associated with the PC-rich phase, PMMA-rich phase, intermediate transition of PC/PMMA multilayers (PMMA Mw = 95,000), pure PC, and pure PMMA (Mw = 95,000).

In order to verify the difference in the determined ΔE values associated with either the glass transition of the pure components or the intermediate relaxations, we have further examined the PC/PMMA multilayers with different molecular weights of PMMA. A second PMMA, V826-100, with a higher Mw of 135,000 was used in the new series of PC/PMMA multilayers, compared to the PMMA, VM-100, with Mw of 95,000, which was used in the first series as discussed previously. Results of the E" vs. temperature curves are shown in Figure 9 for the new series of PC/PMMA multilayers with a higher molecular weight of PMMA, in which an intermediate rexalation is also evident for all the compositions. The intermediate transition

temperature shifts to a higher temperature with an increase in frequency as shown in Figure 10a and 10b for the second series of multilayers with 20 and 50 volume-percents of PMMA, respectively.

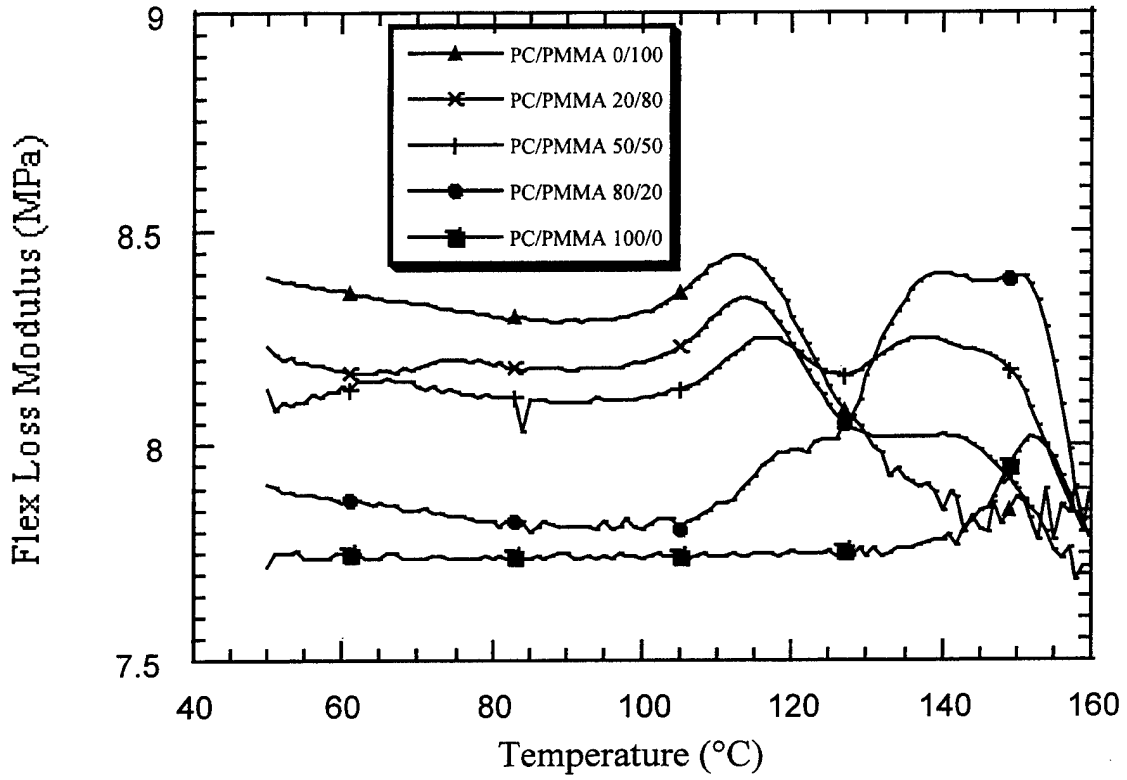

Figure 9. Plots of loss modulus, E", vs. temperature at 1 Hz for pure PC, pure PMMA (Mw = 135,000), and PC/PMMA multilayers with volume-percents of PMMA (Mw = 135,000) being 20%, 50%, and 80%.

The effect of molecular weight on the loss modulus E" curves is shown in Figures 11a and 11b for the multilayers with 20 and 50 volume-percents of PMMA, respectively. Higher glass transition temperature is expected to result from a higher molecular weight; this is seen in T_g of both the pure PMMA and PMMA-rich phase. Similarly, an increase in the transition temperature is also evident in the intermediate relaxation of the multilayers with a higher Mw of PMMA.

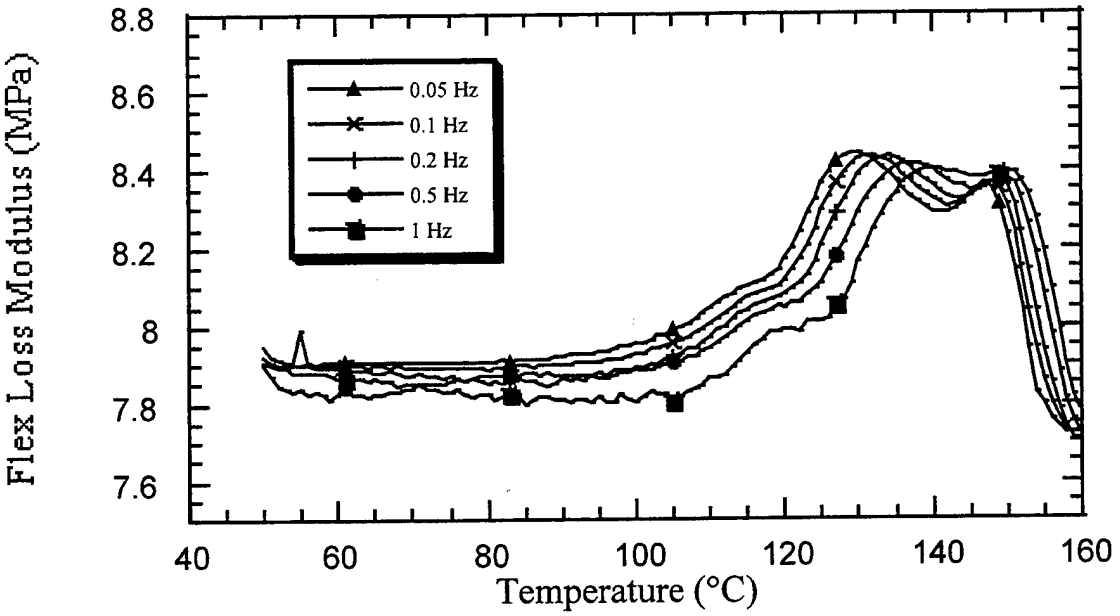

Figure 10a. Plots of E" vs. temperature obtained from multifrequency measurements at 0.05, 0.1, 0.2, 0.5, and 1.0 Hz for PC/PMMA multilayers with 20 volume-percent of PMMA (Mw = 135,000).

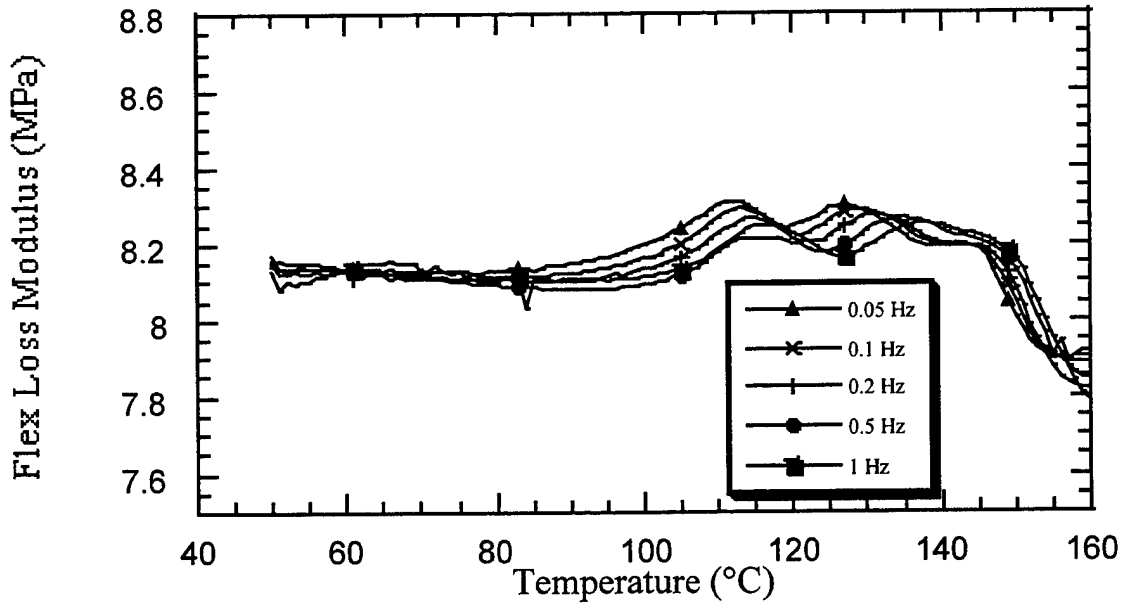

Figure 10b. Plots of E" vs. temperature obtained from multifrequency measurements at 0.05, 0.1, 0.2, 0.5, and 1.0 Hz for PC/PMMA multilayers with 50 volume-percent of PMMA (Mw = 135,000).

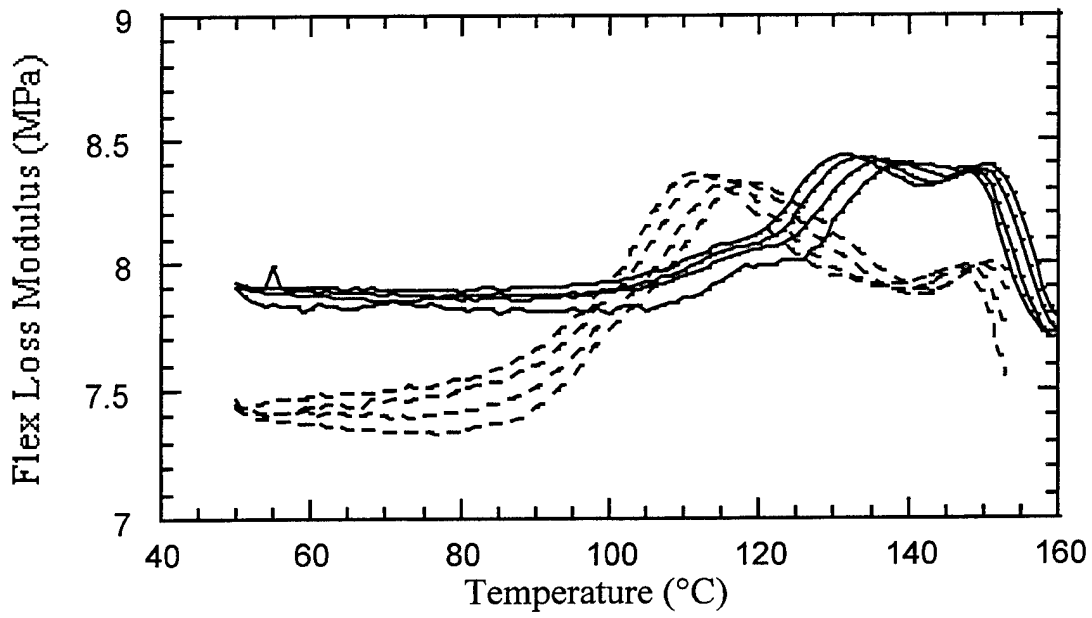

Figure 11a. Comparison of E" vs. temperature curves obtained with multifrequency measurements for PC/PMMA multilayers with 20 volume-percent of PMMA and Mw of PMMA at 90,000 (PMMA 1, ----------) and 135,000 (PMMA 2, ————).

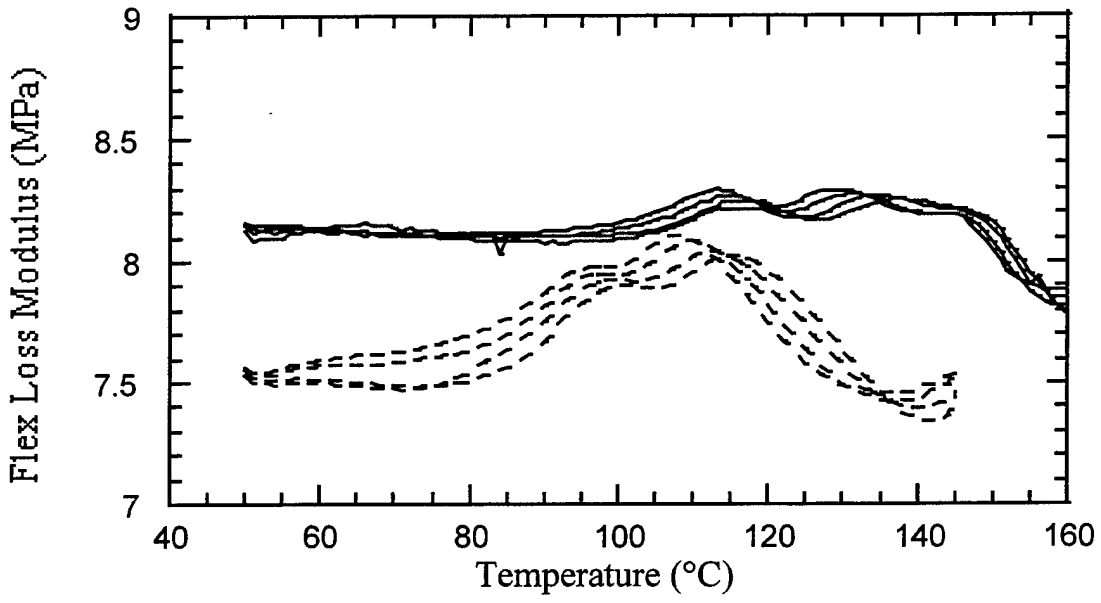

Figure 11b. Comparison of E" vs. temperature curves obtained with multifrequency measurements for PC/PMMA multilayers with 50 volume-percent of PMMA and Mw of PMMA at 90,000 (PMMA 1, ----------) and 135,000 (PMMA 2 , ————).

A linear dependence is also seen in the plots of log (frequency) vs. the reciprocal of peak maximum temperature, as shown in Figure 12, for the PC/PMMA multilayers with a higher Mw of PMMA (Mw = 135,000). The apparent activation energy values for the relevant intermediate relaxation are determined to be 174 ±1% kJ/mol, and ΔE for pure PMMA with Mw of 135,000 is 351 kJ/mol. Figure 13 compares the ΔE values obtained for the intermediate relaxations of the PC/PMMA multilayers with the selected molecular weights. It is clear that these ΔE values are relatively constant with respect to the variation in composition and molecular weight, which are also consistently smaller than those determined for pure PC and pure PMMA.

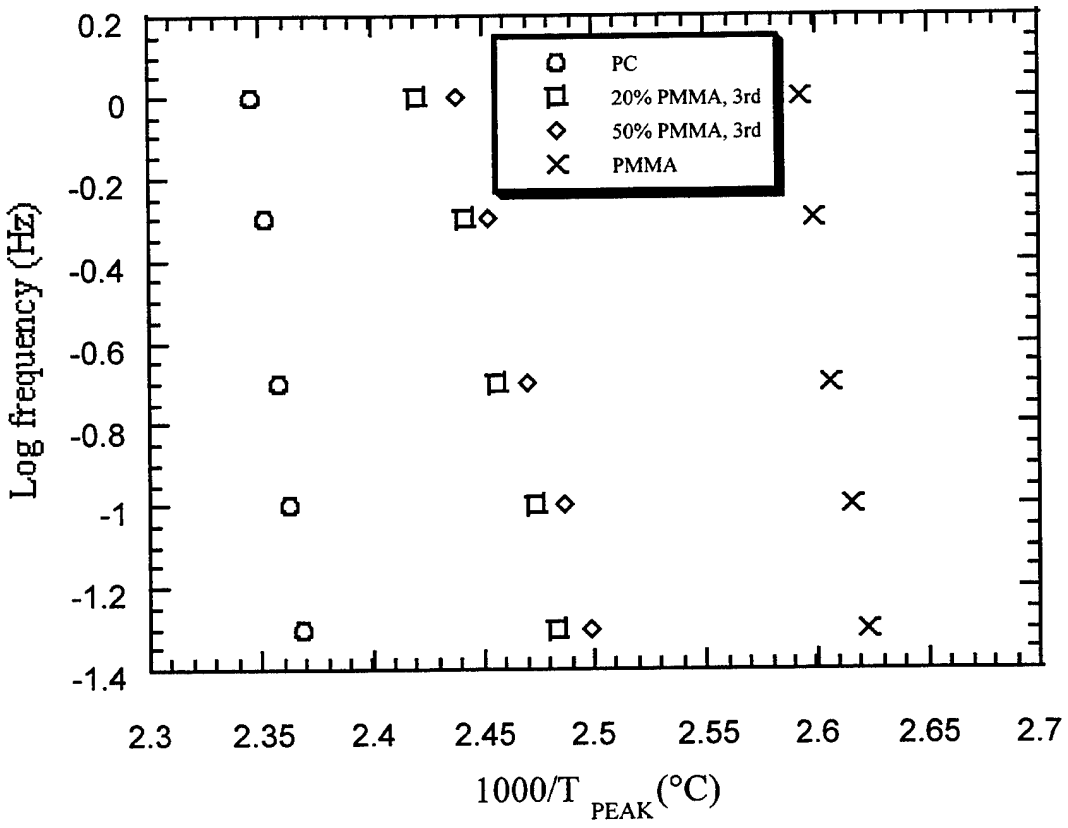

Figure 12. Plots of log (frequency) vs. reciprocal peak temperature data obtained for pure PC, pure PMMA (Mw = 135,000), and PC/PMMA multilayers with 20 and 50 volume-percents of PMMA, respectively (PMMA Mw = 135,000).

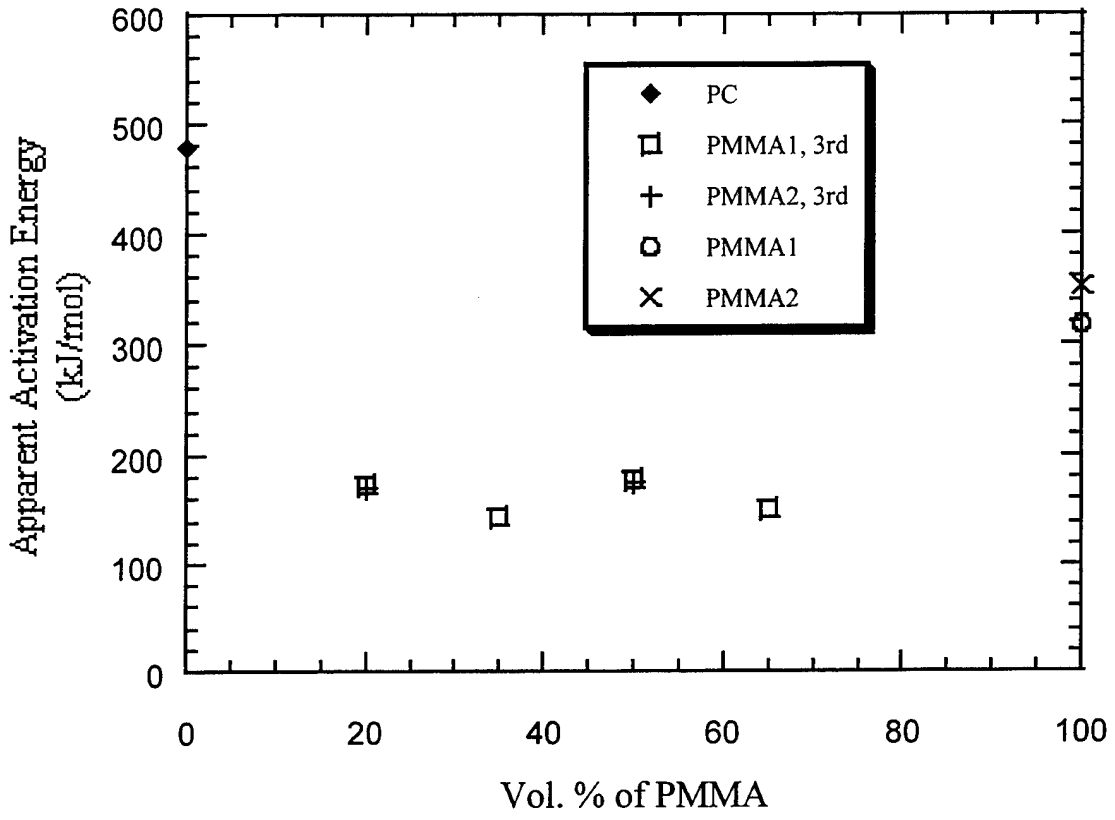

Figure 13. ΔE values determined for pure PC, pure PMMA, and the intermediate relaxation of PC/PMMA multilayers with PMMA1 (Mw = 95,000) and PMMA2 (Mw = 135,000).

Based upon the fact that the transition temperature of the intermediate relaxation depends strongly upon the composition and molecular weight, we propose that the origin of this additional transition is attributed to the relaxation response of an interphase formed between the PC and PMMA layers. A question that remains is whether the formation of an interphase between the PC and PMMA is intrinsic or configuration-dependent. Additional DMA measurements have been carried out on PC/PMMA multilayers with various layer configurations, and the results show that the presence of an intermediate relaxation is consistent in all the PC/PMMA multilayers. This is also true for a PC/PMMA multilayer with only a total of four layers, as shown in Figure 14.

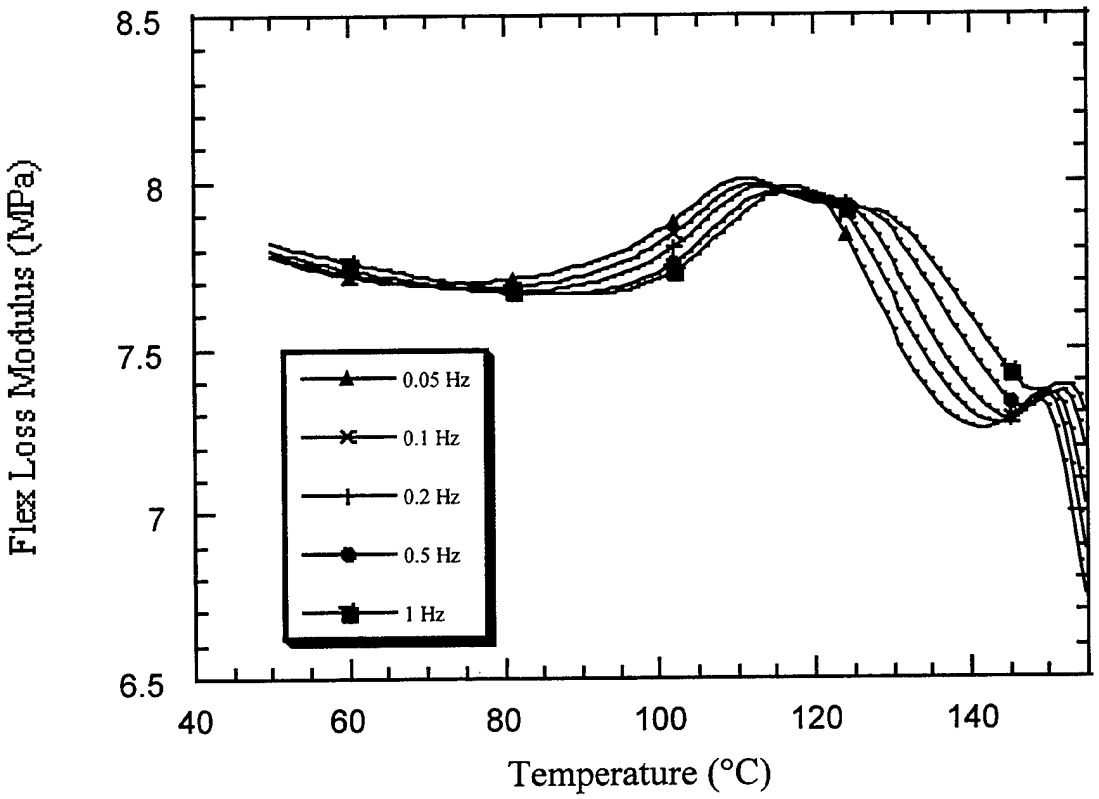

Figure 14. Plots of E" vs. temperature curves for a four-layered PC/PMMA composite with 50 volume-percent of PMMA (Mw = 135,000).

4. Conclusion

This is the first study using the DMA measurements to reveal the presence of an intermediate relaxation at a temperature between the T_g of polycarbonate and PMMA for all the PC/PMMA multilayers. However, this additional transition is not observed with DSC. The intermediate relaxation temperature depends strongly on the composition of multilayers, and it shifts to a higher temperature as the PC content is increased. An increase in the transition temperature is also evident for the multilayers with higher molecular weight of PMMA. The dependence of the transition temperature upon a shift in frequency is more significant compared

to the respective response of the glass transition of either pure component. As a result, the apparent activation energy values determined for the intermediate relaxation are consistently smaller than those for pure PC and pure PMMA. These ΔE values associated with the intermediate transition, however, remain relatively constant with respect to the variation in composition and molecular weight. In addition, the apparent activation energy of the PC-rich phase appears to be very sensitive to the incorporation of PMMA, based on the available experimental data.

We propose the origin of this intermediate transition is due to the molecular relaxation of an interphase between the PC and PMMA layers. The formation of an interphase can result from interdiffusion between two polymer melts, although the nature of the multilayer coextrusion is designed for polymer melts to be under laminar flow instead of interlayer mixing. The dimension of the resulted interphase between the layers may be very small and beyond the resolution of DSC. Nevertheless, the total volume fraction of such interphase can be significant in these interphase-dominated multilayers when proper polymer components are selected. In fact, the extent of interdiffusion not only depends upon the processing conditions, which is also strongly dependent upon the miscibility between the polymer pairs. We speculate that a weak but favorable intermolecular interaction reported to be present between the phenyl rings of PC and carbonyl groups of PMMA can actually enhance the interdiffusion between PC and PMMA, despite their limited miscibility. The hypothesis of an interphase formation is further supported by the evidence that an immediate relaxation is also present in a four-layer PC/PMMA composite. Further investigation of the detailed interphase morphology is currently being undertaken with other characterization techniques.

In summary, this study provides a better understanding of the miscibility and molecular relaxation experienced in the PC/PMMA multilayers. The implications of an interphase between the PC and PMMA allow us to design and develop novel PC/PMMA multilayers with multifunctional properties but without the need of an additional adhesive or compatibilizer.

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1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	July 1998	Final, Oct 96 - Sep 97

4. TITLE AND SUBTITLE
Miscibility Studies of Coextruded Polycarbonate/Polymethyl Methacrylate Composites

5. FUNDING NUMBERS
1L162618AH80

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-1714

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

10.SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Miscibility and molecular relaxation measurements have been carried out using dynamic mechanical analysis (DMA) on the coextruded polycarbonate (PC)/polymethyl methacrylate (PMMA) multilayers with various compositions. Three distinct transitions are observed; two of these are corresponding to the glass transition of the PC-rich phase and PMMA-rich phase. The glass transition temperatures, T_g, of both phases shift slightly toward each other, compared to the T_g of pure PC and pure PMMA, indicating limited miscibility. A third relaxation, which was not observed with differential scanning calorimetry (DSC), is present at a temperature between the T_g of PC-rich and PMMA-rich phases. The transition temperature of this intermediate relaxation increases as the PC composition increases, and it also shifts to a higher temperature with an increase in the molecular weight of PMMA. The origin of the intermediate transition is attributed to the molecular relaxation response of an interphase resulted from interdiffusion between the PC and PMMA. In addition, this intermediate relaxation is more sensitive to the change in frequency compared to the response of glass transition of either pure component. As a result, the apparent activation energy values determined for the corresponding third relaxation are consistently smaller than those measured for the glass transition of pure PC and pure PMMA. The former values, however, remain relatively constant with respect to the variation in composition and molecular weight for all the PC/PMMA multilayers.

14. SUBJECT TERMS
miscibility, relaxation, coextrusion, multilayers, dynamic mechanical analysis

15. NUMBER OF PAGES
29

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

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