

GLASS TRANSITION TEMPERATURE AND MICROHARDNESS OF COMPATIBLE AND INCOMPATIBLE ELASTOMER/PLASTOMER BLENDS

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ABSTRACT

Glass transition temperature (T_g) of core-shell particles-toughened poly(methylmethacrylate) (CSPTPMMA) and natural rubber-toughened PMMA (NRTPMMA), which are basically the PMMA/elastomer blends with different concentrations of elastomer heterogeneously distributed in the samples, was investigated by means of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and microindentation technique (MT). Microhardness (H) of the samples was measured using MT. Core-shell particles (CSP) with a rubbery shell and natural rubber (NR) were used as reinforcing materials for the production of compatible and incompatible blends, respectively. Results reveal a good correlation of the glass transition temperature (T_g) obtained from DSC and DMA, and that deduced from MT. The H -value of each sample is compared with its T_g -value. Increase of T_g with the increase of H , which is a general behavior of polymers, is not maintained in the both blends investigated. Contrary to expectation, H is shown to decrease with increasing glass transition temperature in case of CSP-toughened compatible blends while it decreases with the decrease of T_g -value only in case of NR-modified incompatible blends for lower NR concentration (<1 wt%) and does not depend on T_g for rubber content higher than 1 wt%.

Keywords: Glass transition temperature, microhardness, rubber-toughened poly(methyl - methacrylate), core-shell particle, differential scanning calorimetry

1. INTRODUCTION

A combination of properties, which cannot be achieved by a homogeneous polymer alone, can certainly be obtained by tailoring the morphology of a polymer blend. For instance, poly(methylmethacrylate) (PMMA) is a glassy homogeneous polymer, which on the one hand is very important in many applications due to its outstanding optical transparency but on the other is not suitable in specific end uses due to its brittleness⁽¹⁾. This drawback can be eliminated by incorporation of soft particles into the PMMA matrix, keeping a good adhesion between the components of the blend by means of process control and selection of rubber. Accordingly, PMMA with core-shell particles (CSP) that exhibit rubbery behavior produce compatible blends, which are designed and manufactured in order to meet the requirement of improving fracture toughness⁽¹⁻⁹⁾.

Furthermore, the toughness of PMMA can be enhanced not only by introducing CSP but also by adding elastomers such as natural rubber (NR), which is in principle incompatible with PMMA. In a recent work, we have studied micromechanical and thermal properties of a PMMA-NR blend by means of microindentation experiments⁽¹⁰⁾.

It is worthwhile to note that compositional variation in polymeric materials can influence the transition temperature, where differential scanning calorimetry serves as a popular method for the minute detection of this thermal transition. A relation between glass transition and composition in homogeneous blends has been reported⁽¹¹⁻¹²⁾. However, more data for making such a relation in heterogeneous blends, for instance CSP-toughened PMMA (CSPTMMA) and natural rubber-toughened PMMA (NRTPMMA), with compositional variation of CSP or NR are still absent. A further point of interest is that, till now, data regarding micromechanical properties obtained using the microindentation technique and glass transition temperatures determined by various techniques for heterogeneous compatible/incompatible blends are missing. Within this context, the research on either CSPTMMA or RTPMMA blends is of particular technical importance.

Owing to its simplicity, the microindentation test is a well-established method in the quest of valuable information about mechanical properties of polymeric materials⁽¹³⁾. This method has been successfully applied to the determination of the glass transition temperature of polymers and their blends^(10,13,14). The primary aim of this paper is to study glass transition temperatures and microhardness values of the compatible and incompatible PMMA-rubber blends following different methods and make a correlation among them.

2. EXPERIMENTAL

2.1 Materials

NRTPMMA samples were prepared in our laboratory following the solution method. PMMA was produced from the monomer MMA (Merck, Germany) by the radiation polymerization technique using a dose of 0.8 kGy of γ -rays from a Co⁶⁰ source. NR films were prepared from concentrated rubber latex, which was single centrifuged with a Saito Separator Ltd., Japan. Thereafter, these films and the neat PMMA were separately dissolved in toluene (Merck, Germany) and the two solutions were mixed together in different proportions. From the physical appearance of the solution, it was observed that the increase of the rubber component (>5 wt%) gave rise to inhomogeneous solutions even after long stirring times using a magnetic bar. Therefore, solution blends with the NR content ranging 0–5 wt% were made and poured on leveled glass dices to produce the films by evaporation. The presence of a sharp phase boundary around rubber particles, as shown in Fig. 1a, is an indication that NR is unlikely to make an impact with the matrix and is incompatible in nature with PMMA. For the sake of description, this series of samples is hereinafter abbreviated as Blends-I.

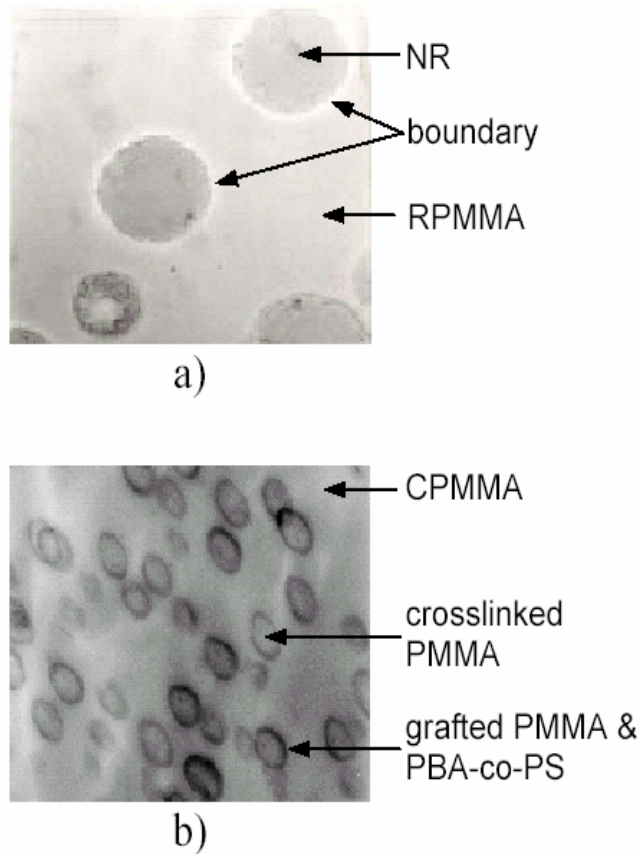


Fig. 1 a) optical micrograph of NRTPMMA containing 5 wt% NR content and b) TEM micrograph showing surface morphology of CSPTPMMA containing 17.5 wt% CSP content.

On the other hand, pellets of neat PMMA, CSP and CSPTPMMA were supplied from a commercial source, Röhm GmbH, Darmstadt, Germany. Films of these samples were prepared by hot-pressed method. The detail preparation procedure of CSPTPMMA was described elsewhere⁽¹⁵⁾. PMMA was blended with three-layered CSP of spherical shape. The surface morphology of a CSPTPMMA is shown in a transmission electron micrograph (Fig. 1b). The central core of the particles consists of crosslinked PMMA with a diameter in the order of 180 nm, which is surrounded by a rubbery shell of random poly(butylacrylate-co-styrene) having a thickness of about 40 nm. The outermost shell is a thin layer (20 nm) of grafted PMMA producing good adhesion between CSP and the PMMA matrix. The overall diameter of the particles is about 300 nm. The total volume content of CSP in the blends was about 8.5, 17.5 and 35 wt% corresponding to low impact, middle impact and high impact materials. For the sake of clarity, original PMMA is hereinafter abbreviated as PMMA; 8.5, 17.5 and 35 wt% CSP-modified PMMA

samples are denoted to low impact PMMA (LIPMMA), middle impact PMMA (MIPMMA) and high impact PMMA (HIPMMA), respectively. For ease of discussion, this series of samples is termed hereafter as Blends-II. For distinguishing the two different neat PMMAs, we define laboratory-produced neat PMMA as RPMMA and commercially supplied neat PMMA as CPMMA.

2.2 Techniques

A. Microindentation hardness

A Vickers square-based diamond indenter was employed to measure the microhardness (H) from the residual impression on the sample surface after an indentation time of 0.1 min. Loads of 98, 147, 245 and 490 mN were used to derive a load-independent value of H (MPa) that was estimated by the following equation:

$$H = K \frac{P}{d^2} \quad (1)$$

where d (mm) is the indentation diagonal, P (N) the applied load and K a geometric factor equal to 1.854⁽¹³⁾. During measurements, 10 imprints were taken for each load and the H -values for all samples were determined within an error of $\pm 3\%$.

The microhardness technique (MT) can be applied to measure the glass transition temperature (T_g) of a material. For this purpose, the same load and loading time were used to observe the H variation as a function of temperature (T). A hot stage that can be controlled between room temperature and 200°C was used in the experiment. The actual temperature was calibrated after melting known standards on the sample surface. Then, the T_g value was measured following the thermal variation of microhardness in the range of $T=30\text{--}120^\circ\text{C}$ using a load of 490 mN and a fixed loading time of 0.1 min.

B. Differential scanning calorimetry (DSC)

Each sample was heated by a differential scanning calorimeter in the temperature ranging from -60 to 150°C using a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen gas flow. The DSC data was analyzed by appropriate software to derive the T_g .

C. Dynamic mechanical measurements

Dynamic mechanical analysis (DMA) was performed using a DMTA Torsion Rheometer System (Rheometric Scientific) in torsion and temperature-sweep mode. The measurements were carried out at a frequency of 1 Hz within a temperature range from -140 to 150°C and at a heating rate of $1^\circ\text{C}/\text{min}$, which is assumed to be small enough to eliminate the thermal gradient problems of the samples during measurements. The glass transition was determined from the maximum of $\tan\delta$ peaks as a function of temperature.

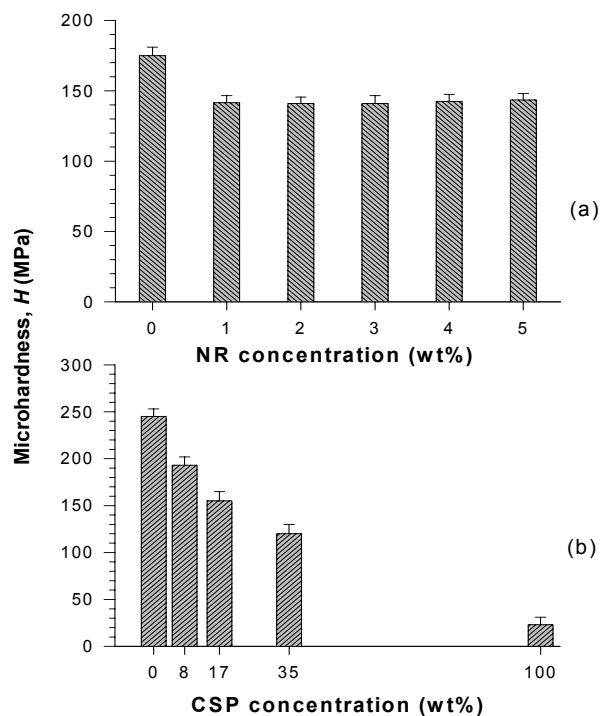


Fig. 2 Plots of hardness, H , at various a) NR and b) CSP concentrations.

3. RESULTS AND DISCUSSION

3.1 Variation of microhardness with rubber content

Figures 2a and b show the H values at various NR and CSP concentrations for Blends-I and Blends-II, respectively. The maximum hardness value of Blend I is about 175 MPa (Fig. 2a) and decreases to about 140 MPa by inclusion of >1 wt% of NR. Thus the total hardness decrease obtained is about 20%. At NR>1 wt%, variation of H is practically irrespective to NR and slightly fluctuates up and down from a minimum value. Several reasons may be taken into account of this anomalous H changes with NR particles in NRTPMMA. Of these, inhomogeneous distribution of NR particles and its incompatibility with PMMA may be the major consequences.

Blends-II exhibits an H -decrease from 245 MPa for neat commercial PMMA to 120 MPa for 35 wt% CSP modified PMMA, showing a total hardness decrease to about 50%. This value gives an indication of the maximum decrease in hardness for the commercial samples without destroying any optical transparency. The decrease of the H -value with increasing particle content can be attributed to both the increasing contribution to H from

the softer particle-matrix interphases⁽¹⁰⁾ and the growing capacity of the PMMA matrix around the rubbery particles to absorb part of the stress energy.

3.2 Glass transition temperatures

Figures 3a and b illustrates the DSC curves for the Blends-II. Two different scales are used to show obvious and notable transition peaks. The T_g values are obtained from the midpoint of the step-transition found for each sample. It is interesting to note that the neat CSI sample shows a step-transition at -18°C (Fig. 3a) in a temperature scale from -50 to 30°C and a clear step-transition at 115°C in the range of 30 – 150°C (Fig. 3b). Of blends-II, CPMMA (PMMA) and CSPTMMA samples indicate a shoulder transition around 50°C only and a step-transition above 110°C (Fig. 3b) as they are characterized by the β -relaxation temperature of the clusters of PS segments inside the CSP.

The T_g values for Blends-I other than the neat NR film, which was not investigated due to the restriction of DSC apparatus, were measured and then evaluated by the same way as before. However, the glass transition temperature of NR found in the literature is about -70°C ⁽¹⁶⁾.

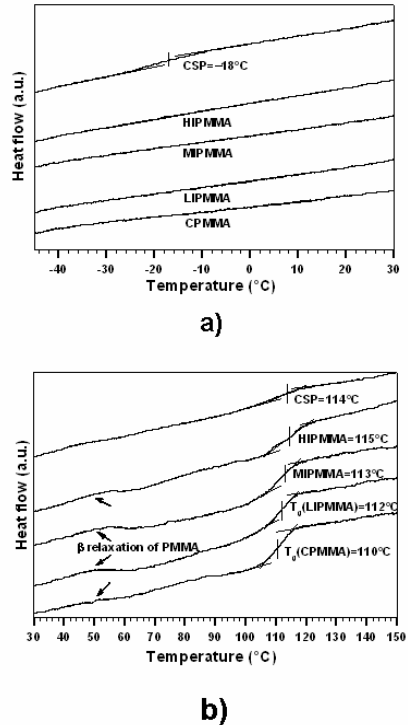


Fig. 3 DSC thermograms of the CSP samples in the temperatures ranging a) from -50 to 30°C and b) from 30 to 150°C .

The T_g values, determined for both types of blends, are presented in Table 1. In case of Blends-I, T_g decreases only up to 1 wt% NR concentration above which it is independent with NR. The soft NR phase with very lower T_g value possibly induces PMMA molecules of the matrix towards an early transition, thereby causing an apparent T_g decrease of the whole material. But higher NR concentration in the Blends-I results in inhomogeneous distribution of rubber particles for which anomalous changes of T_g occur. The considerable difference of T_g values for two neat PMMA samples may be due to the difference of their molecular weights as they had different origins of preparation.

Table 1.
Glass transition temperature of Blends-II and I measured by DSC.

Blends-II	CSP (wt%)	T_g (°C)	Blends-I	NR (wt%)	T_g (°C)
CPMMA	0.7	110.0	RPMMA	0	79.0
LIPMMA	8.5	112.0	RTPMMA1	1	75.0
MIPMMA	17.5	113.0	RTPMMA2	2	74.5
HIPMMA	35	115.0	RTPMMA3	3	74.2
		114.0			
CSP	100	-18.0	RTPMMA4	4	74.1
		-18			
			RTPMMA5	5	74.0

The T_g of Blends-II shows a slight increase with CSP concentration up to 35 wt%, although the neat CSP exhibits a negative T_g value. Generally, the harder is the polymer, the more is the T_g value. In this respect, a well-established relation between hardness and glass transition temperature of some polymers was published⁽¹³⁾. Therefore, decrease of T_g value with the increase of softness in a material is desirable, but increase of T_g with the increase of soft particles in the CSPTMMA is in contrast to the expectation and indicates a peculiar influence of these soft particles in the overall materials.

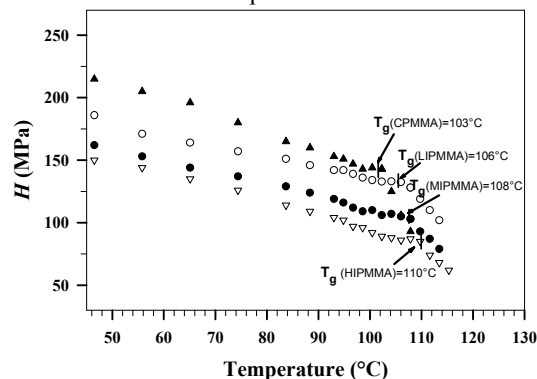


Fig. 4 Hardness (H) as a function of temperature. The intersection of the two straight lines defines the T_g value: CPMMA (\blacktriangle), MIPMMA (\circ)MIPMMA (\bullet) and HIPMMA (\blacksquare).

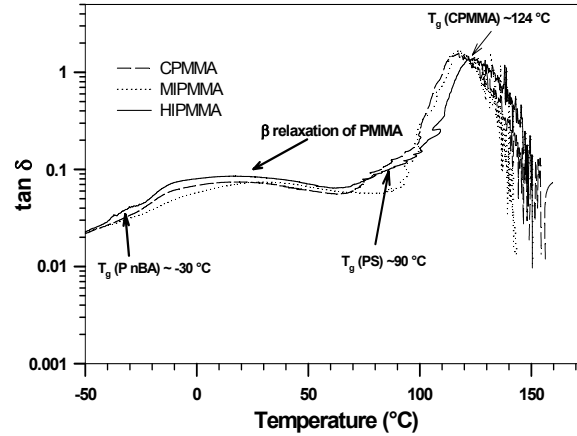


Fig. 5 Glass transition temperature as observed by dynamic mechanical analysis.

Using DMA, the T_g values derived from the maximum of $\tan \delta$ -temperature plot (Fig. 5) are larger than those obtained from DSC (in our case for HIPMMA $T_g \sim 124^\circ\text{C}$ while for MIPMMA, $T_g \sim 118^\circ\text{C}$). Although the T_g values of DMA are higher than those of DSC and MT, the trend of T_g variation is similar to that described for other two methods. Moreover, the β -relaxation temperature appears nearly at an identical temperature-range, as observed by DSC. In Table 1, we have presented the T_g values only measured by DSC because of its delicacy and high precision over other two techniques. The MT and DMA were merely followed to verify the nature of T_g changes.

DSC, DMA and MT clearly reveal an uncommon behaviour of T_g changes of Blends-II with respect to the change of microhardness as also mentioned earlier. One possibility to explain the variation of T_g with particle concentration is to use the Gordon-Taylor additivity relation and the Fox relation for compatible blends as⁽¹¹⁻¹²⁾:

$$T_g = W_1 T_{g1} + W_2 T_{g2} \quad (2)$$

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (3)$$

where, T_g is the glass transition temperature of the blends and W_1 , W_2 and T_{g1} , T_{g2} are respectively the weight fraction and glass transition temperatures of the PBA-co-PS shell within the CSP, or NR and the PMMA.

By introducing known values for the parameters in eqs. 2 and 3, in principle one can estimate the T_g value. The calculation of the T_g from equations 2 and 3, for CSPTMMA, shows values that respectively lie below and above the observed range. The calculated T_g values of NRTPMMA using above equations show similar variation as that observed for CSPTMMA. Therefore, equations 2 and 3 applied to the heterogeneous blends investigated here do not explain either the effect of CSP or of NR on T_g . Two possible reasons that might justify the observed increase of T_g with CSP could be either the change

in particle morphology or the modification of the PMMA matrix. We can assume that the crosslinked PMMA can, in general, be attributed to toughen the overall material, and the grafted PMMA of CSP can easily penetrate into the PMMA matrix and can make a good adhesion between the two components. Thus, one could expect that the occurrence of crosslinking and grafting of PMMA within CSP should give rise to higher T_g -values of blends from that of pure PMMA.

On the other hand, in case of NR-modified blends, the sharp boundary of rubber particles clearly shows an incompatibility of NR with PMMA. Besides, an easy movement of the PMMA molecules can occur around the boundary of rubber particles at lower temperature. It is also worthy to note that the distribution of rubber particles in PMMA matrix is not homogeneous. Therefore, the decrease of T_g with the increase of NR (>1wt%) may be due to the presence of soft NR phase in PMMA matrix and to its incompatibility with PMMA. The inhomogeneous distribution of NR particles in PMMA matrix may be a reason for no remarkable contribution to variation of T_g .

CONCLUSIONS

- i) While the inclusion of NR into PMMA does not show any significant decrease of hardness, the inclusion of 35 wt% CSP in the PMMA matrix lowers the hardness values to about 50% of the initial value. The H decrease is due to the rising plastic deformation of the matrix and to the increasing amount of toughening particles.
- ii) The addition of CSP into the matrix unexpectedly gives rise to a gradual increase of the glass transition temperature, whereas the increase of NR does not substantially change the T_g values of blends.
- iii) The decrease of T_g with soft phase in the core-shell modified blends is due to the particle morphology and their impact with PMMA matrix. On the other hand, the slight decrease of T_g in natural rubber toughened blends is due to the presence of soft NR phase into PMMA matrix and to the presence of sharp boundary surrounding the rubber particles.

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