

Thermal and mechanical analysis of urethane acrylate graft copolymer

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ABSTRACT

Microphase separation occurred in all polymethyl methacrylate graft urethane copolymer (PMMA-g-UM2) and poly normal but methacrylate (PnBMA-g-UM2) copolymers: two glass transitions temperatures corresponding to the PMMA or PnBMA and UM2 fractions, respectively, were observed. On the other hand, Dynamic mechanical analysis (DMA) and Differential scanning calorimetry (DSC) results showed that in most graft copolymer products the two respective component parts PMMA-g-UM2 or PnBMA-g-UM2 were compatible, because only one T_g was observed. Two glass transitions occurred for PMMA or PnBMA and UM2 when the amount of UM was increased to 55 wt % during copolymerization and microphase separation was evident in DSC, DMA and Transmission electron microscopy TEM measurements. Thermal stability and storage modulus (stiffness) of all the synthesized PMMA-g-urethane and PnBMA-g-urethane copolymers increased as the concentration of urethane macromonomer in the copolymerization feed increased, as confirmed in TGA and DMA results.

Keyword words: polyurethane, polyacrylate, graft copolymer, microphase separation and thermal stability

المخلص:

تم في هذا البحث فصل الطور الدقيق في جميع البوليمرات المشتركة من البولي ميثيل ميثاكريلات من اليوريثان (PMMA-g-UM2) والبوليمرات العادية المتعددة ولكن

ميثاكريلات (PnBMA-g-UM2): تم فيها ملاحظة درجتي حرارة انتقاليتين للزجاج بالاعتماد على جزيئات PMMA أو PnBMA و UM2 ، على التوالي. من ناحية أخرى ، أظهرت نتائج التحليل الميكانيكي الديناميكي في الاجهزة المستخدمة (DMA) و DSC ، أنه في معظم منتجات الكسب غير المشروع من البوليمر المشترك ، كان الجزءان المكونان المعينان PMMA-g-UM2 أو PnBMA-g-UM2 متوافقين ، لأنه تمت ملاحظة Tg واحدة فقط. حدث انتقالان للزجاج لـ PMMA أو PnBMA و UM2 عندما تمت زيادة كمية UM إلى 55٪ بالوزن أثناء البلمرة المشتركة وكان فصل الطور الدقيق واضحاً في قياسات DSC و DMA و TEM. زاد الاستقرار الحراري ومعامل التخزين (الصلابة) لجميع البوليمرات المصنعة من PMMA-g-urethane و PnBMA-g-urethane مع زيادة تركيز اليوريثان الكبير في تغذية البلمرة المشتركة ، كما تم تأكيده في نتائج التحليل الحراري الوزني (TGA) و التحليل الميكانيكي الديناميكي (DMA).

1. Introduction

Properties and applications of polymers can be extended by copolymerization with other polymers to give new materials with tailored properties and performances[1]. The ability to produce polymers with well defined and controlled structures has led to the study of structure-property relationships in polymer materials. An understanding of this relationship is essential in predicting polymer properties and in designing materials with new properties. Many researchers have studied creating specialized copolymers of various architectures, for offering new properties [2,...,6]. One of the most attractive copolymers is graft copolymers, which contain polymer units that are incorporated as side chains on a backbone polymer, and which cause that polymer to exhibit good phase separation.[7,8]. Graft copolymers have been used for a variety of applications, such as impact-resistant plastics, thermoplastic elastomers, compatibilizers, polymeric emulsifiers, hydrogels, drug delivery polymers, and gas permeation membranes [9,...,11]. Graft copolymers are generally prepared by three general methods: the grafting-onto, grafting from, and the macromonomer method [12].

The UM2 was synthesized with better solubility in common chromatographic solvents and compatibility with the polymethacrylates backbone. Polyaddition polymerization was used to synthesize UM2 using a prepolymer method to introduce a polymerizable functional group into the urethane polymer chain[13].

Most graft copolymers are formed by the reaction of a parent polymer, containing reactive sites (macromonomer technique), with a second type of monomer. Urathane macromonomer (UM2) was grafted with metyl methacrylate (MMA) and with normal butler methacrylate (n-BMA) , respectively. All the graft copolymers were synthesized by using solution free radical copolymerization in which various quantities of UM2 were copolymerized with various amounts of MMA, and with various quantities of n-BMA, respectively. The procedure that was used to synthesize novel methacrylic-urethane graft copolymer was described previously[13].

Methacrylic-urethane copolymer formulations

Formulations used of the preparation of the different PMMA-g-UM2 and PnBMA-g-UM2 copolymers are shown below in Table 1

Table 1: Formulations for the preparation of PMMA-g-UM2 and PnBMA-g-UM2 graft copolymers

Reagents	Mass of reagents used in various experiments			
	EXP.1* (g)	EXP.2* (g)	EXP.3* (g)	EXP.4* (g)
MMA	5.00	4.50	3.75	2.25
AIBN**	0.05	0.045	0.037	0.025
UM2	0.00	0.50	1.25	2.75
DMF solvent	35.12	35.10	35.15	35.13
nBMA	5.00	4.50	3.75	2.25
AIBN**	0.05	0.045	0.037	.025
UM2	0.00	0.50	1.25	2.75
DMF	35.32	35.19	35.14	35.12

*The concentrations of the UM2 were between 0 and 50 wt % (relative to MMA), and the amounts of urethane macromonomer and MMA in all copolymerization feeds were based on 5 g.

** The concentration of initiator (AIBN) was varied between 0.7 to 1% by weight according to n-BMA. This is however actually considered slightly high, and will affect the molecular weight of graft copolymers.

Characterization of UM2 and methacrylate-g-urethane copolymers

Different techniques were used in this study to analyze and characterize the UM2 and methacrylate-g-urethane copolymers

TGA Thermogravimetric analysis

TGA analyses of the UM2 and acrylate-UM2 graft copolymers were carried out using a TGA- 50 SHIMADZU thermogravimetric instrument with a TA-50WSI thermal analyzer connected to a computer. Samples (10-15 mg) were degraded in nitrogen or air (flow rate 50 ml/min) at a heating rate of 2.5 °C /min

Dynamic mechanical analysis DMA

DMA was carried out on a Perkin Elmer DMA 7e using the thin-film extension mode. The frequency was 1 Hz and the heating rate was 5 °C/min. The sample was a 0.3-mm thick, solution-cast film, which was dried before testing.

Differential scanning calorimetry DSC

DSC was performed on a Du Pont DSC 913 or a Perkin Elmer Pyris instrument, depending on the samples. The glass transition temperatures were obtained from samples that had been pressed and secured in crimped aluminum pans. Scans were run at 5 °C/min and the reported T_g values were obtained from the second heat after a quench cool from the first run. Three scans were performed, all at a standard 5 °C/min rate, for each sample. The samples were first heated to 220 °C and held isothermally for 5 min to remove all thermal history. The cooling cycle followed, with the sample cooled to -40 °C and then held at that temperature for 5 min. The temperature was then increased to 200 °C for the second heating cycl.

Transmission electron microscopy TEM

TEM images were recorded out at the University of Cape Town's electron microscopy unit. TEM was used to directly visualize the morphology of the acrylate-g-urethane copolymers. Bright-field TEM images were recorded on a JEM 200CX (JEOL Tokyo, Japan) TEM at an accelerating voltage of 120 kV. Prior to analysis, samples of urethane-acrylate graft copolymers were stained with OsO₄, then embedded in epoxy resin and cured for 24 h at 60 °C. The embedded samples were then ultra-microtomed with a diamond knife on a Reichert Ultracuts ultra-microtome at room temperature. This resulted in sections with a nominal thickness of ~100 nm. The sections were transferred from water at room temperature to 300-mesh copper grids, which were then transferred to the TEM apparatus.

Results and Discussion:

Thermal stability of urethane macromonomer

A complex compound like polyurethanes has the onset of degradation of Pus governed by the weakest link in the chain, whereas the most available group in the chain is the dominant factor for overall thermal stability. Ultracut thermal decomposition patterns of UM2 were determined by TGA. Typical thermograms along and its derivative curve (DTG) were recorded in a nitrogen atmosphere and results shown in Figure 1

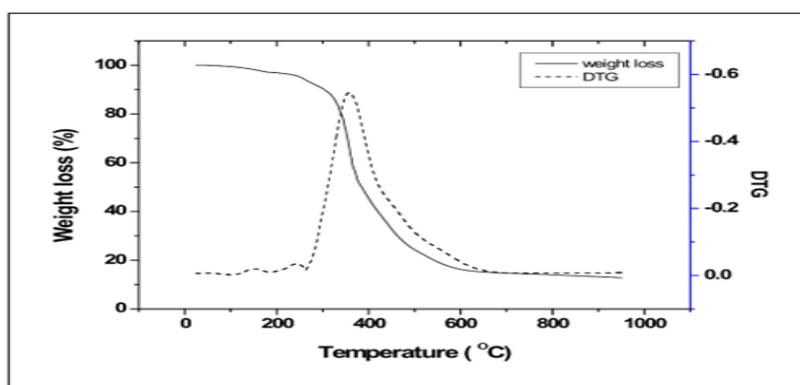


Figure 1: TGA thermogram of UM2 and its derivative curve

Figure 1 indicates the three-stage thermal degradation of UM2. The first stage and second stage degradation are very small, and took place in the range 105–160 °C and 160–264 °C respectively. The weight loss in these two steps was 2% and 1% respectively which might be due to some water and unreacted raw martial still present in the UM2 sample. The third stage degradation in the temperature range 264–623 °C occurred with a weight loss of 92%. This could be due to thermal decomposition of all the segments of UM2. In this step the weight loss may be due to liberation of HCN, nitriles or aromatic carbon and ethers. This stage ends with the loss of all volatile fractions, and a mass loss that does not change much after 603 °C

PMMA-g-UM2 copolymers

Primary TGA curves for MMA copolymerized with different amounts of UM2, in the range from 0–55% by weight according to MMA, are shown in Figure 2(a). The decomposition patterns for all the graft copolymer samples were similar. There was a slight improvement in thermal stability as the amount of UM2 increased, which might be due to optimum morphological interaction between PMMA and the urethane

segments. PMMA degrades in three steps, and is virtually completely destroyed by 465 °C. The first stage of degradation occurs in the temperature range 205–290 °C, which is attributed to depolymerization after cleavage of weak links, i.e., head-to-head linkages. The second stage of the degradation takes place in the temperature range 290–390 °C, which is attributed to a larger mass loss due to end chain unsaturation. The third stage of degradation occurs in range 390–450 °C which accounts for the majority of the degradation, and is due to random scission..

The weight loss obtained from TGA thermograms for different degradation steps and the ash content are given in Table 2. Figure 2(b)-(f) revealed three-step thermal degradation process for all PMMA-g-UM2 copolymers

Table 2: Thermal data obtained from TGA scans for PMMA-g-UM2

Compositio n of UM1/PMM A (wt/wt)	Degradati on stages	Temperature range (°C)			Weight loss (%)
		Ti	Tmax	Tf	
0/100	1	133	181	241	12.3
	2	241	313	347	20.4
	3	347	406	465	67
	ash				0.3
10/90	1	207	282	318	6.3
	2	318	349	409	31.3
	3	409	474	536	61.4
	ash				1.7
25/75	1	243	285	333	4.3
	2	263	328	377	28.2
	3	377	438	538	63.1
	ash				2.5
55/45	1	263	255	330	12
	2	300	400	438	17.4
	3	438	483	607	63.9
	ash				6.4
100/0	1	105	135	160	24
	2	160	239	264	68.7
	ash				6.3

Table 2 shows that the copolymers, especially in the low temperature range (where PMMA starts at 133 °C and UM2 at 105 °C), are very much more stable; the first signs of degradation appear at 263 °C for the 55/45 copolymer.

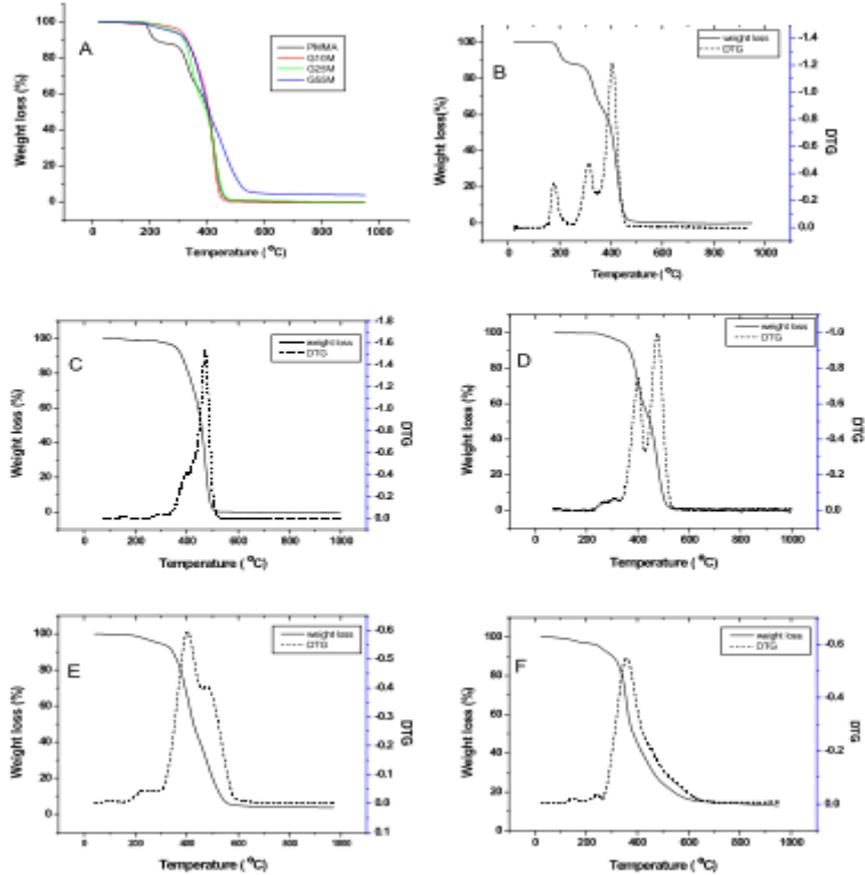


Figure 2: TGA thermograms and their derivate curves for: (A) TGA curves of MMA copolymerized with different amounts of UM2, (B) 0/100, (C) 10/90, (D) 25/75, (E) 55/45, and (F) 100/0 UM2/MMA copolymers.

PnBMA-g-UM2 copolymers

Primary TGA curves for n-BMA copolymerized with different amounts of UM2 are shown in Figure 3(a). The decomposition patterns for all graft copolymers samples were similar. There was however a slight improvement in thermal stability as the amount of UM2 in the graft copolymer increased, which might be due to better morphological interaction between PnBMA and UM2 segments.

Figure 3(b) shows that PnBMA is degraded in three steps. The weight loss obtained from TGA thermograms for different degradation steps and ash content are given in Table 3. Figure 3 (b)-(f) revealed a two-step thermal degradation process for PnBMA-g-UM2 copolymers. The first stage of degradation occurs in the temperature range 255–390 °C occurred with a weight loss of 38–57%. As the percentage of UM2 in the PnBMA-g-UM2 is increased the onset decomposition temperature (T_i) is shifted towards higher temperature. The weight loss during the first stage of degradation was found to decrease with the increase in PnBMA content in the PnBMA-g-UM2.

The second stage of degradation of PnBMA-g-UM2 in the temperature range 355–549 °C occurred with a weight loss of 57–71%. The above observation was supported by the fact that as the UM2 content in the PnBMA-g-UM2 copolymer decreased, weight loss in this step was increased.

Table 3: Thermal data obtained from TGA scans for PnBMA-g-UM2

Composition of UM1/PnBMA (wt/wt)	Degradation stages	Temperature range (°C)			Weight loss(%)
		T_i	T_{max}	T_f	
0/100	1	190	255	275	7
	2	275	334	351	28.4
	3	351	402	491	64.2
	ash				0.3
10/90	1	255	326	355	38
	2	355	395	497	60.3
	ash				1.7
25/75	1	261	356	377	47.7
	2	377	397	519	49.7
	ash				2.5
55/45	1	265	366	390	57.1
	2	390	414	549	40.4
	ash				6.5
100/0	1	105	138	163	2
	2	163	237	264	1
	3	264	353	603	91
	ash				6.9

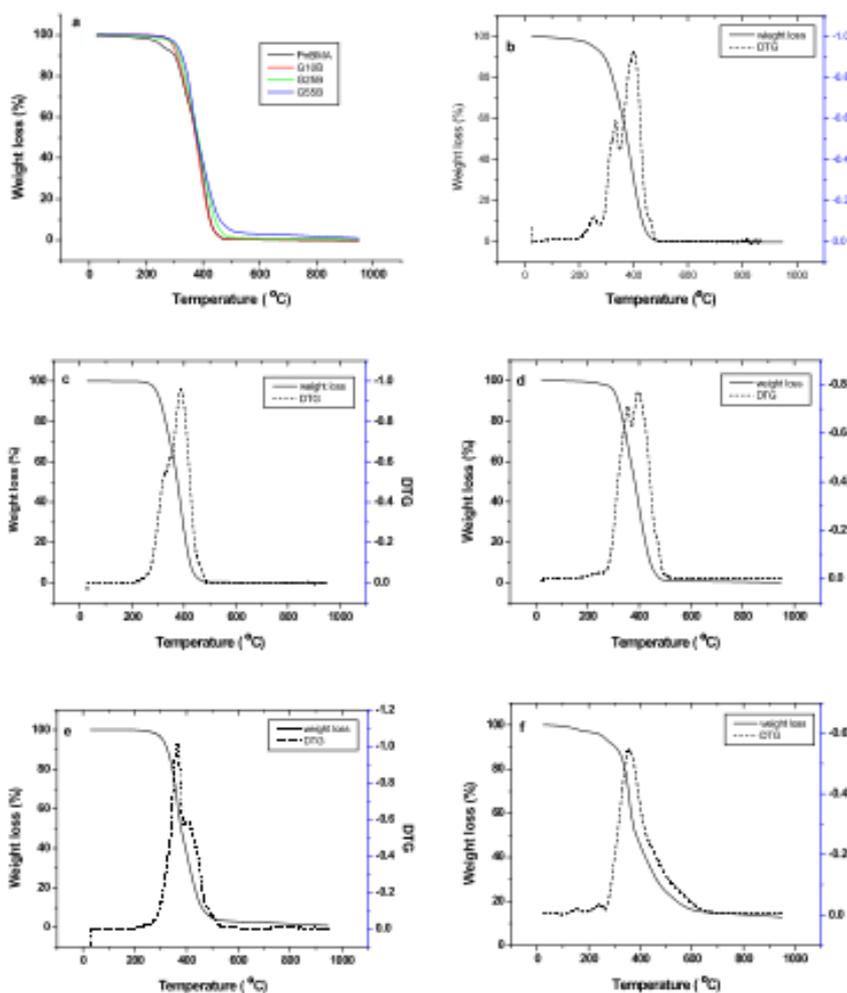


Figure 3: TGA thermograms and their derivate curves for: (a) TGA curves of n-BMA copolymerized with different amounts of UM2, (b) 0/100, (c) 10/90, (d) 25/75, (e) 55/45, and (f) 100/0 UM2/n-BMA copolymers.

DMA analysis:

The dynamic mechanical behaviour of a graft copolymer depends on the miscibility of the polymer pair. If the polymer pair is

miscible, only one phase is formed and one sharp glass transition will be observed. Conversely, if two polymers are totally immiscible, two glass transitions will be observed, that is, at the glass transitions of the homopolymers.

Structural differences between soft and hard blocks normally result in phase separation. The degree of phase separation affects the properties of the 36.1wt % incorporation of UM2 onto the graft copolymers there is a small secondary storage modulus at 107 oC to 145 °C, where separation reoccurred. Figure 4 also shows dramatic increases in modulus as the amount of UM2 incorporated into the graft copolymers was increased for example, the sample containing 36.50 wt % UM2 shows a storage modulus that is about 2.35 greater than that of PMMA. Overall, DMA analysis reveals that the PMMA-g-UM2 copolymers are much stiffer and can withstand higher temperatures compared to the PMMA homopolymer. The effect of the amount of UM2

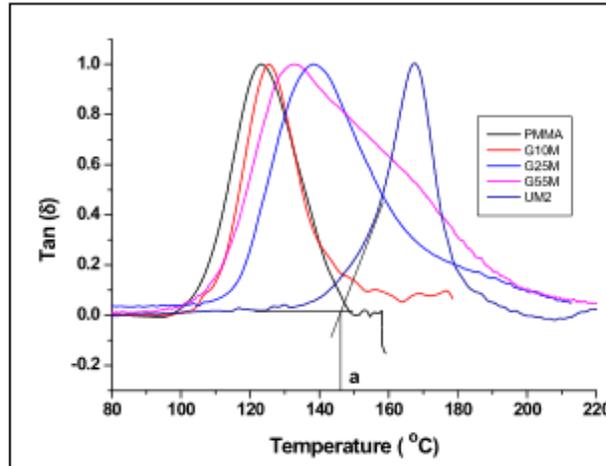


Figure 4: tan δ traces of PMMA, UM2 and PMMA-g-UM2 copolymers.
Note (a: extrapolated Tg at onset of UM2 tan δ).

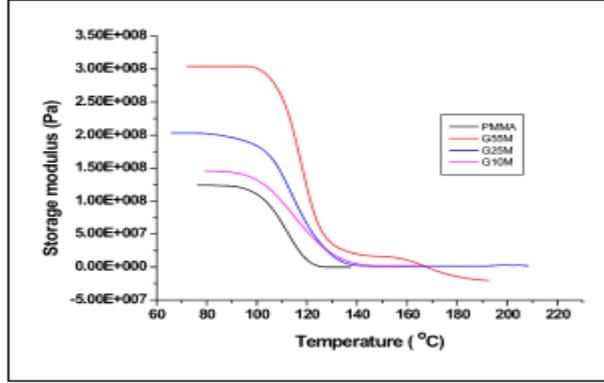


Figure 5: Storage modulus traces of PMMA and PMMA-g-UM2 copolymers

Figure 5 shows that G55M has partial compatibility when incorporation is low while for that was incorporated into the PMMA-g-UM2 copolymer and that affects the storage modulus value, is shown in Table 4

Figure 6 shows the loss modulus of PMMA-g-UM2 copolymer containing 36.50 wt % UM2, which confirms a significant degree of mixing, especially at the interfacial areas of two phases, as a peak containing a single shoulder is found, not two peaks.

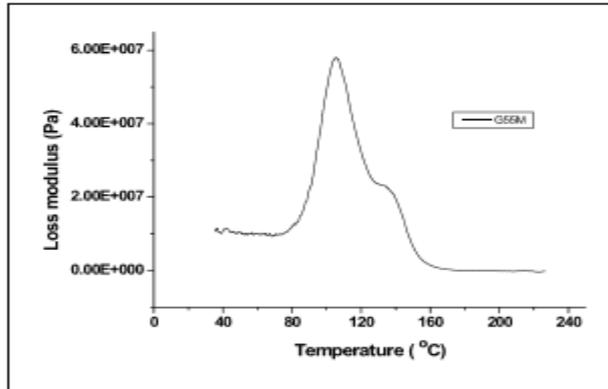


Figure 6: Loss modulus of PMMA-g-UM2 copolymer containing 36.50 wt % UM2PnBMA-g-UM2 copolymers

The variation of dynamic mechanical properties such as $\tan \delta$, and storage modulus versus temperature of the homopolymers and graft copolymer are shown in Figures 7 to 9. The $\tan \delta$, storage modulus, and loss modulus show a transition arising at 40-45 °C due to the segmental motion. This corresponds to the glass-transition temperature (T_g) of PnBMA. UM2 shows a glass transition temperature at 135 °C as shown in the extrapolated peak in Figure 7. When n-BMA was copolymerized with UM2 the T_g of the copolymer shifted to a higher temperature, to between the T_g values of the UM2 and PnBMA. The $\tan \delta$ traces and storage modulus (E'') of graft copolymer showed only a single peak between the PnBMA and UM2 peaks, which suggested a homogeneous (i.e. not phase separated) material. The T_g was measured as the onset temperature, and the T_g values of the PnBMA-g-urethane copolymers varied between 38-45 °C. It was also observed that the T_g values of PnBMA-g-UM2 graft copolymers had single T_g values and that the value increased with increasing UM2 content. This confirmed that the UM and PnBMA segments were largely compatible and that copolymers were formed. The T_g values of all the synthesized PnBMA-g-UM2 copolymers are tabulated in Table 5. (T_g defined here as extrapolated onset peak of $\tan \delta$)

When the amount of UM2 added was increased to 55 wt % during copolymerization (to give 37.99% UM2 incorporation into the graft copolymers), partial microphase separation occurred. Two T_g values are observed in all $\tan \delta$, loss modulus (E'') and storage modulus UM2 graft copolymers had single T_g values and that the value increased with increasing UM2 indicated that there was a degree of microphase separation. Detection of glass transition temperatures associated with each of the respective homopolymers indicated that the UM2 segments and PnBMA segments in the above case were locally separated (microphase separation) into distinct regions. However, the increase in the onset T_g over 34 °C of PnBMA shows minor mixing, due to short backbone sequences and short branch sequences (a result of the addition synthesis)

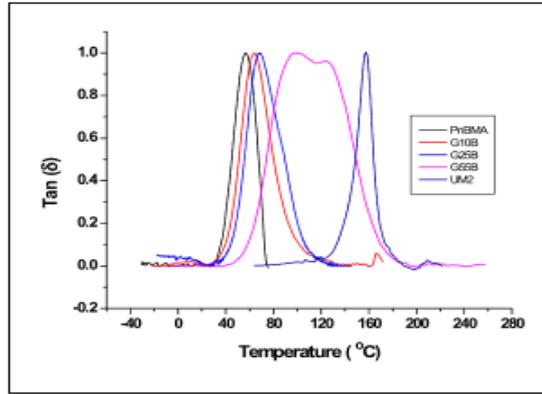


Figure 7: $\tan \delta$ traces of PnBMA, UM2 and PnBMA-g-UM2 copolymers

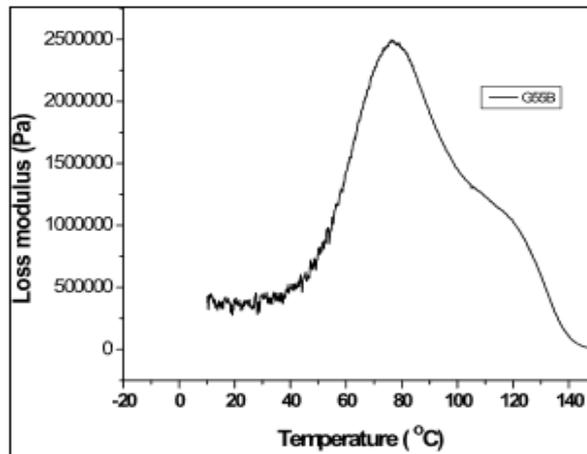


Figure 8: Loss modulus of PMMA-g-UM2 copolymer containing 37.99 wt % UM2.

On other hand, the PnBMA-g-UM2 copolymers show dramatic increases in modulus as the amount of UM2 incorporated into graft copolymers was increased. For example, the sample containing 37.99 wt % UM2 shows a storage modulus about 3.73 times that of PnBMA. This modulus increase shows partial compatibility and matches the increases in the T_g . The overall DMA analysis reveals

that the PMMA-g-UM2 copolymers are much stiffer and can withstand higher temperatures compared to PMMA homopolymer. The effect of the amount of UM2 that was incorporated into PMMA g-UM2 into the storage modulus value is shown in Table 5

Table 5: DMA results for PMMA-g-UM2 and PnBMA-g-UM2 copolymers at varying UM2 ratio in polymerization feed

	Sample code	UM2 feed ratio (wt %)	UM2 incorporated into copolymers as calculated by ¹ H-NMR (wt %)	T _g (°C) at onset	T _g (°C) at max peak height	E'X10 ⁸ (Pa)
PMMA-g-UM2	PMMA	0	-	108	125	1.3
	G10M	10	3.09	113	136	1.5
	G25M	25	20.35	115	138	2.0
	G55M	55	36.50	107,147	132	3.0
PnBMA-g-UM2	PnBMA	0	-	34	56	0.7
	G10B	10	6.16	37	63	1.8
	G25B	25	16.96	40	68	2.2
	G55B	55	37.99	45, 130	90	2.5

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a commonly used tool to determine molecular organization changes, such as phase separation, and glass transition, both the mechanical and thermal properties of the copolymer can be affected dramatically by phase mixing. Interaction between the soft and hard segments can increase the glass transition temperature of the soft segment and decrease the T_g of the hard segment. The glass transition temperatures of the graft copolymer and the macromonomers were determined using DSC. The results for all graft copolymers and macromonomers are

shown in Table 6. UM2 showed T_g at 150 °C, the T_g of the PMMA is about 108 °C) and the T_g of PnBMA is about 34 °C. The DSC results of both PMMA-g-UM2 and PnBMA-g-UM2 copolymers with high UM2 content shows the presence of two T_g values, which indicates the formation of phase separation, where the UM2 region aggregates separately from methyl methacrylate and from n-butyl methacrylate. These results correspond well with the DMA results (Table 6). The T_g decreased with a decrease in the macromonomers content. This is expected, due to an decrease in the number of (hard chain) UM2 chains which have relatively high T_g. This decrease in the T_g could be explained as follows. At low macromonomer content there are less very long chain branches which can assimilate and form a separate phase. In the case of the high macromonomer content the longer grafts in the copolymer can better find themselves and can assimilate more resulting in high T_g. From the thermal properties of grafts, the T_g is affected by the macromonomer content and here there are sufficient short branches and sterically hindered branches that form mixing.

$$T_{g \text{ mix}} = \alpha_{\text{PMMA}} T_{g \text{ PMMA}} + \alpha_{\text{UM2}} T_{g \text{ PMMA}}$$

where α is volume present

Table 6: DSC results for PMMA-g-UM2 and PnBMA-g-UM2 copolymers at varying UM2 ratios in polymerization feed.

	Sample code	UM2 feed ratio(wt %)	UM2 incorporated into copolymers as calculated by ¹ H-NMR (wt %)	T _{g1} (°C)	T _{g2} (°C)
PMMA-g-UM2	PMMA	0	-	118	-
	G10M	10	3.09	113	-
	G25M	25	20.35	115	-
	G55M	55	36.50	117	148

PnBMA-g-UM2	PnBMA	0	-	34	-
	G10B	10	6.16	37	-
	G25B	25	16.96	40	-
	G55B	55	37.99	57	150

Figures 10 and 11 show DSC results for the PMMA-g-UM2 and PnBMA-g-UM2 copolymers, respectively. The two T_g values of the graft copolymers are similar to those PMMA and UM2, or PnBMA and UM2 (measured by DMA). This offers additional evidence for incorporation of UM2 into the graft copolymers, and their phase separation

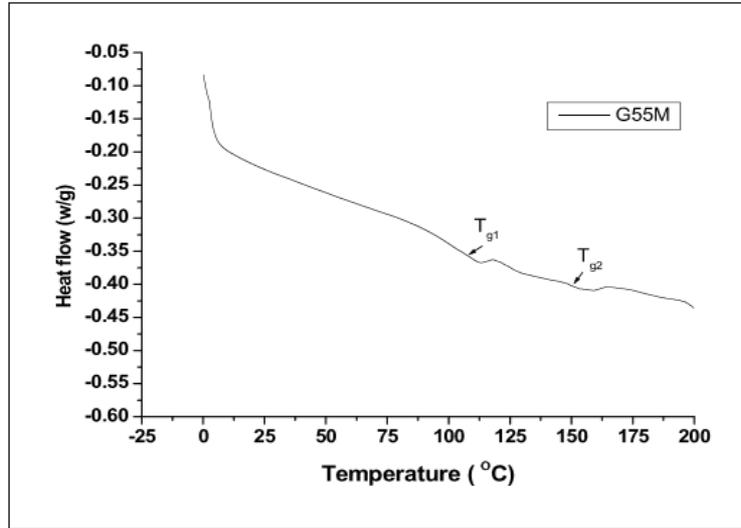


Figure 10: DSC trace of PMMA-g-UM2 copolymer containing 37.99 wt % UM2

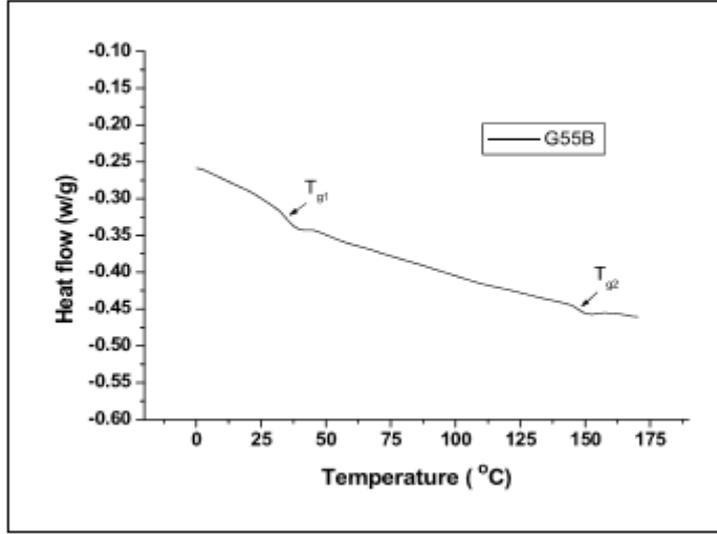


Figure 11: DSC trace of PnBMA and PnBMA-g-UM2 copolymer containing 36.50 wt % UM2

Transmission electron microscopy

The presence of a two-phase nature has been strongly confirmed from the DSC and DMA results listed above. In order to confirm this hypothesis more directly, transmission electron microscopy was conducted. As shown in Figures 12 and 13, TEM images below show evidence of phase segregated morphologies on both graft copolymers PMMA-g-UM2 and PnBMA-g-UM2 copolymers. In the images the difference in the electron densities of the PMMA, PnBMA and urethane components in the graft copolymer allow the various components to be distinguished by TEM. UM2 is more electrodense due to the aromatic backbone and will tend to show darker regions in the TEM which appear to form a spherical phase. PMMA and PnBMA are less electro dense and show lighter in the image. The images in Figures 12 and 13 show evidence of darker and lighter regions which strongly suggest results of nanophase segregation.

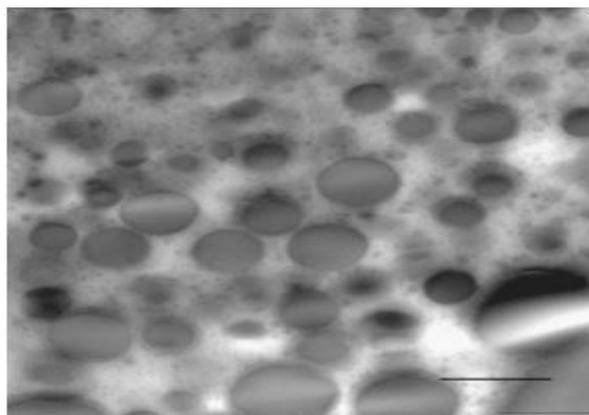


Figure 12: TEM image of PMMA-g-UM2 copolymer containing 37.99 wt % UM2 tinted with osmium tetroxide. The light regions are soft PMMA domains and the dark regions are hard urethane domains. Bar = 100 nm

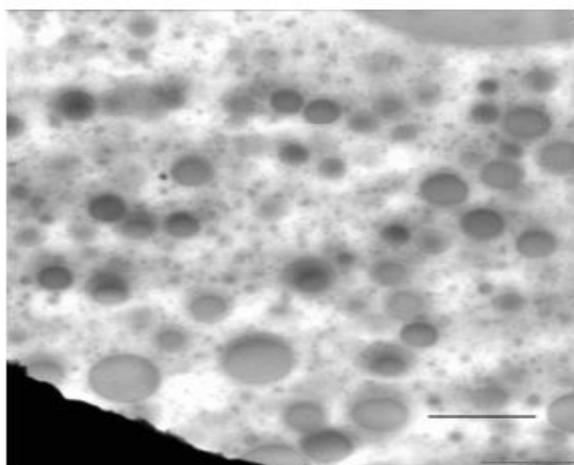


Figure 13: TEM image of PnBMA-g-UM2 copolymer containing 36.50 wt % UM2 tinted with osmium tetroxide. The light regions are soft PnBMA domains and the dark regions are hard urethane domains. Bar = 100 nm

Conclusion:

Graft copolymers decreased as the concentration of the urethane macromonomers in the copolymerization feed increased. As the concentration of urethane macromonomer in the copolymerization feed increased, more urethane macromonomer was incorporated into the PMMA and PnBMA backbones, and better thermal stability was found in both PMMA-g-UM2 and PnBMA-g-UM2. In most of the graft copolymers a large measure of compatibility was observed, as was evident from in DSC and DMA results. The Tg values increased as the concentration of urethane macromonomer was increased in the PnBMA-g-UM2 copolymer. A single peak, indicating compatibility, was observed in most of the graft copolymers. Yet in the case of the copolymer with the high UM2 content (both PMMA-g-UM2 a PnBMA-g-UM2 copolymers) there were two glass transition temperatures, corresponding to the PMMA or PnBMA, and UM2 fractions, respectively. The result also indicated that the PMMA or PnBMA and UM2 moieties exhibited partial nanophase separation, as confirmed by TEM.

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