Properties of polyurethane–poly(methyl methacrylate) graft copolymers

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An unsaturated polyurethane macromonomer was synthesized by the step growth polymerization of poly(tetramethylene ether glycol), butane-1,4-diol, glyceryl monomethacrylate and diphenyl methane diisocyanate. Graft copolymers were prepared from this macromonomer by copolymerization with methyl methacrylate in dimethyl formamide solution at 80°C, using various concentrations of 2,2′-azobisisobutyronitrile as radical initiator. For some reaction mixtures, the graft copolymers were isolated by preparative gel permeation chromatography. The properties of samples of the polymeric reaction mixtures and isolated graft copolymers were examined by differential scanning calorimetry, stress–strain, impact and rheological tests and by scanning electron microscopy. Samples of the mixed polymer and isolated graft copolymers showed little evidence of phase separation in solution or the solid state.

(Keywords: graft copolymers; polyurethane; polymethyl methacrylate; macromonomer)

INTRODUCTION

There has been continuing interest[1–3] in the use of graft copolymers as interfacial agents for the successful blending of glassy polymers, such as poly(methyl methacrylate)s (PMMAs), and rubbery polymers such as polyurethanes (PUs), to give rubber-toughened blends. The synthesis of interpenetrating networks, (IPNs), involving PMMAs and PUs has also been investigated by other workers[4,5] but these systems have more limited, specialized applications.

Previous papers have described the synthesis and characterization of PU–PMMA graft copolymers by first incorporating either the unsaturated diol, glyceryl monomethacrylate (GMM) or the unsaturated isocyanate, α,α-dimethyl *meta*-isopropenyl-benzyl isocyanate[3] (TMI) into the PU to make a PU macromonomer. In the syntheses attempted, it was possible to produce macromonomers of PU containing an average of about one double bond per molecule of macromonomer.

The unsaturated group from GMM was pendent along the PU backbone and the macromonomer was termed PUGMM. The macromonomer involving TMI was at the end of the PU chain and was termed PUTMI. Hence radical copolymerization of PUGMM and PUTMI with methyl methacrylate (MMA) gave poly(urethane-*g*-methyl methacrylate)s[2], (P(U-*g*-MMA)s) and poly(methyl methacrylate-*g*-urethane)s[3] (P(MMA-*g*-U)s), respectively.

In this paper, we report the radical copolymerization of one sample of an unsaturated PUGMM with MMA at 80°C in dimethylformamide (DMF) solution. The reaction products consisted of graft copolymers, P(U-*g*-MMA)s, together with unreacted PUGMM. Several experiments were performed varying the initiator concentration, reaction time and chemical nature of the initiator.

Separation of the reaction products was performed in some instances to isolate the graft copolymers, P(U-*g*-MMA)s, themselves. Some physical properties of the mixtures of graft copolymers and unreacted PUGMM, and of the isolated graft copolymers are described. Physical techniques involved were differential scanning calorimetry (d.s.c.), stress–strain, impact tests, rheological tests including viscometry and dynamic oscillation, and scanning electron microscopy.

The aim of this research was to demonstrate that radical grafting of unsaturated PUs by MMA was possible and to indicate some of the physical effects of such grafting.

EXPERIMENTAL

The purification of the solvents dimethyl sulphoxide (DMSO), isobutylmethyl ketone (IBMK) and *N*,*N*-dimethylformamide, has been described in an earlier paper[2]. Details of the synthesis of the macromonomer PUGMM, based on the step growth polymerization of purified butane-1,4-diol (BD), GMM, 4,4′-diphenyl methane diisocyanate (MDI), poly(tetramethylene ether glycol) 2000 (PTMEG) have also been described[2]. A trace of dibutyl tin dilaurate was added to catalyse PU formation.

MMA and 2,2′-azobisisobutyronitrile (AIBN) were purified before use[2] while benzoyl peroxide (BPO; BDH Ltd, UK) was recrystallized from chloroform, dried and stored in the freezer until required.

The graft copolymerizations of PUGMM with MMA were performed in a flask fitted with a Suba-seal. A solution of PUGMM (1.50 g), MMA (4.00 g) and AIBN was made up in DMF (20 cm^3), purged with nitrogen

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Table 1 Reaction conditions and g.p.c. analysis of the unseparated polymers in grafting experiments

Experiment no.[a]	AIBN (g)	BPO (g)	Reaction time (h)	Total yield (g)	Yield of P(U-*g*-MMA) (g)	PU (%) in P(U-*g*-MMA) in mixture
1[b]	0.0046	–	24	4.14	3.34	21
2	0.0125	–	24	3.65	2.71	21
3	0.0514	–	24	4.08	3.10	17
4	0.0054	–	48	3.82	2.90	20
5	0.0510	–	48	4.65	3.7	14
6	–	0.0746	24	4.53	3.44	12

[a]All experiments involved PUGMM (1.50 g), MMA (4.00 g), DMF (20 cm^3), initiators AIBN or BPO, and were at 80°C
[b]The polymer products for experiment 1, for example, consist of unreacted PUGMM and graft copolymer P(U-*g*-MMA)-1

gas and reacted at 80°C for 24 or 48 h. In the series of experiments 1–5, the quantity of AIBN used was altered systematically, while in experiment 6 benzoyl peroxide was used as initiator. Synthetic details are given in *Table 1*. The polymeric products were precipitated into distilled water, washed, dried *in vacuo* and the percentage yields of all polymers isolated from any reaction were calculated.

Previous work[2] established that the only successful method of separation of graft copolymers from unreacted PUs was by gel permeation chromatography (g.p.c.). G.p.c. of the crude reaction products showed that the PUGMM acted as a true macromonomer and underwent copolymerization with the MMA. No pure PMMA homopolymer was formed and clearly the pendent methacrylate unit of the PU was sufficiently exposed to undergo copolymerization. Details of the preparative and analytical g.p.c. equipment used in this work have already been given[2] and extensive use of these techniques was necessary in the isolation and characterization of the graft copolymers. I.r. spectroscopy of polymer films was performed using a Perkin-Elmer 457G Grating spectrophotometer. ^1H n.m.r. spectra were recorded using a 5% w/v solution of the polymers in d_6-DMSO (Aldrich) on a Bruker WM-250 spectrometer. Typical spectra of the copolymers have been reported previously[2].

D.s.c. was carried out using a Du Pont Instruments thermal analysis system 9000 fitted with a plug-in module, cooling unit and high temperature unit. The rate of heating was 10°C min^{-1}. Samples were scanned from −100°C to room temperature and then immediately from room temperature to 250°C. Samples were scanned twice, one scan after the other following cooling, to see if physical changes had occurred within the sample. When analysing the data, the glass transition temperature, T_g, of the sample was considered to be the half-way point of the inflexion in the curve.

The stress–strain properties of the polymers were measured at room temperature using a Polymer Laboratories miniature materials tester (Minimat) interfaced to an IBM personal system-2 computer. Polymer films of thickness 100–150 μm were cast from THF; dimensions of samples were measured with a micrometer. A crosshead speed of 10 mm min^{-1} was used for the stress–strain measurements.

Impact tests by the 'falling dart' technique were performed using a Rosand Precision Limited instrumental falling weight impact tester type 5 interfaced to a Commodore 8032-SK computer. The instrument was fitted with a Charpy striker.

Some rheological properties of the graft copolymers in solution were investigated using a Bohlin rheometer VOR interfaced to an IBM personal computer XT. For the oscillatory tests, values of the dynamic sheer modulus, G^*, the moduli G' and G'', the dynamic viscosity, η', and the phase angle, δ, were measured at different frequencies of oscillation. The measurements were taken from the lowest frequency to the highest and then repeated in the reverse direction.

Scanning electron microscopy was performed using a 10 keV Joel T200 electron microscope. Polymer films with a thickness of about 200 μm were cast from THF and carefully dried. The surface of each sample was coated with a thin layer of gold and magnifications were relatively low, 1000–5000×.

RESULTS AND DISCUSSION

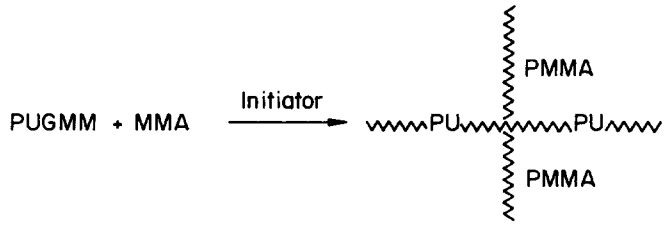
PUGMM

The basic PU macromonomer, PUGMM, was synthesized[2] with a reactant mole ratio of MDI:PTMEG 2000:BD:GMM of 11:2:8:1. Although ideally each molecule of PUGMM would have contained only one unit of GMM, in reality a distribution of molecules containing no GMM to those containing several units was possible.

It was established by separate experiments, coupled with g.p.c. analysis, that no homopolymerization of PUGMM alone occurred under conditions similar to those employed in later graft experiments. This was probably due to the combination of the low concentration of active unsaturated sites to the copolymers and the difficulty of homopolymerization due to steric effects.

P(U-g-MMA)s in polymer mixtures

The reaction conditions for the synthesis of graft copolymers of PUGMM with MMA are shown in *Table 1*. The PUGMM would have copolymerized with MMA typically to produce T-shaped or criss-crossed polymers. It would be possible for a small number of copolymer molecules to contain several PU units:



Examination of the unseparated products produced in experiments 1–6 by g.p.c. showed the presence of two materials observable by the u.v. detector. One of the materials was unreacted PUGMM while the other had a larger molecular size. Since the u.v. detector responded only to the PU, the new material was a graft copolymer of PUGMM and MMA.

The chromatograms obtained from the refractive index (r.i.) detector resolved the mixture into two peaks corresponding to the unreacted PUGMM and P(U-*g*-MMA)s. There was no PMMA homopolymer, suggesting that the reaction followed the general rules of copolymerization. Disproportionation would probably have been the most dominant termination mechanism in copolymerization as PMMA terminates exclusively by this mechanism above 60°C[6].

Quantitative analysis of the g.p.c. data for the unseparated products gave the results shown in *Table 1*. Increasing the initiator concentration, in experiments 1, 2 and 3 seemed to reduce slightly the quantity of PU in the graft copolymers. Experiments 3 and 6, resulted in a lowering of the %PU in the P(U-*g*-MMA), although the initiators, (AIBN and BPO), and their respective concentrations were different. Doubling the reaction times for experiment 1 slightly lowered the %PU of the resulting P(U-*g*-MMA) (experiment 4). The same effect is observed on comparing experiments 3 and 5. This suggests that there is an increase in grafting with increased reaction times, as expected.

Separation of P(U-g-MMA)s from mixtures with unreacted PUGMM

The removal of unreacted PUGMM from the P(U-*g*-MMA)s proved difficult. For example, Soxhlet extraction with toluene (a non-solvent for PUGMM but a solvent for P(U-*g*-MMA)) extracted both polymers due to the graft copolymer acting as a surface active agent to form micelles or aggregates which solubilized the PUGMM. The successful separation was by g.p.c. using the preparative g.p.c. equipment already described[2]. In this paper, the polymeric products from experiment 1 (unreacted PUGMM and graft copolymer), will be designated 1-mix. The isolated graft copolymer from experiment 1 will be designated P(U-*g*-MMA)-1. A similar type of notation will be used for each experiment and its corresponding products.

The results of molecular weight analysis by g.p.c. of the separated graft copolymers are shown in *Table 2* together with data for the original PUGMM. Both the u.v. and r.i. detectors gave values of the weight average ($\bar{M}_w$) and number average ($\bar{M}_n$) molecular weights for the isolated graft copolymer. The g.p.c. was calibrated with linear polystyrene standards and so the values are nominal and again, the lower fractions of the graft copolymers were probably lost on initial precipitation. The values of molecular weights are, of course, markedly affected by the efficiency of the g.p.c. columns used in the study.

As the concentration of AIBN in the initial reaction mixture increased (experiments 1 and 2) the apparent $\bar{M}_n$ values decreased, as expected. Changing from AIBN to a slightly higher concentration of BPO, (experiments 3 and 6), increased the values of $\bar{M}_w$ and $\bar{M}_n$. Increasing the reaction times (experiments 1 and 4, also 3 and 5) did not greatly affect the graft molecular weights. Polydispersities, ($\bar{M}_w/\bar{M}_n$), were higher than expected even when allowing for the fact that the initial PUGMM had a broad molecular weight distribution. There is the possibility of limited branching occurring in the PUGMM–MMA polymerizing systems, although no polymerization was observed when attempts were made to polymerize PUGMM alone in the presence of AIBN in DMF at 80°C.

The structure for the criss-crossed type of copolymers, previously shown, suggests that if g is the average number of branch points in the copolymer molecule:

$$\%\text{PU(w/w) in copolymer} = g\left[\frac{\bar{M}_n(\text{PUGMM})}{\bar{M}_n(\text{graft copolymer})}\right]$$

The average number of branches per graft copolymer molecule is given in *Table 1* using both u.v. and r.i. g.p.c. data and there was reasonable agreement between these results.

D.s.c. studies of the PUs, PUGMMs and P(U-g-MMA)s

D.s.c. was performed on several samples of the PUGMMs and their respective isolated graft copolymers, P(U-*g*-MMA)s. For the PUs, three consecutive runs were carried out on the same sample. The first two runs were between −100 and 200°C and the third was from −100 to 250°C. Run 1 showed a transition between −80 and −50°C, centred on −65°C, which corresponded to the T_g of the polyether soft segments in the PU. This indicated some degree of phase separation between the hard and soft segments. Then a slight and broad transition occurred between 30 and 80°C, probably corresponding to a partial breakdown in ordering within the hard segments. This was followed by a broad melting transition starting at ~150°C which peaked at ~175°C.

Run 2, with the same PUGMM samples, again showed a T_g at ~−65°C but now a strong melting transition

Table 2 Molecular weights of P(U-*g*-MMA)s found by g.p.c., number of branches and molecular weight of PUGMM

Sample	U.v. detector		R.i. detector		Number of branches (u.v. detector)	Number of branches (r.i. detector)
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$		
P(U-*g*-MMA)-1	156000	33636500	279000	43570000	2.1	2.7
P(U-*g*-MMA)-2	130000	11425000	166000	12989500	1.7	1.6
P(U-*g*-MMA)-3	41500	454000	86500	414500	0.4	0.7
P(U-*g*-MMA)-4	125000	27832000	172500	18669000	1.6	1.6
P(U-*g*-MMA)-5	40000	232000	61900	156300	0.4	0.4
P(U-*g*-MMA)-6	121000	3464000	120000	2851300	0.9	0.7
PUGMM	15700	72000	21800	70000	–	–

was noticed at 20°C corresponding well to the melting point, T_m, of the PTMEG 2000 homopolymer. Some disruption of the hard segments occurred in the range ~30–110°C and a sharp melting transition for these segments occurred above ~185°C. Run 3 showed a weak T_g of the soft segments at ~−60°C, and a very strong T_m of the PTMEG segments at ~20°C. The T_m of the PU hard segments peaked at 208°C and a weak decomposition exotherm occurred at 225–240°C. The principal features of the d.s.c. results for run 3 with PUGMM samples are shown in *Figure 1*. Thus, *Figure 1a* shows the T_g of the amorphous PTMEG soft segments, *Figure 1b* shows T_m for the crystalline PTMEG segments and *Figure 1c* shows both the T_m of the hard segments and the subsequent slight decomposition exotherm at ~225–240°C.

G.p.c. of samples of the PUGMMs after d.s.c. indicated that some low molecular weight polymers were produced. Also, separate g.p.c. studies with PTMEG 2000 homopolymer alone, after d.s.c. up to 200°C, indicated that slight decomposition had occurred. Thus there may have been some soft segment decomposition in run 1 leading to crystallization of the soft segment fragments on cooling, giving rise to the observed T_m at ~20°C for the crystalline PTMEG. It is considered more likely, however, that run 1 caused relaxation of the soft PTMEG segments, followed by their subsequent crystallization on cooling, resulting in the T_m value noticed in runs 2 and 3.

Two consecutive d.s.c. analyses were performed on each sample of graft copolymer from −100 to 200°C and immediately afterwards from −100 to 250°C. Run 1 showed no transition of the polyether section of the PU, possibly due to the presence of the PMMA portions of the graft copolymer giving a one-phase system. Two broad endothermic transitions occurred at 10–70°C and 100–150°C. The first of these transitions was probably due to the relaxation of the carbomethoxy side group of the PMMA and the second transition was considered to be due to an interaction between PMMA in the graft and PU in the backbone. This interpretation follows the suggestion of other workers[7] who examined PMMA grafts and different types of PU. An endotherm at ~125°C was the T_g of the PMMA segments, probably in the syndiotactic form. After this heat treatment, run 2 showed an endotherm at about −70°C, the T_g of the PU soft segment. This observation again agreed with the results of Axcelrod and Gomes[7] that for graft copolymers with a low PU content, heat treatment was necessary before the T_g of the PU soft segment was observed.

In run 2, an endotherm was seen centred at ~25°C with no apparent stress relaxation due to the side groups of the PMMA. The broadening of this transition, as in run 1, was not visible, indicating that the graft copolymer had undergone rearrangements and that phase mixing had been eliminated by run 1 treatment. The T_g of the PMMA graft appeared at ~112°C and a decomposition exotherm at ~225°C.

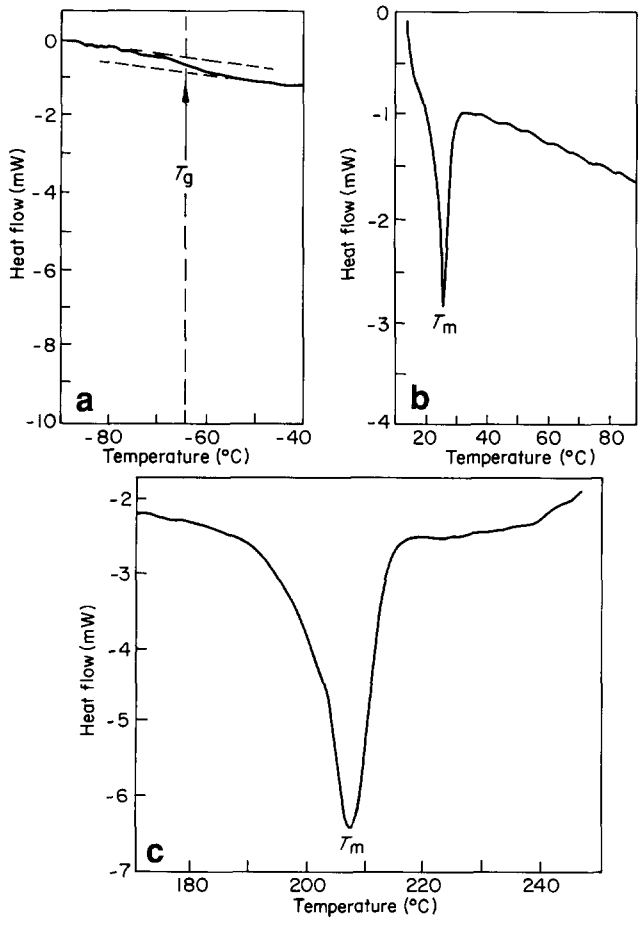


Figure 1 D.s.c. thermograms for PUGMM: (a) T_g for the soft segment PTMEG; (b) T_m for PTMEG; (c) T_m for hard segments

Stress–strain tests

Table 3 lists the results obtained for the stress–strain tests performed on samples of PMMA, graft copolymers, P(U-*g*-MMA)s and blends of the graft copolymers with unreacted PUGMMs.

The films cast for all mixtures of products were opaque, indicating that there was a degree of phase separation in the blends. The films of the pure graft copolymers were usually clear or slightly cloudy. However, occasionally white films were produced. Re-casting formed a clear film, indicating that the whiteness was caused during the drying of the film.

Necking occurred for certain samples, particularly in the case of the blends of unreacted PU and graft copolymer. During the process, the materials underwent stress whitening. For the samples that underwent necking, values of ultimate strength are quoted at the yield point and at the point of break.

For the pure graft copolymers, the results can be summarized as follows:

Young's modulus, E	≈ PMMA homopolymer
	> corresponding PU
Ultimate strength	< PMMA homopolymer
	> corresponding PU
Breaking strain	> PMMA homopolymer
	≪ corresponding PU

For the unseparated products, the results suggest:

Young's modulus, E	≈ PMMA homopolymer
	> corresponding PU
	≈ corresponding graft copolymer

The samples yielded and the stress decreased with increasing strain before breaking. However:

Maximum stress	≈ PMMA homopolymer
	> corresponding PU
	≈ corresponding graft copolymer

Table 3 Stress–strain and impact results for PMMA, mixtures and isolated graft copolymers

Sample	Young's modulus ($E \times 10^{-8}$, Pa)	Ultimate strength ($\times 10^{-7}$, Pa)	Breaking strain (%)	Impact velocity ($m\ s^{-1}$)	Secant modulus ($\times 10^{-8}$, Pa)	Ultimate strength (peak stress) ($\times 10^{-7}$, Pa)	Breaking strain (%)
PMMA	5 (±2)	2 (±1)	4.0 (±0.8)	(±0.04)	3.74 (±0.06)	0.45 (±0.04)	1.19 (±0.07)
1-mix	2.9 (±0.8)	0.91 (±0.07) at yield 0.4 (±0.2) at break	12 (±2)	0.417 (±0.001)	7.7 (±0.6)	2.86 (±0.05)	3.7 (±0.4)
P(U-*g*-MMA)-1	3.2 (±0.7)	1.5 (±0.3) at yield 0.7 (±0.4) at break	33 (±3)	–	–	–	–
2-mix	3.9 (±0.3)	1.7 (±0.1) at yield 1.0 (±0.2) at break	10 (±2)	0.427 (±0.006)	6.1 (±0.3)	1.3 (±0.3)	2.0 (±0.4)
P(U-*g*-MMA)-2	1.9 (±0.7)	0.9 (±0.3)	9 (±2)	–	–	–	–
P(*U*-*g*-MMA)-3	3.3 (±0.7)	1.1 (±0.2)	6 (±1)	–	–	–	–
6-mix	6.1 (±0.3)	1.68 (±0.02) at yield 1.0 (±0.1) at break	45 (±2)	0.428 (±0.004)	2.3 (±0.2)	0.33 (±0.04)	1.45 (±0.05)
P(U-*g*-MMA)-6	4.1 (±0.4)	1.7 (±0.2) at yield 1.2 (±0.1) at break	17.3 (±0.5)	–	–	–	–

Breaking strain > PMMA homopolymer
< corresponding PU
> corresponding graft copolymer

In general, it appeared that a combination of a relatively high molecular weight graft copolymer ($\bar{M}_n \approx 150000$) and a PU content of 10–20% w/w for the graft copolymer gave a good mechanical performance for the blend. It appeared from other experiments[8] that copolymers were capable of producing stabilized blends with free PU provided that the molecular weights of the graft copolymers were sufficiently high, and that their PU contents were constrained within certain limits.

Impact tests

The materials tested were only the blends of graft copolymer with unreacted PU. *Table 3* lists the results obtained. For the majority of the materials, higher values were obtained than for the sample of PMMA homopolymer. Again, a combination of a relative high molecular weight graft copolymer with a PU content of 10–20% w/w seemed to give the best performance.

Rheological properties of the graft copolymers and their blends with unreacted PU

In order to produce meaningful results for the tests performed, the minimum concentration of polymer in solution in DMF was 20% w/v. Since only small quantities of the pure graft copolymers could be isolated at one time by prep-g.p.c., the samples whose rheological properties were investigated were the blends of the graft copolymers with their unreacted PU.

Viscometry tests

For the viscometry tests, values of the viscosity, η, and shear stress, σ_s, were measured for each sample for a series of different shear rates, $\dot{\gamma}$. Readings were made initially with the shear rate gradually increasing. The measurements were then repeated with the shear rate decreasing to see if any time-dependent effects were to be seen. If thixotropy or rheopexy did not occur, the value of η or σ_s for a particular shear rate was taken to be the average of the two readings.

Figure 2 shows the results of the viscometry tests for PMMA, 1-, 2-, 3- and 6-mix. The samples of the blends showed no pseudoplastic effects. It appeared, therefore, that little aggregation of molecules or high frictional forces between molecules occurred in the solutions. Alternatively, any aggregates formed were stable under the shear rate ranges used. Pseudoplastic behaviour is a beneficial property for the formulation of a surface coating. Other P(U-*g*-MMA)s of different composition and branch frequency exhibited such behaviour[8].

Dynamic (oscillation) tests

The oscillation tests were performed on fresh samples of the solutions used for the viscometry tests. Values of the phase angle, δ, the storage modulus, G', the loss modulus, G'', the complex modulus, G^*, and the dynamic viscosity, η', were measured for a series of different frequencies of oscillation. Values of these parameters are shown in *Table 4*. For each sample, except 3-mix, G'' was much greater than G', indicating that each solution was behaving as a viscous liquid. More energy

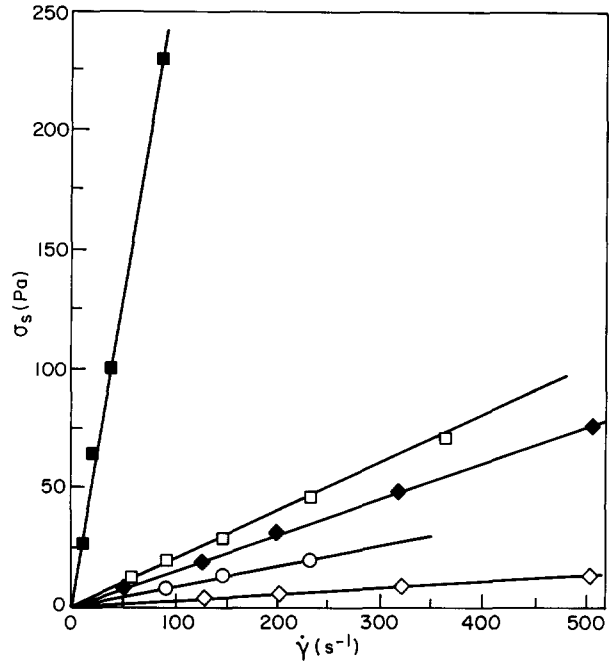


Figure 2 Plot of shear stress (σ_s) against shear rate ($\dot{\gamma}$) for 20% w/v solutions in DMF of: ■, PMMA ($\eta = 2.9 \pm 0.3$ Pa s); □, 1-mix ($\eta = 0.21 \pm 0.02$ Pa s); ○, 2-mix ($\eta = 8.8 \pm 0.5 \times 10^{-2}$ Pa s); ◇, 3-mix ($\eta = 2.9 \pm 0.2 \times 10^{-2}$ Pa s); ◆, 6-mix ($\eta = 0.17 \pm 0.02$ Pa s)

Table 4 Results of the oscillation test on the 20% w/v DMF solutions of PMMA and the mixtures of graft copolymers with unreacted polyurethanes

Sample	Freqnency range (Hz)	δ (·)	G' (Pa)	G'' (Pa)	η' (Pa s)
PMMA	0.05–10.0	84 (±6)	0.05 (±0.04)–51 (±1)	1.0 (±0.2)–161 (±1)	3.1 (±0.5)
1-mix	0.2–10.0	84 (±6)	0.038 (±0.006)–3.06 (±0.01)	0.40 (±0.01)–17.2 (±0.2)	0.30 (±0.03)
2-mix	0.1–10.0	80 (±10)	0.004 (±0.001)–1.28 (±0.04)	0.0610 (±0.0005)–6.26 (±0.09)	0.10 (±0.05)
3-mix	0.05–5.00	30 (±5)–76 (±3)	0.22 (±0.03)–0.20 (±0.04)	0.12 (±0.01)–0.76 (±0.01)	0.39 (±0.04)–0.0240 (±0.001)
6-mix	0.01–5.0	87 (±7)	0.020–0.13 (±0.02)	0.113 (±0.008)–5.06 (±0.05)	0.18 (±0.02)

was being lost per cycle than was being stored. The value of δ was relatively high for most samples and since tan δ was a measure of the energy lost compared to the energy stored per cycle, this was again an indication that the solutions were behaving as viscous liquids. The value of η' decreased with increasing frequency for samples 3-mix, although the values of η' for this sample were very low. However, the value of η' for 3-mix was almost equal to η, its steady flow viscosity, at low frequencies. Other samples of P(U-*g*-MMA) did show pseudoplasticity[8]. Therefore, changing the overall shape and molecular weight of the graft copolymers affected their rheological behaviour.

Scanning electron microscopy

Scanning electron microscopy (SEM) was performed on gold-coated samples of PUs, graft copolymers and blends of graft copolymer with free PU. SEM effectively probed the surface of the gold-modified samples. The electron micrograph for the PUs indicated that at the magnifications available, the polymer surface appeared to be featureless. Thus, no separate hard or soft segment domains were observed. Samples of PMMA were analysed. However, these were rapidly damaged by the heating effect of the electron beam.

A micrograph of the copolymer P(U-*g*-MMA)-3 had to be photographed very quickly as the sample underwent dramatic changes under the influence of the electron beam. Overall, the surface of the graft copolymer also appeared to be featureless. However, black spots rapidly grew on the surface of the film, probably due to film damage following graft copolymer degradation.

CONCLUSIONS

This research has demonstrated that radical grafting of an unsaturated PU by MMA is feasible and that pure graft copolymers can be separated by g.p.c. Examination of some physical properties of graft copolymers and unseparated reaction mixtures, by techniques including d.s.c., stress–strain, impact and rheological tests, showed little evidence of phase separation in solution or solid states. Further work is necessary to successfully correlate physical properties and structure.

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