Physical Properties of Model Graft Copolymers and Their Use as Blend Compatibilizers

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SYNOPSIS

The present investigation pertains to the structure–property relationships of highly structured graft copolymers. The specific model graft copolymers are based on an elastomeric backbone, i.e., poly(ethyl acrylate), and monodisperse thermoplastic grafts, i.e., polystyrene. The synthesis of these graft copolymers is based on the free-radical polymerization of ethyl acrylate and an anionically polymerized polystyrene macromonomer. It is clearly demonstrated that grafts significantly enhance tensile properties. The level of improvement is directly related to the graft level, i.e., number of grafts/chain, and graft molecular weight. In addition, blending these graft copolymers into their respective homopolymer mixture results in a mechanical performance strikingly dependent on the molecular characteristics of the graft copolymer. For example, tensile strength is maximized at a level between one and two grafts per chain. This result parallels observations noted in blend compatibilization using diblock and triblock copolymers. It is also demonstrated that using mutually grafted copolymers produces an interesting variety of compatibilized ternary (or higher) component blends. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Recently, a significant amount of research has been devoted to modifying the physical and chemical properties of polymeric materials. A wide range of scientifically interesting and technologically important materials have been produced by introducing specific functional groups onto the polymer chain. These groups can be associating, e.g., via ionic, hydrogen bonding, coordination-type interactions[1-6] or, alternatively, these functionalities are capable of reacting with complementary groups on other structurally distinct chains.[7-10] In the latter instance, covalent bonds are formed between the chains. The primary purpose of the associating groups has been to modify the solution and melt rheology and mechanical characteristics of the polymer itself. Recently,[11-13] these groups have been found useful in markedly improving the physical properties of poly-

mer blends. Although reactive groups may also be associating, one primary purpose in their utilization has been to control the structure of the assembly of molecular chains or their segments. This is achieved through covalent bonding, as noted previously, which results in the formation of block and/or graft copolymers. These materials are very effective compatibilizers for polymer blends. However, since the process occurs through the reaction of randomly positioned groups, graft copolymers are inevitably formed. Although these types of graft copolymers are not well defined in terms of molecular architecture, they are very effective in enhancing the mechanical properties of blends.

To more precisely structure the appropriate graft copolymer required for various applications, the copolymerization of a macromonomer with a low molecular weight monomer is generally considered to represent one of the most reliable synthetic techniques for the synthesis of graft copolymers.[14-20] This is true even with the knowledge that the reactivity of macromonomers is controlled by steric, polar, and electronic effects, but also by the excluded volume effect.

In this report, we detail the preliminary results of the properties of graft copolymers of defined structure and their structure–property relationships in a binary component blend. The blends are composed of the structurally controlled compatibilizers melt-mixed with homopolymers identical in structure to the components of the graft copolymers. The properties of the unmixed graft copolymers were initially examined and followed by blends with a specific ratio of thermoplastic, i.e., polystyrene, and elastomeric component, i.e., poly(ethyl acrylate). The latter component concentration was typically 20 wt % since this is in the range where rubber-toughened blends are formed.

EXPERIMENTAL

Styrene monomer was initially purified by extensive washing with a 10 wt % sodium hydroxide solution and subsequently distilled under reduced pressure. sec-Butyllithium (Aldrich Chemical Co.) was used as received. Ethylene oxide (Eastman Kodak Co.), 1,1-diphenylethylene (Eastman Kodak Co.), and ethyl acrylate, methyl ethyl ketone, and methacryloyl chloride (Aldrich Chemical Co.) was used as received.

The methacrylate-terminated polystyrene macromonomers were synthesized by end-capping anionically polymerized polystyrene anions with ethylene oxide, and, subsequently, terminating the reactive end group with methacryloyl chloride:
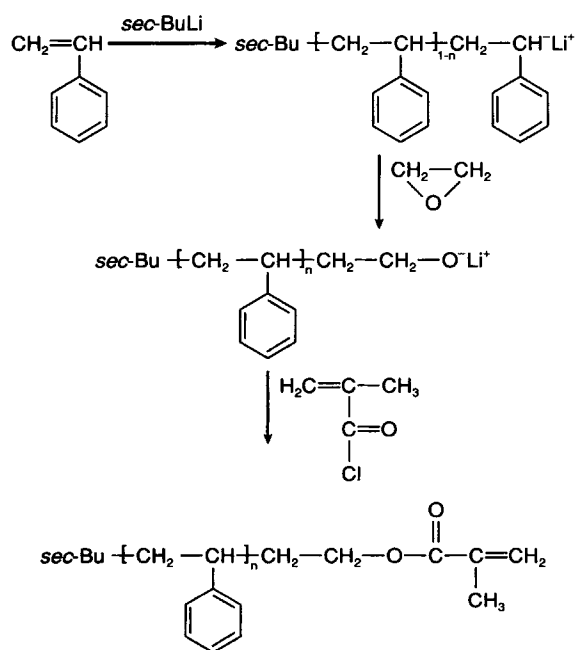
The specific synthesis procedure is described by Milkovich et al.[14] The products were precipitated, washed with a large excess of methanol, and dried in a vacuum oven for 48 h at 50°C. The molecular weight and distribution were determined by gel permeation chromotography using tetrahydrofuran as the elution solvent with the instrument calibrated with monodisperse polystyrene standards. ^{1}H-NMR was used to confirm the macromonomer end-group structure. The macromonomers used in this study are shown in Table I.

The poly(ethyl acrylate)–polystyrene-based macromonomers were synthesized by dissolving ethyl acrylate and the macromonomer in methyl ethyl ketone, degassing with nitrogen gas for 2 h, while simultaneously heating the solution to 60°C for 24 h. The polymerization was initiated with azobisisobutylonitrile. The copolymer was precipitated in a large excess of n-butanol and then extracted with a 50/50 decalin/petroleum ether mixture. The copolymer was dried in a vacuum oven for 24 h at 60°C. This particular graft copolymer structure was synthesized because of the high degree of immiscibility between polystyrene and poly(ethyl acrylate).[21] As previously noted, the product contains approximately 20% by weight poly(ethyl acrylate).

In Tables II–IV are shown the characteristics of the graft copolymers used in this study. The styrene/ethyl acrylate composition was determined by elemental analysis and ^{1}H-NMR. The average number of grafts per chain (n) was estimated by $n = M_n \times W_{PS}/M_n^{PS}$, where M_n is the number-average molecular weight of the graft copolymer as determined by GPC; M_n^{PS}, the molecular weight of the PS branch; and W_{PS}, the weight fraction of the polystyrene component in the graft copolymer. The average molecular weight between grafts is estimated from M_n and M_n^{PS}. The graft efficiency was determined from GPC measurements and extraction results.

An examination of the data in Tables II–IV shows the anticipated trend that as the graft level is enhanced, the average molecular weight between grafts

Table I Molecular Weight Characteristics of the Polystyrene-based Macromonomers

Designation	M_w (g/mol)	M_n (g/mol)	M_w/M_n
PSMA (6.9 K)	6,900	5,900	1.2
PSMA (14.6 K)	14,600	11,600	1.2
PSMA (35.6)	35,600	20,000	1.8

Table II   Charateristics of Graft Copolymers PSMA (6.9 K)

Designation	Styrene Content (Weight Fraction)	Graft Level (n)	Graft Efficiency (%)	Molecular Weight $\times 10^{-3}$ (g/mol)	Av Molecular Weight Between Grafts $\times 10^{-3}$ (g/mol)
146-1	0.0	—	—	123.0	—
156-1	0.041	0.85	98.6	142.5	73.9
156-2	0.139	2.84	97.2	140.2	31.4
156-3	0.275	7.00	97.4	175.2	15.9
156-4	0.467	9.21	96.4	135.6	7.0

is decreased. It is also noteworthy that the average graft level is decreased with increasing graft molecular weight.

The graft copolymers were formed through compression-molding into approximately $2 \times 2 \times 0.002$ in. films using the following conditions: 3 min preheat at 200°C, followed by a 3 min press cycle at 29 tons (200°C), and a 3 min cooling procedure to room temperature, also under 29 tons pressure.

Stress–strain properties were tested at room temperature with an Instron Tensile Tester Model 1122. Samples used were microdumbbells that were cut with a die from compression-molded pads. A crosshead speed of 0.02 in./min was used in all the tensile measurements.

Blends comprising mixtures of polystyrene, (Styron 666, product of Dow Chemical Co.), poly(ethyl acrylate) (synthesized under the same conditions as the graft copolymers), and the graft copolymers were melt-mixed in a Brabender mixer at 200°C for 7 min at a mixing speed of 100 rpm. Tensile specimens were prepared under the identical conditions as detailed for the unblended graft copolymers. As a rule, the weight percentage of the added components remain invariant, i.e., elastomeric and thermoplastic compositions are 20 and 80 wt %, respectively.

RESULTS AND DISCUSSION

A substantial amount of the research related to the formation of graft copolymers utilizing macromonomers is directed at the synthesis of the macromonomers itself. Only recently[22] has attention begun to focus on a systematic study of their mechanical properties in either the unblended or blended state, although substantial data exists on block copolymers.[23-27] It is generally understood that, to enhance the mechanical properties of blends, polymeric compatibilizers need to be added or formed in situ. As noted previously, graft copolymers are the common structural form of these compatibilizers. Figures 1 and 2 show the tensile properties of the poly(ethyl acrylate)-g-polystyrene copolymers as a function of graft level. Throughout the entire composition range explored, the properties are dramatically enhanced as compared to those composed of physical mixtures of poly(ethyl acrylate) and the unreacted macromonomer. In the latter instance, it was extremely difficult to form a coherent tensile specimen at any blend composition. This lack of cohesion is due to the strong repulsive interactions between the two phases, which results in very poor interfacial adhesion. The data show that this limitation is eliminated through chemical bonding between the elastomeric and thermoplastic phases.

Table III   Characteristics of Graft Copolymers PSMA (14.6 K)

Designation	Styrene Content (Weight Fraction)	Graft Level (n)	Graft Efficiency (%)	Molecular Weight $\times 10^{-3}$ (g/mol)	Av Molecular Weight Between Grafts $\times 10^{-3}$ (g/mol)
146-1	0.0	0	—	123.0	—
146-2	0.10	1.0	95.5	150.8	68.1
146-3	0.28	3.2	92.3	164.1	28.0
146-4	0.47	5.2	94.6	159.5	13.5

Table IV   Characteristics of Graft Copolymers PSMA (35.6 K)

Designation	Styrene Content (Weight Fraction)	Graft Level (n)	Graft Efficiency (%)	Molecular Weight $\times 10^{-3}$ (g/mol)	Av Molecular Weight Between Grafts $\times 10^{-3}$ (g/mol)
146-1	0.0	—	—	123.0	—
158-1	0.185	0.756	92.6	145.4	67.5
6-1	0.471	1.80	91.3	136.5	25.9
6-2	0.649	3.05	91.4	167.4	14.5

This strong phase-separation tendency also enhances the properties of this system.

An examination of the tensile data in Figures 1 and 2 shows a number of general trends. The modulus is observed to increase by four orders of magnitude even at relatively low graft content. The more effective enhancements occurs with the higher molecular weight grafts. It is noteworthy that poor properties result when the molecular weight of the grafts is below about 4000 g/mol. It is also observed that the tensile strength has increased by several orders of magnitude, whereas the elongation to break has decreased by an approximately similar amount as expected. These parameters are a strong function of the graft molecular weight.

These results point to the fact that the strong phase-separation tendency produces a system of graft-containing domains resulting in highly effective physical cross-links. Apparently, the number and size of the domains are directly linked with the tensile properties, i.e., low molecular weight grafting and a modest graft level produce poor mechanical performance.

When the molecular weight of the polystyrene grafts is kept invariant, the tensile strength increases and the elongation to break (see Fig. 2) decreases with increasing styrene content. When the styrene content is low, the mechanical properties are quite inferior. With increasing graft levels, the graft copolymers possess properties similar to thermoplastic elastomers with very acceptable tensile strength and elongation at break. At the highest graft levels studied, the graft copolymer behaves essentially like a toughened plastic rather than like a thermoplastic elastomer. If a compatabilized blend analogy can be used in this instance, then these properties could be related to phase inversion from a discrete polystyrene phase to a more or less continuous phase.

It is well known that thermal annealing can have a profound influence on the properties of polymeric materials. These graft copolymers are not an exception in this regard. Extended thermal conditioning at 100°C or higher markedly enhances the tensile

strength and reduces the elongation at break. The specific details regarding the structure–property relationships of this phenomenon are presently under
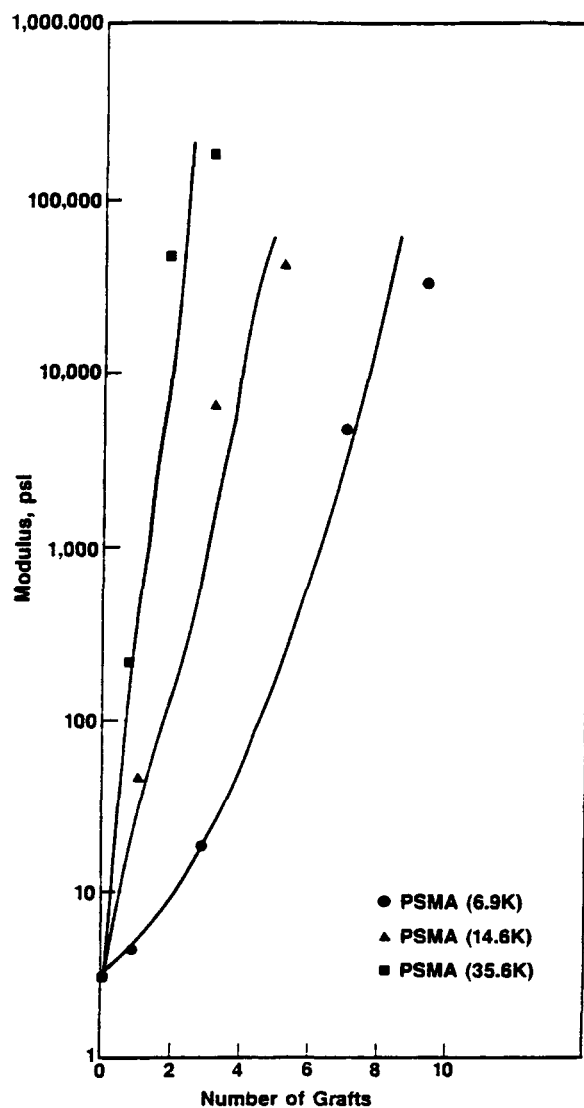

Figure 1   Modulus of poly(ethyl acrylate)-g-polystyrene copolymer as a function of graft level. The molecular weight of the grafts (PSMA) are listed in the parentheses. K denotes 10^3.
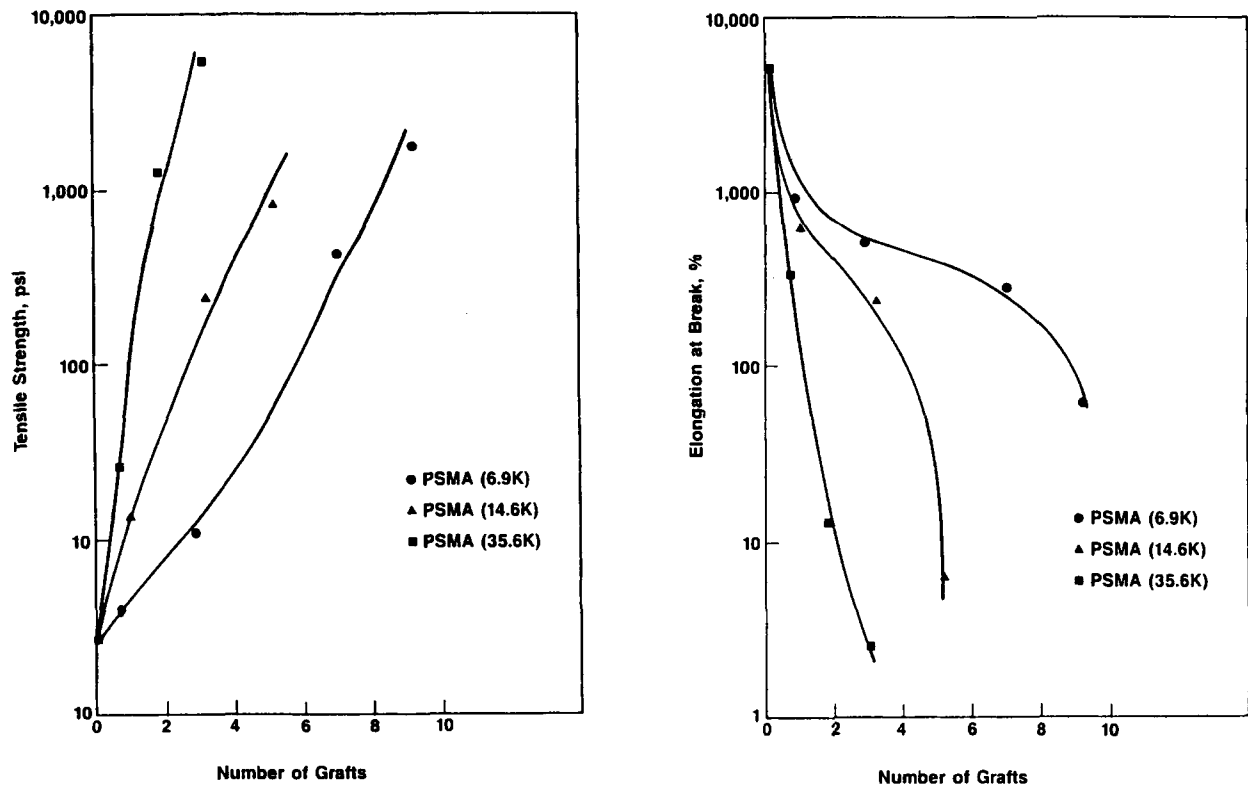
Figure 2 Tensile strength (left) and elongation at break (right) of the poly(ethyl acrylate)-g-polystyrene copolymer vs. graft level and graft molecular weight. The latter quantity is listed in parentheses. K denotes 10^3.

study, but it is apparent that improved perfection of the phase-separated regions is occurring.

Figure 3 shows the relationship between the tensile properties and graft level of ternary component blends containing the previously described graft copolymers and the two corresponding homopolymers. As anticipated, the tensile strength without a graft copolymer compatibilizer is poor, but marked enhancement in blend properties is observed with their addition. The performance level of each graft copolymer is intimately related to both the graft level and its molecular weight. For example, the tensile strength is inversely related to graft level and directly related to the graft molecular weight.

The partial phase separation of these graft copolymers in the interfacial region between the phase-separated homopolymers accounts for the markedly enhanced properties. The data also suggest that the grafts can more strongly interact with the polystyrene phase of the blend if its molecular weight is increased. This phenomenon can be due to simple adhesion, i.e., due to solubility of the graft into its respective homopolymer phase, but also to an increase in chain entanglements between the two components. However, it is observed that the prop-

erties deteriorate with graft level at a constant molecular weight. This phenomenon again can be related to decreased adhesion of the chain backbone in the elastomeric phase, i.e., poly(ethyl acrylate), which may decrease with a reduction in the molec-
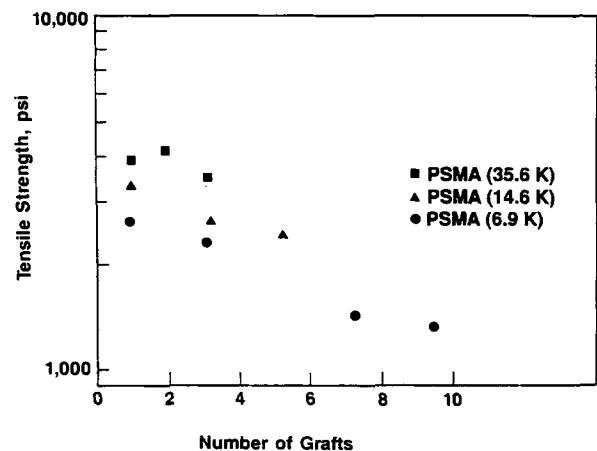

Figure 3 Tensile strength as a function of graft level and graft molecular weight for ternary component blends containing polystyrene, poly(ethyl acrylate), and poly(ethyl acrylate)-g-polystyrene copolymers.

ular weight between grafts. Therefore, it may not be too surprising that properties rise in value as the entanglement molecular weight of the poly(ethyl acrylate) backbone[28] is approached and exceeded.

It was noted previously that the mechanical properties of the unblended graft copolymers (having low graft content) had relatively poor mechanical properties in their own right. However, an examination of the data in Figure 3 confirms that these materials are very effective blend compatibilizers. In fact, if the very low tensile strength (< 300 psi) of the uncompatibilized blend is incorporated in the data of Figure 3, then maximum effectiveness of the compatibilizer occurs with approximately one to two grafts per chain. In qualitative terms, these structures approximate diblocks and triblocks, respectively, without the blocks tethered end to end. Teyssie et al.[26] noted that the interfacial activity of diblock copolymers is more pronounced than that of graft copolymers based on morphological observations and is further supported by the mechanical properties. It appears that a graft copolymer absorbs primarily onto the interface between the phase-separated regions because of conformational constraints, whereas each block of a diblock structure can easily penetrate the corresponding homopolymer phase. A low level of grafting appears to produce materials of comparable activity to diblock copoly-

mers. Along these lines, the graft copolymers containing one to two grafts are quite effective at low concentration levels (2–3 wt %), whereas those with higher graft levels are effective at high graft contents (5–10 wt %).

Finally, it is noteworthy that these graft copolymers can interact with other graft copolymers in which the grafts on each chain are identical in structure, i.e., miscible, with each other. As a result of mutual graft phase separation, unique ternary component blends can be produced. An example of this type of compatibilized blend system is shown in Table V in which the properties of a poly(methyl methacrylate)-g-polystyrene and poly(ethyl acrylate)-g-polystyrene blend are given. The data show, over almost all the entire composition range, that the mechanical properties of the ungrafted blends cannot be measured due to the very poor interfacial adhesion between the phases. Alternatively, blend components containing grafts have a very high modulus, tensile strength, and elongation at break. It is clear that mutually interacting grafts situated in both phases of these blends markedly improve the interphase adhesion, possibly in a similar manner when graft copolymers are added to a blend of homopolymers.

CONCLUSION

The structure–property relationships of a series of poly(ethyl acrylate)-g-polystyrene copolymers were studied extensively with modification in the graft level and molecular weight. As compared to the tensile properties of the ungrafted materials, several orders in magnitude enhancement in modulus, tensile strength, and elongation to break are observed. This is certainly due to the covalent bonds linking the grafts to the chain backbone, but also to the strong tendency of the grafts to phase separate. These physically associated structures are the primary reason for the property improvement through the tight knitting together of the chains.

Although low graft levels produce materials with relatively low performance parameters, these copolymers are very effective blend compatibilizers. It is observed that "optimized" property enhancement occurs with approximately one to two grafts per chain. In qualitative terms, this indicates that diblock- and triblocklike structures are the preferred molecular architecture for blend compatibilization.

These findings have implications in designing precise molecular structures for the compatibilization of blends, in general, especially with regard to the level of grafting. If the graft copolymers are

Table V   Mechanical Properties of Ungrafted and Grafted Poly(methyl methacrylate)–Poly(ethyl acrylate) (PMMA–PEA) Blends

Composition	Modulus (kpsi)	Tensile Strength (psi)	Elongation at Break (%)
PMMA : PEA, Wt %			
100 : 0	a	a	a
90 : 10	a	a	a
75 : 25	a	a	a
50 : 50	a	a	a
25 : 75	0.924	3.1	53
10 : 90	2.58	3.7	335
0 : 100	a	a	a
PMMA-g-PSMA13 : PEA-g-PSMA 13, wt %			
100 : 0	400.9	3410	1.6
90 : 10	307.2	2760	2.3
75 : 25	48.1	570	3.8
50 : 50	10.3	50	99.7
25 : 75	4.3	41	401
10 : 90	1.0	38	530
0 : 100	a	a	a

a Blends lacked sufficient cohesion to form an acceptable tensile specimen.

formed *in situ* in the melt phase as in reactive processing conditions, then relatively low levels of functionalization would be required. Of course, the extent of the reaction would be direct functions of the backbone and graft molecular weight, melt temperature, mixing time, and efficiency. These types of investigations are presently underway and will be reported on at a later date.

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