

The Physical Limits of Grafting in Two-Phase Polymerization Reactions

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Synopsis

When rubber-reinforced thermoplastics are produced, conversion of monomer to glassy polymer takes place in two thermodynamically incompatible phases. Regardless of the chemical nature of the grafting process, monomer which is converted in the glassy phase can never be grafted to rubber simply because it is never in contact with rubber. A simple model has been developed which describes quantitatively the upper limit of grafting arising from the physical nature of the process as a function of conversion and monomer-to-rubber ratio in the charge.

INTRODUCTION

The use of dispersed particles of rubber to enhance the toughness of a normally brittle glassy plastic is well established. It is generally agreed that grafting of the glassy polymer to the rubber particles is important to obtain maximum benefit from the rubber.¹

The chemistry of the grafting process has been studied in some detail. It has been observed that certain monomers will graft to certain polymers while other pairs will not.² Furthermore, certain initiators, e.g., benzoyl peroxide, seem to promote grafting, while others, e.g., azobisisobutyronitrile, do not.³ Studies of the efficiency of grafting are always complicated by the difficulty in separating the two ungrafted homopolymers and the graft to allow determination of the extent of grafting with certainty.

A fact which seems to have been overlooked until now is that the physical nature of the reacting systems and the way the reactions are carried out commercially place an upper limit on the amount of grafting which can be achieved, regardless of the chemical nature of the grafting process. This limit arises from the inherent incompatibility of polymer pairs, i.e., no two high polymers can coexist at appreciable concentrations in a homogeneous phase. If there is to be *any* possibility of grafting glassy monomer to rubber, the monomer must be polymerized in the physical presence of the rubber, i.e., in a molecular solution with it. As soon as an appreciable quantity of glassy polymer is produced, it will form a separate and distinct phase. Monomer which polymerizes in this latter phase can never be grafted to the rubber, simply because it is never in contact with the rubber. This work develops a simple model which provides a quantitative estimate

of the upper limit placed on the amount of grafting by the physical nature of the polymerization process.

THEORY

One commercially important technique for producing rubber-reinforced thermoplastics is emulsion polymerization. Glassy monomer is added to a rubber latex. According to classical emulsion polymerization theory, some monomer diffuses into the rubber particle, which uniformly reaches an equilibrium degree of swelling (point a in Fig. 1), and polymerization commences with the addition of a water-soluble free-radical initiator.⁴ (To achieve maximum grafting, the rubber particles must obviously be the exclusive loci of polymerization.) As glassy polymer is formed, it diffuses outward, forming a shell around the rubber particle (of composition b in Fig. 1), since it cannot remain dissolved in the rubber. The particle continues to grow as monomer diffuses in and is converted to additional glassy polymer.

The second commercially important method of producing "grafted" rubber-reinforced thermoplastics is bulk polymerization. Rubber is dissolved in glassy monomer to form a homogeneous solution (point c on the phase diagram in Fig. 1). Polymerization is started with an organic-soluble free-radical initiator, and the reaction proceeds along the path indicated in Figure 1 as glassy monomer is converted to glassy polymer. At some relatively low level of conversion (point d), a two-phase system is formed, and the thermodynamics of polymer incompatibility dictate that before long, each phase contains nearly pure polymer, points e and f. The product at 100% conversion is point g. There is a possibility that a certain amount of supersaturation could occur, i.e., a homogeneous solution would persist beyond the thermodynamic phase boundary, because energy is needed to generate the new surface area in a two-phase system. How-

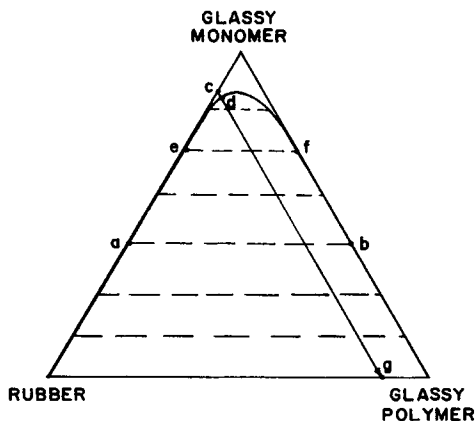


Fig. 1. Schematic phase diagram for a glassy monomer-glassy polymer-rubber system. Dotted tie lines connect equilibrium phase compositions.

ever, surface tensions in these systems are very low, and the energy needed is easily supplied by the agitation systems in commercial reactors, so this effect is probably undetectably small.

Under certain conditions, all the glassy polymer formed within the monomer-swollen rubber may not be able to diffuse out and so will form glassy inclusions within the rubber particle.⁵ For the analysis which follows, all that matters is that the glassy polymer exist in a separate phase, which is necessitated by the incompatibility of the two high polymers.

If the early homogeneous stage of the reaction (which accounts for a few per cent of the total conversion) is neglected, the same analysis is applicable to this type of reaction also.

To simplify the analysis, it will be assumed that:

a. The densities of all components of the reacting system—rubber, monomer, glassy polymer, and various solutions thereof—are the same, and therefore mass and volume fractions are equal.

b. Rubber and glassy polymers are swelled uniformly to an equal extent by the monomer, i.e., that the tie lines in Figure 1 are horizontal and that the reaction proceeds at the same rate in each phase. This is probably a conservative assumption, as it is likely that the monomer would prefer its own polymer, further reducing the possibility of grafting.

c. The lifetime of a growing chain is much less than the reaction time, as is usually the case in free-radical polymerization.

The fraction of monomer in the rubber phase at any instant in time is $v_r/v_r + v_g$, according to assumptions (a) and (b) above. The differential fraction of monomer polymerized *in the rubber phase* over the conversion increment dx ($x = v_g/v_g + v_m = v_g/v_{m0}$, since $v_{m0} = v_g + v_m$) is

$$df = \frac{v_r}{v_r + v_g} dx. \quad (1)$$

The volume of glassy polymer formed, v_g , is proportional to the conversion of monomer to polymer,

$$v_g = v_{m0}x. \quad (2)$$

Combining eqs. (1) and (2) gives

$$df = \frac{v_r dx}{(v_r + v_{m0}x)}. \quad (3)$$

When $x = 0$, $f = 0$ (no monomer has been polymerized at all). Integrating with this boundary condition gives

$$f = \frac{v_r}{v_{m0}} \ln \left(1 + \frac{v_{m0}}{v_r} x \right). \quad (4)$$

The quantity f is the fraction of the monomer charged which has been converted to polymer while in the presence of rubber. Another quantity of interest would be the maximum grafting efficiency, ϕ . This is the fraction

of all glassy polymer formed at a given conversion which has been formed while in the presence of rubber. Since x is the total fraction of monomer charged which has been converted to polymer (in both rubber and glass phases),

$$f = \phi x. \quad (5)$$

DISCUSSION

Figure 2 shows f and ϕ as functions of conversion for monomer charged/rubber ratios $v_{m0}/v_r = 5, 10,$ and 20 . At low conversions, the maximum grafting efficiency ϕ is high. The small amount of polymer which has been formed has been formed largely within the rubber phase. It drops rapidly with conversion, however, as more and more of the polymer formed has originated in the growing glassy phase. At complete conversion, $x = 1$, $\phi = f$, and v_{m0}/v_r also represents the glass/rubber ratio in the final composite.

Figure 3 illustrates the maximum possible fraction of grafted polymer at complete conversion as a function of glass/rubber ratio. Also shown in Figure 3 is the ratio of the maximum amount of grafted glassy polymer to rubber (i.e., maximum possible grams grafted/gram of rubber) $f(v_{m0}/v_r)$ at complete conversion as a function of glass/rubber ratio. This is of interest in view of the commercial practice of producing a grafted stock at a low glass/rubber ratio and bringing it up to the desired final ratio by mechanical blending with glassy polymer. This provides flexibility in producing a product line with different rubber levels with a minimum of reaction formulations. According to the analysis, it also cuts down on the maximum possible amount of grafting as compared to a material of equivalent rubber level produced directly in the reactor. The difference may not

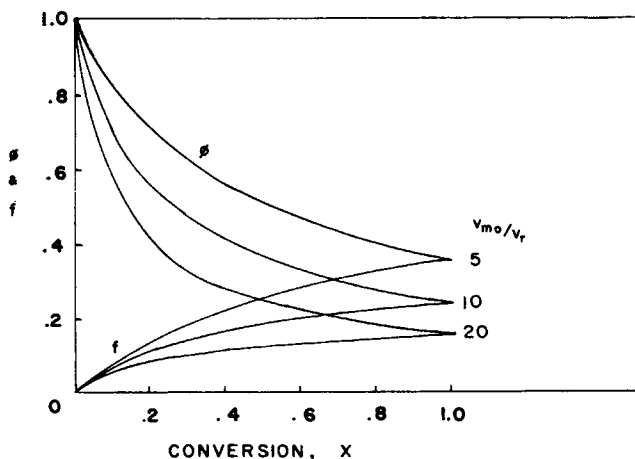


Fig. 2. Maximum possible fraction of monomer charged which has been grafted to the rubber, f , and fraction of glassy polymer formed which could possibly be grafted, ϕ , vs. conversion.

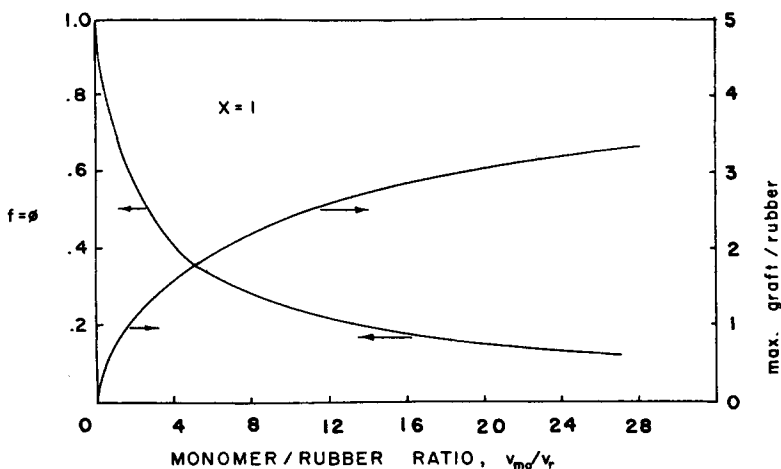


Fig. 3. Ratio of maximum amount of grafted glassy polymer to rubber at 100% conversion vs. glass/rubber ratio.

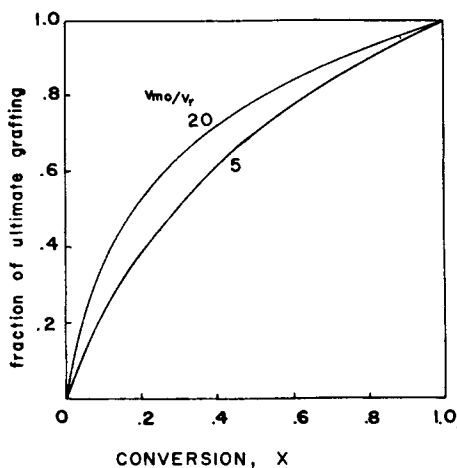


Fig. 4. Fraction of ultimate grafting vs. conversion.

be great, however, because the curve tends to level off at high glass/rubber ratios. The success of this blending procedure also indicates that grafting, beyond a certain low level, has much less of an influence on properties than does rubber level. This is reasonable, because from the standpoint of maximum compatibility, the rubber particle need only be "coated" with grafted polymer.

Figure 4 illustrates the fraction of ultimate grafting, $f(v_{m0}/v_r)/f(v_{m0}/v_r)_{x=1}$ as a function of conversion. The important point here is that most of the grafting which can ultimately be obtained is obtained in the early stages of the reaction. This effect becomes more pronounced as the rubber content of the composite is reduced. This allows the producer to concentrate on grafting in the early stages of the reaction, while worrying about other

properties later on. For example, in a bulk reaction, a peroxide initiator might be used in early stages of the reaction to promote grafting, while azobisisobutyronitrile could be added at higher conversions to minimize the problem of color formation often associated with peroxides.

CORE-SHELL MORPHOLOGY

In the preceding analysis, it was assumed that polymerization in emulsion took place according to classical theory, i.e., that the growing particle was uniformly swollen with monomer. Williams and co-workers^{6,7} have recently presented evidence for a core-shell emulsion polymerization process, in which most of the polymerization takes place in a monomer-rich outer shell of the growing particle, while very little, if any, polymer is produced in the monomer-starved core. If this is the case, much less grafting than is predicted above will be possible. According to the core-shell model, the rubber particle will be coated with glassy polymer at low conversions. Subsequent polymerization will take place entirely within the glassy shell and can never result in any grafting. An analytic solution for the maximum extent of grafting can be obtained subject to the approximation that Δr , the thickness of the monomer-rich shell, is small compared to the particle radius r . These results will not be presented here because the actual magnitude of Δr is uncertain at this point. Suffice it to say that if $\Delta r \ll r$, the predicted maximum extent of grafting is negligible, as would be deduced by qualitative reasoning alone.

CONCLUSIONS

Regardless of the chemical nature of the grafting process, the physical nature of two-phase polymerizations limits the maximum amount of glassy polymer which could possibly be grafted to the rubber. The maximum *efficiency* of grafting (fraction of glassy polymer grafted) decreases with glassy monomer/rubber ratio and conversion, but the ratio of grafted polymer to rubber increases with glass/rubber ratio and conversion. Most of the grafting which can occur in such reactions is accomplished during the early stages of the reaction.

Nomenclature

- v_g volume of glassy polymer
- v_m volume of monomer
- v_{m0} volume of glassy monomer charged, i.e., v_m at $x = 0$
- v_r volume of rubber
- x fractional conversion of monomer to polymer
- f fraction of monomer charged which has been converted to polymer in the rubber phase
- ϕ maximum grafting efficiency, the fraction of glassy polymer formed which has been formed in the rubber phase

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Received October 2, 1972