Properties of composite materials based on high-impact polystyrene

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SUMMARY

In order to improve the physical and mechanical properties of specimens of high-impact polystyrene, a graft copolymer of atactic polypropylene with styrene was introduced into its composition. The graft copolymer is distinguished by the fact that there is no homopolymer of the monomer being grafted, i.e. polystyrene, in its composition. It was found that, depending on the length and distribution frequency of the grafted chains, the introduction of the graft copolymer helps to improve the breaking stress, bending strength and impact strength of the composite material.

High-impact polystyrene (HIP) is one of the commonest of plastics, and is quite widely used in a number of areas of technology. The main reason why it is put to such effective use is its satisfactory physical/mechanical and functional qualities, along with its capacity to be processed using virtually any type of equipment for the processing of plastics. Meanwhile, however, attempts at further improvements to the properties of polymers, including HIP, remain permanently on the agenda for many researchers. The reason why this is so is that nowadays increasingly severe functional demands are being advanced for polymers, and these demands are driving research into how to achieve yet more improvements to their quality characteristics. Such properties as mechanical and impact strength and elongation are fundamental criteria for assessing the quality and structural properties of styrene plastics, which, when taken together, govern the range of grade ratings for them.

The objective of the present work was to apply the most effective modifiers to provide a substantial improvement in the main physical and mechanical indicators for commercial specimens of HIP.

A solution to this problem that involves the creation of composite materials has always been the simplest and most effective way of modifying the structure and properties of polymer materials. There appeared to be two main ways of ensuring an improvement to the qualities of polymer composites: through selection of alloying additives or by using various types of modifier [1-12]. One of these ways consisted in the use of various types of alloying additive, which was intended to provide a certain positive benefit in improving the properties. Its effect was manifested through the interphase zone, and consisted in their incompatibility with components of the polymer composite. The second way consisted in the use of modifiers, or compatibilisers, which provide a quite substantial benefit in improving properties through increasing the compatibility of the reacting components in the interphase zone. In both cases the same goal was being pursued, namely to improve the quality characteristics of polymer composite materials.

Based on the assumption that like dissolves in like, in the present work modification of a commercial HIP specimen was carried out using a compatibiliser which was a true graft copolymer (without styrene homopolymer): a graft copolymer of atactic polypropylene (a-PP) with polystyrene – poly-(a-PP-pr-styrene), hereinafter referred to as the graft copolymer (GC). This enabled us not only to study the qualitative impact of the GC, but also to evaluate the role of the microstructural factor – the length and statistical mean frequency of distribution of grafted polystyrene chains on the mechanism of shaping of the structure and properties of HIP composites. This approach to study of the mechanism of modification
of the structure and properties of multiphase polymer composite materials (PCMs) enables answers to be provided to a number of questions which have been under discussion for a long time and have constrained the potential to carry out a systematisation of studies in this field into one overarching theory.

EXPERIMENTAL

Synthesis of graft copolymers was carried out using the method given in work [13]. The synthesised specimens differed not only in the degree of grafting of styrene to a-PP (24, 52 and 76% by wt), but also in the length and frequency of distribution of grafted polystyrene chains along the macro-chain of the rubber matrix.

a-PP is a by-product of polypropylene from the OOO Tomskneftekhim works and has a viscosity-average molecular weight of 38000, polydispersion of 5.3, and a number of double bonds per 1 mol polymer of 0.4. The viscosity-average molecular weight was determined by measuring the characteristic viscosity in benzene at 23°C using the formula:

\[ [\eta] = 2.7 \times 10^{-4} M_0^{0.71} \quad (1) \]

As the results of selective washing of GC with dimethylformamide showed, there was no homopolymer of the grafted monomer, i.e. polystyrene, in the latter. The graft copolymer concentration was determined from the difference in the weights of the graft copolymer (after synthesis) and the initial a-PP.

The grafted chain length was evaluated from the results of analysis of the kinetic patterns for the process of graft copolymerisation of styrene with atactic polypropylene, i.e. it was determined from the number-average degree of polymerisation \( P^* \) from the ratio of the rate of growth of the grafted chain to the initiation rate. The number of grafted chains in a section of 1000 C atoms of a-PP macro-chain or the grafted chain distribution frequency was determined using the formula [14,15]:

\[ n_0 = \frac{[M]_0}{\alpha/P^*} C_{1000C} \quad (2) \]

where \([M]_0\) is the initial monomer concentration (styrene) in the reaction medium, mol/l;

\(\alpha\) is the degree of conversion of the styrene;

\(P^*\) is the number-average degree of polymerisation;

\(C_{1000C}\) is the concentration of sections of a-PP macro-chain (per 1000 C) in the reaction medium, mol/l.

\[ C_{1000C} = \frac{m}{M_{1000C}} \quad (3) \]

where \(m\) is the weight of the initial a-PP, g/l;

\(M_{1000C}\) is the molecular weight of a 1000 C section of a-PP macro-chain, which is 21000.

Evaluation of the grafted chain distribution frequency in a 1000 C section will enable a standardised approach to be implemented for calculation of the size of this indicator for different polymer systems. The need to find such an approach is entirely justified, and the reason for that is that if the calculation of \( n_0 \) is performed for the whole macromolecule of the polymer base, it will be dependent on its molecular weight. Thus, for example, for the same weight of a-PP in the reaction medium, degree of styrene grafting and length of grafted polystyrene chains in the copolymer, as the molecular weight of the initial matrix rises, the macro-chain concentration in the solution will fall, and correspondingly more grafted chains will be attributable to each a-PP macro-chain.

The main object used in the study, for modification and the production of composite materials based on it, was a commercial specimen of high-impact polystyrene of moulded grade UPM-0503L (HIP).

Mixing of GC composites with HIP was carried out using hot rolls at a temperature of 190-200°C for a period of 7-8 minutes. The GC concentration in the HIP varied from 0 to 20% by wt. To produce specimens for testing, the polymer composites were subjected to pressing at 190-200°C. Tests for tensile breaking strength, bending strength, impact strength and elongation of specimens were carried out in line with the standards GOST-11262-80 and GOST-19109-84.

RESULTS AND DISCUSSION

In works [14, 15] we showed that synthesis of graft copolymers with comparatively long grafted chains takes place at a relatively low temperature (343-348 K) in the initial reaction medium with an increase in monomer concentration and a decrease in initiating system concentration. The decrease in monomer concentration and increase in initiating system concentration when synthesis is performed at a higher reaction medium temperature (373-403 K) helps to produce styrene graft copolymers with relatively short grafted chains. To establish the selective impact of the size of the grafted styrene chains on the main physical and mechanical properties of HIP, we used 6 GC specimens with relatively short \( M_p = 4500-6000 \) and long \( M_p = 25000-35000 \) grafted chains as modifier. The results of evaluation of the length and distribution frequency of chains of these specimens are shown in Table 1.

The GC synthesised by us is an a-PP macro-chain with side branches of grafted polystyrene chains. As may be seen from Table 1, the graft copolymer specimens differ in the length and distribution frequency of the grafted chains. With an identical degree of grafting, graft copolymer specimens have short, but more frequently arranged grafted polystyrene chains or long but less arranged chains. We were consequently interested in
looking at the impact not only of the composition, but also of the structural features of the GC on the mechanism of modification of the structure and properties of a commercial HIP specimen.

It was also demonstrated in works [14-24] that the length of the grafted chains of graft copolymers based on polyolefins and acrylic monomers has a selective impact on their structure and properties. Similar studies were also performed by us based on styrene plastics, where clear proof was obtained of the substantial role played by the size and sequential order of the grafted chains in shaping the structure and properties of graft copolymers [25-28]. From numerous studies that have been performed with a view to establishing the selective impact of the side branch length (grafted chains) on the structure and properties of graft copolymers it has become clear that the process of analysis of the “structure – property” relationship itself requires a fairly detailed and integral treatment of the patterns that are identifiable in polymer systems. The usual and established concepts on evaluation of the structure and properties of polymer systems are not always adequate or acceptable for an exhaustive interpretation of the study objects under consideration.

Figure 1, for example, shows a graph of breaking stress for a polymer mixture based on a commercial HIP sample as a function of the composition, structural features and concentration of the modifier GC. Analysing the curves in this figure, we may see that depending on concentration and composition (with grafted chain length \( M_p \) of 25000) there is an ambiguous tendency in their patterns. Thus for example at a degree of grafting of styrene in GC of between 52 and 76% by wt, an increase in their composition in the HIP composite from 0 to 20% by wt leads to a substantial rise in the composite's tensile strength (curves 1 and 2). But at a degree of grafting of 24% by wt, an increase in the GC concentration leads to the creation of a peak at a 10-12% content of it in the HIP composite (curve 3). This difference in the pattern of variation in properties may apparently be interpreted by saying that at a low degree of styrene grafting (24% by wt) in GC, the proportion of the rubber component is relatively high. By mixing HIP with a GC specimen featuring a relatively low grafted component content, therefore, we are actually helping to increase the proportion of the rubber component (α-PP) in the composite, which has an effect in reducing the breaking stress.

According to the data in Table 1, at a relatively high degree of styrene grafting in GC there is a significant rise in the distribution frequency of short grafted chains, from 2.25 to 8.18, and of long chains from 0.42 to 1.52 per 1000 \( C \). It is quite evident that if the sizes of the grafted chains become commensurate with the length of the macro-chain of the polymer matrix, then we should expect a more effective impact of long grafted blocks on the actual process of shaping of the two-phase structure of the composite. Bearing in mind that for α-PP, \( M_p \) is 38000, the latter confirms our conclusions concerning the commensurateness of the main and side chains in evaluation of the strength characteristics of graft copolymers.

The commercial specimen of high-impact polystyrene is a two-phase system, the ratio of the volume of each of which has a crucial impact on the whole set of properties of the specimen and the way in which it is technically processed [28-31]. What we are essentially looking at is a polymer mixture shaped at the stage of

<table>
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<tr>
<th>No.</th>
<th>Degree of grafting of styrene to α-PP, %</th>
<th>Length of grafted chains (molecular weight) ( M_n )</th>
<th>Grafted chain distribution frequency per 1000 ( C ) ( n^o )</th>
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<td>2.</td>
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<td>6.</td>
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Figure 1. Impact of GC concentration on breaking stress of HIP composites: GC with long grafted chains \( M_p = 25000 \)\(-35000 \) (1, 2, 3) and with short grafted chains \( M_p = 4500\)\(-6000 \) (1', 2', 3'), and with a degree of grafting – 1, 1' - of 76% by wt, 2, 2' - 52% by wt, and 3, 3' - 24% by wt
HIP synthesis. This mixture is free polystyrene shaped after phase inversion in the form of a disperse medium, polystyrene “occluded” inside the rubber, butadiene-styrene rubber that is free of grafted component and grafted polystyrene-rubber copolymer. In the case in point the grafted copolymer plays a particular role as a “buffer” zone created at the phase/disperse medium interface, where the “occluded” and free polystyrene of the disperse medium remain isolated from one another.

The unique effect of the GC is governed by its partial compatibility with polystyrene and butadiene-styrene rubber at the inter-phase boundary, as a result of which the “buffer zone”, like a “staged module”, becomes responsible for improving the strength characteristics of HIP composites. There is reason to suppose that as the GC proportion in the HIP rises, there is an increase in the number of phases with “occluded” polystyrene, as a result of which the proportion of free polystyrene in the disperse medium diminishes, and this makes for an improvement in the homogeneity and uniformity of phase distribution [28-32]. It is this circumstance which actually helps to improve the main physical and mechanical indicators of polymer composites. In the first two GC specimens the grafted styrene concentration was comparatively high, which turned out to be quite an effective way of improving compatibility of the components of a polymer mixture and their quality characteristics. Increasing the compatibility of two-phase polymer systems typically increases the likelihood of synergy in terms of a number of their important physical and mechanical characteristics. In the polymer mixtures of high-impact plastics, compatibility may typically only be ensured on condition that dispersions are stabilised and adhesion between phases is improved [33-36]. Weak adhesion between phases is one of the main causes of deterioration of the strength characteristics in multi-phase polymer systems. It is this that explains why, the higher the degree of grafting of styrene in GC (from 24 to 76%), the greater the likelihood of an improvement in the homogeneity and uniformity of phase distribution and compatibility with polystyrene and butadiene-styrene rubber which help to improve strength characteristics.

In the case of GC with short grafted chains (with $M_p$ 6000), presented in Figure 1 as a broken line (1’-3’), the curves quite clearly show the substantial impact of the structural factor of the modifier macro-chain in altering the strength characteristics of the HIP. In the event that a GC with short grafted chains is used, strength indicators were comparatively low. The impact of the size of the grafted chains is most clearly seen when GC specimens with a relatively high grafted component content (52 and 76% by wt) are used as modifier. When a GC with a grafted polystyrene content of 24% is used, the impact of the size of the grafted chains is virtually imperceptible. This is clearly because at a high degree of grafting of styrene in GC a polystyrene disperse medium is formed, while at low grafted component concentrations (24% by wt), rubber serves as the disperse medium [25-29, 31].

There are grounds for thinking that in the process of mixing of polymers, the long grafted polystyrene GC chains interact not just among themselves, but also with the grafted links of the baseline HIP, with the disperse medium polystyrene and with the “occluded” polystyrene in the rubber matrix. This mutual penetration of long polystyrene chains goes a long way to assist even GC dispersion in the polymer matrix and, as a consequence, to improve compatibility of the components of the HIP mixture, reinforce the structure and enhance the tensile strength of the modified polymer composite.

With an identical degree of grafting, short grafted polystyrene chains are comparatively more frequently arranged along the a-PP macro-chain. This latter circumstance to some extent helps to reduce the mobility of the grafted copolymer macro-chain in GC, thus not allowing their effective mutual dispersion in the HIP polymer mass. As a result, the tensile strength becomes somewhat lower than for GC composites with long grafted chains.

To provide an explanation for the fact described above, we shall look at the HIP morphology, which, as is known, features spherical domains of free polystyrene arranged in a continuous butadiene matrix [29-31, 34, 35]. We may say that because of the relatively lower molecular weight of the grafted polystyrene chains, the size of the domains in the GC will be slightly smaller. Aggregation of grafted chain segments of a single type may take place in a variety of directions: through the interaction of grafted chains of one rubber macromolecule or grafted chains of different macromolecules. In turn, the sections of the rubber macro-chain that are free of grafted chains may themselves interact with one another to form a rubber disperse phase [25, 28]. With this spread of GC structure in styrene plastics, we may say that the shaping of a disperse medium takes place more fully in the event that the sizes of the grafted chains are commensurate with the sizes of the macromolecules of the rubber base or the free polystyrene in the HIP.

In other words, under the influence of van der Waals forces, intramolecular cooperative interaction between grafted chains and rubber macro-segments in the GC enables a particular class of high-molecular compounds to be synthesised, which provide a basis for them to be considered as branched macromolecules with complementary polymer components of the base-base and graft-graft type [31, 36].

We found equivalent patterns when evaluating the bending strength ($\sigma$) of the above specimens. As may be seen from Figure 2, in the case in point, as the GC concentration rises, a rise in $\sigma$ is seen in the first two specimens (curves 1 and 2), which, as we know, have a high degree of styrene grafting. Introduction of 10-
12% GC (with a degree of styrene grafting of 24% by wt) into the HIP composition leads to the production of specimens with a δp value peak in this area. The grafted chain length of a given GC specimen has virtually no major impact on the specimen’s bending strength (curve 3). When a GC with a comparatively high grafted component content is introduced into the HIP (curves 1, 1' and 2, 2'), the impact of the grafted chain length becomes quite substantial.

One of the main indicators for high-impact plastics is impact strength, which, taken overall, characterises whether they belong to this class of polymers. Figure 3 presents a graph of composite impact strength against GC concentration in the HIP composition. From analysis of the data we may ascertain that in all cases, pretty much regardless of the grafted component concentration, the impact strength of composites rises as the GC concentration increases. In contrast to the two preceding figures, regardless of the degree of styrene grafting in the GC, an increase in its concentration in the HIP composite is accompanied by a steady rise in impact strength. So the essential factor in increasing the impact strength of polymer composites is an increase in the grafted copolymer content in its composition. The best results are attained for specimens in which copolymers with 52% by wt grafted styrene content are used as GC. As we have noted above, the grafted copolymer helps to improve the compatibility of the vitreous and rubber components in the HIP composition, as a result of which the process of transfer of stress between these phases is itself facilitated. It seems that in order to provide an explanation for the patterns identified, it would be appropriate to interpret the data obtained in line with the crazing theory [29]. According to this theory, an increase in graft copolymer [poly(a-PP-pr-styrene)] content will help to provide an increase in the number of “occluded” polystyrene, micro-heterogeneity of phase distribution, an enhancement of the HIP rubber component, and thus a significant blocking of the likelihood of crack formation and deep crack propagation [11].

Figure 4 presents the results of a study of specimen elongation in relation to the degree of grafting, the GC concentration in the HIP composite and the grafted chain length. A comparative analysis of the curves in this figure indicates that, regardless of the grafted chain length, an increase in GC concentration leads to an insignificant rise in elongation. GC specimens containing 24% by wt grafted styrene have somewhat higher composite elongation values.

CONCLUSIONS

So if we summarise the data obtained, we may conclude that, when assessing the main physical and mechanical characteristics of high-impact plastics, we should take into account not only the quantitative content of modifier, but also the structural features of the GC (length and distribution frequency of grafted chains), which play an important role in the overall shaping of the micro- and...
macro-structure, and also of the resultant properties of the HIP composite, which govern its areas of application in industry.

REFERENCES