

# **TOUGHNESS ENHANCEMENT OF POLYMERS**

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## ABSTRACT

Toughness is an important mechanical property and often the deciding factor in materials selection. The continuing growth in the use of plastics for engineering and other applications is due in no small measure to the development, during the past five decades, of new and tougher plastics materials.

The problem facing the raw materials manufacturer is not simply to increase toughness. For many applications, the requirement is for a moderately priced polymer which can be moulded easily, and which exhibits adequate stiffness and toughness over a wide range of temperatures. Most of the major plastics manufacturers have devoted a significant part of their research and development effort to the search for materials with these characteristics.

There are two basic solutions to this problem. One is to produce completely new polymers, based upon novel monomers, as in the case of polycarbonates and polysulphones. The second approach consists in modifying existing polymers through the addition of a second rubbery component. Rubber-toughened plastics constitute a commercially important class of polymers, which are characterised by a combination of fracture resistance and stiffness. The best known members of the class are toughened polystyrene, or HIPS, and ABS, but there are also toughened grades of polypropylene, PVC, epoxy resin, and a number of other polymers.

The paper reports on the work carried out by the Department of Polymer Engineering, UTM, in these areas. It will discuss the results of the recent investigations which have been conducted to enhance the toughness of three commercial polymers that is PP, PVC and PS.

## INTRODUCTION

Toughness is the ability of materials to absorb strain energy under any applied force, without fracture. Plastics materials are viscoelastic and are therefore strain rate dependent. Under impact (high velocity) loading conditions, embrittlement is a problem often encountered and therefore impact resistance is an important attribute required in a plastics materials for their successful use in many load-bearing applications. Impact resistance is defined as 'the ability of a material or a structure to withstand the application of a sudden load without failure'.

One of the most important aspects in the materials development of engineering thermoplastics is to achieve a good combination of properties and processability at a moderate cost. As far as mechanical properties is concerned, the main target is to strike a balance of stiffness, strength and toughness. Therefore, toughness is an important mechanical property and often the deciding factor in materials selection. The continuing growth in the use of plastics for engineering and other applications is due in no small measure to the development, during the past five decades, of new and tougher plastics materials.

The problem facing the raw materials manufacturer is not simply to increase toughness. Improvements in fracture resistance must be achieved without undue impairment of other properties; nor must costs be neglected. For many applications, the requirement is for a moderately priced polymer which can be moulded easily, and which exhibits adequate stiffness and toughness over a wide range of temperatures. Most of the major plastics manufacturers have devoted a significant part of their research and development effort to the search for materials with these characteristics.

There are two basic solutions to this problem. One is to produce completely new polymers, based upon novel monomers, as in the case of polycarbonates and polysulphones. The second approach consists in modifying existing polymers through the incorporation of a rubbery component into a rigid plastic matrix. Such a method presents the distinctive advantage of being, in general, more economically attractive, since the development of new synthetic methods is a long and costly process. The resulting blend is characterized by a considerably higher fracture toughness than the parent polymer. However, there is an inevitable reduction in the modulus and tensile

strength but these losses are far outweighed by the improvement in fracture toughness

## OVERVIEW OF RUBBER TOUGHENED POLYMERS

Extensive research and development work has therefore been carried out to formulate polymers with high impact resistance. The history of rubber-toughened plastics can be traced back as far as 1927. In that year, Ostromislensky patented a process for making toughened polystyrene by polymerising a solution of rubber in styrene monomer. The process was not developed, because the product was found to be crosslinked, and therefore could not be moulded. The availability of cheap styrene monomer led to an expansion of polystyrene production during the 1940s, and revived interest in the rubber-toughening process. With this stimulus, the Dow Chemical Company mounted a research programme which led to the announcement in September 1948 that it was marketing a new, impact-resistant grade of polystyrene.

This series of inventions laid the foundations for a substantial new sector of the plastics industry. Rubber-toughened plastics constitute a commercially important class of polymers, which are characterised by a combination of fracture resistance and stiffness. Besides toughened polystyrene (high impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS)), there are also toughened grades of polypropylene, PVC, epoxy resin, and a number of other polymers.

The understanding of the toughening mechanism in rubber toughened polymers is important to account for the factors affecting property optimisation. This subject of toughening mechanism in the area of rubber-toughened polymers has attracted substantial interest. Much of the early work on toughening mechanisms centered on HIPS since it was the first rubber modified plastic of commercial importance. The first explanation for the toughening mechanism was proposed by Mertz *et al.* who suggested that the increased energy absorption in a heterogenous blend represented the energy required to fracture the glassy matrix added to the work to break the rubber particles as the crack passed through them. However, the main disadvantage of this theory is that it is concerned primarily with the rubber rather than the matrix. Later, Newman and Stella showed that this model was incorrect. They demonstrated that the excess energy absorption gained by addition of rubber far exceeds that required to break the rubber, even in the

unlikely event that the rubber particles were stretched to a very high breaking strain. Consequently, this mechanism plays only a minor role in the toughening of rubber-toughened polymers.

Further toughening theories concentrated on the deformation mechanisms associated with the matrix, which are enhanced by the presence of the rubber phase. The whitening which accompanies the deformation or fracture of rubber-toughened polymers suggested an alternative means of energy absorption. Schmitt and Keskkula proposed that the whitening and the energy absorption arise from the formation of many microcracks around the rubber particles. However this hypothesis was rejected since it requires the expenditure of very large quantities of surface energy in microcrack formation and also provides little explanation for the increased elongation and cold drawing tendencies of rubber-toughened polymers.

Newman and Stella demonstrated that the matrix absorbed more energy than the rubber particles and proposed that the rubber particles in fact triggered yielding in the matrix. The increased energy absorption in rubber-modified plastics is caused by increased cold drawing of the glassy matrix polymer. The idea that toughening in polymers is enhanced by shear yielding (i.e. local deformation in the matrix) was thus founded. However, this proposal did not account for stress whitening, a characteristic of rubber toughening. Further studies have elucidated a better understanding of the detailed micromechanisms of systems which deform preferentially by shear yielding. The major toughening mechanisms are thought to be cavitation of rubber particles and shear yielding of the matrix. The cavitation of the rubber particles explains the observed stress whitening as light scattering occurs which is enhanced by the holes enlarging.

Based on the toughening mechanism in rubber toughened polymers, conditions for optimum impact strength are as follows (Bucknall, 1977):

- i. The elastomer particles are finely and uniformly dispersed in the plastics matrix.
- ii. The modulus of the elastomer is much less than that of the plastics.
- iii. The crystallinity of the elastomer is low.

- iv. A certain degree of interfacial adhesion is attained between the elastomer particle and the plastics matrix.
- v. The cohesive strength of the elastomer is large.
- vi. A certain degree of entanglement of high-molecular weight polymer chain is attained in the plastics matrix.

After having giving an overview and introduction on rubber toughened polymers, the recent development and research carried out by UTM researchers will now be given.

### **TOUGHENING OF POPLYPROPYLENE**

For several decades, polypropylene (PP) has been very successfully used for blown film, injection molded and extrusion applications. Although PP has a most remarkable combination of physical properties, it has poor impact strength especially at low temperature due to the inherently high glass transition temperature ( $T_g$ ) and high crystallinity. The opportunity to improve their flexibility, impact resistance and tear strength by rubber modification, has enable PP be used in more products. The ethylene-propylene copolymer (EPM) and the ethylene-propylene-diene terpolymer (EPDM) are often used as impact modifiers for PP. Typical rubber-modified PP resins contain about 15% modifier, and effective impact toughening is obtained when small rubber particles ( $<0.5 \mu\text{m}$  in diameter) are distributed homogeneously in the PP matrix.

The last twenty years have seen a spectacular growth in the use of these elastomer modified thermoplastics for automobile components. These materials which can withstand low-speed collisions without breaking are ideally suited for bumpers and spoilers radiator grills. This impact-modified thermoplastic constitutes a new range of modulus which bridge the hardness/modulus gap between conventional rubbers and thermoplastics.

Recently, the blending of various rubbers with PP to provide improvements in its properties, especially in impact resistance at low temperatures and at any given stiffness, has been widely studied. Physical blends of natural rubber (NR) and PP, which form a thermoplastic natural

rubber (TPNR), have been developed into a semi-rigid and impact-resistant plastic. These hard grades of impact modified PP has a flexural modulus in the range 300–1000 MPa. These materials are often used in automotive applications when low temperature impact strength is required, especially where the vehicles are subject to very cold climates. In this respect, NR based materials offer advantages over PP/EPDM materials on account of NR inherent low temperature performance.

Compounds produced by blending PP with NR increases the consumption of NR which benefits Malaysia as a natural rubber producing country, greatly. The use of NR in this study as a impact modifier is viable and has a commercial advantage because the cost of NR is much cheaper than EPDM

As previously mentioned, rubber toughening of thermoplastic always decreases the tensile and flexural properties. Therefore improving the mechanical properties such as modulus and tensile strength of rubber modified PP have been the subject of research for many years. The addition of a suitable third polymer is expected to improve the impact properties of the NR toughened PP without much sacrifice in rigidity. It has been reported by Elliott (1990) that the addition of small amounts of HDPE to the blend of PP and NR would improve adhesion between the disperse rubber phase and the polyolefin matrix.

To further improve the mechanical properties, compatibility of the polymers is another very important issue in polymer blending. To overcome the incompatibility and produce a compatible blend, the mixing of the two polymers during blending require an agent that can induce interactions within the phases, between phases or at the interface.

The study by Tinker demonstrated that good impact strength at low temperatures can be achieved by blending PP with NR in the presence of m-phenylenebismaleimide (HVA-2). The compatibilizer introduces a low degree of crosslinking in the NR phase and forms graft copolymers at the PP and NR interface. It is viewed as a multifunctional radical acceptor and has the potential to improve the interfacial adhesion and the cohesive strength of the rubber phase in

the PP/NR blends, thus NR can compete with ethylene propylene rubber as an impact modifier for PP.

Polyoctenamer (TOR) produced from metathesis polymerization of cyclooctene can also be used as compatibilizer with many polymers. In the study by Mohd. Ambar *et al* (1992), it is found that the incorporation of small quantity of TOR in PP/NR blend showed some effect on the distribution and particle size of NR in PP matrix.

### **Objectives of the Study**

The main objectives of the study are as follows:

- (1) To study the effect of LLDPE as the third component on the mechanical properties such as tensile, flexural and impact of PP/NR blend.
- (2) To study the effect of HVA-2 and TOR on the mechanical properties of PP/NR/LLDPE ternary blends.
- (3) To determine the optimum blend composition of impact-modified PP which possess satisfactory impact strength and rigidity.
- (4) To relate the mechanical properties of the blends with the morphology.

### **CONCLUSION**

The impact strength and elongation at break of the blend increased as the rubber concentration increased from 0 to 30% in the PP/NR binary blends. With similar increase of NR content, the tensile strength and flexural modulus reduced. Partial replacement of PP with LLDPE in the PP/NR blends improved the impact strength but with a corresponding reduction in the tensile strength and modulus. The addition of LLDPE in the PP/NR/LLDPE improves the dispersability of NR resulting in the reduction of NR particle diameter.

For uncompatibilized blend, based upon impact strength and flexural modulus, the composition which shows the optimum properties are the blends with 20 - 30% NR and the replacement of PP

with LLDPE is more than 10 %. For the compatibilized blend, the composition which shows optimum properties are blend HC3 (64/20/16 PP/NR/LLDPE + 0.75% HVA-2) and PCI (64/20/16 PP/NR/LLDPE + 2.5% TOR.).

The two type of compatibilizers used in this study, HVA-2 and TOR are effective in modifying the mechanical properties of the PP/NR/LLDPE ternary blends. The elongation at break and impact strength of the ternary blends improved with the incorporation of HVA-2 and TOR. No significant influence on the flexural modulus is observed. The mechanism whereby HVA-2 improves the impact strength is by increasing the cohesive strength of NR and interfacial adhesion between the phases. TOR improves the impact strength by lowering the viscosity of NR resulting in smaller NR particles diameter. The other mechanism is by increasing the interfacial adhesion between PP phase and the NR particles. There is also a good correlation between the results obtained from SEM and impact testing. It was found that smaller rubber particles are more effective in enhancing the impact strength.

## **TOUGHENING OF PVC**

### **INTRODUCTION**

Currently, PVC is one of the world's leading synthetic polymers with global consumption of approximately 16 million tonnes per annum. It was first recognised and characterised more than 100 years ago, but poor thermal stability makes processing difficult. However, with the development of suitable stabiliser and additive systems, this problem has been overcome and the first commercial production started in Germany in the early 1930's. Shortages of rubber during World War 2 created opportunities for plasticized PVC in applications such as sheeting and electrical insulation. Since then, PVC has been used extensively due to it being relatively cheap and versatile. The versatility of this polymer is its ability to incorporate additives to suit many different applications, and other factors responsible for rapid growth of PVC are:

- (i) good physical, chemical and weathering properties
- (ii) processability by a variety of techniques

However unmodified PVC-U (unplasticised PVC) has the disadvantage of being prone to occasional brittleness and is notch sensitive. Rubber toughened PVC-U is one such important class of rubber toughened plastics material which has been developed to overcome the problem. It consists of PVC and a rubber component known as impact modifiers. There are several types of impact modifiers available which include chlorinated polyethylene (CPE), ethylene vinyl acetate (EVA), and acrylate modifiers. One of the areas in which rubber toughened PVC-U is important is in the manufacture of window frames and associated (tough and weatherable) products. Window profile started in the early 1960s in Germany and grew relatively quickly in Central Europe. High impact resistance is important in the window frames application for:

- (i) problem-free transport, installation and assembly where the end products are subjected to occasional impact loading.
- (ii) retention of mechanical properties during long term use.

Traditionally, window profile has been made from wooden materials. Timber window profile has a major advantage of being a thermal insulator but its major drawback is its low resistance to weather which can be minimised only with regular maintenance. Window frames made from PVC-U have already achieved a proven record of performance in a demanding role. The advantages of PVC-U window profile are its durability and toughness, flame retardancy, weather resistance and chemical inertness. The ease of designing and production, coupled with ease of installation also promote the increasing used of PVC-U

PVC foam represents another area of interest in the current PVC applications. Impressive market growth rates are forecast for rigid PVC foams, particularly in timber-replacement applications in the building and construction industries, for which the weather resistance and high specific stiffness of such materials are important attributes. The other benefits that PVC foam offers are low cost per unit volume, high specific rigidity, light weight, improved thermal insulation, and most importantly, the ease and versatility of being able to be machined. The impact strength of structural foam is, however, usually lower than the solid counterpart material, due to the lower density, and stress concentrations in the cellular structure. The mechanical

properties of structural foam depend on the through-thickness density, the size and uniformity of the cells, the relative amounts of dense skin and foamed core, and surface texture.

## OBJECTIVES

The main objectives of the study are as follows:

- (1) To use an instrumented falling weight impact test method to determine ductile-brittle transitions in acrylate elastomer modified PVC-U and to study the effects of :
  - impact modifier particle size
  - strain rate
  - temperature
- (2) To develop techniques using the Scanning Electron Microscope (SEM) and the Transmission Electron Microscope (TEM) for the study of the deformation, toughening and fracture mechanisms in acrylate modified PVC, under high velocity loading.
- (3) To enhance the impact resistance of PVC-U foam through impact modification with acrylate elastomers.
- (4) To study the effect of the following parameters on impact, fracture and flexural properties on extruded PVC-U foam compounds:
  - impact modifier addition level
  - blowing agent addition level, hence profile density.
- (5) To provide an overview of impact failure in solid and foamed PVC profiles modified by acrylate elastomers
- (6) To suggest how property enhancement may best be achieved, according to end-applications

## CONCLUSIONS

The main objective of this research is to improve the impact strength of both solid and foamed PVC-U with the use of acrylate rubbers as impact modifiers

The study revealed that effectiveness in shifting the ductile brittle transition to a lower temperature and higher strain rate increases with decreasing impact modifier particles size. From the TEM studies on the hinge break impact tested samples, it was proposed that the mechanism of impact reinforcement is based on the enhancement of localised shear yielding in the vicinity of the rubber modifier particles.

The study on the free-foamed PVC-U revealed that the rubber particles are much smaller than the foam cell and therefore the foaming of the PVC matrix does not prevent the stress field of the particles from interacting with each other in enhancing the matrix yielding. From this, it can be concluded that the toughening mechanism in acrylate rubber for both toughened foamed and solid PVC-U are similar.

The advantage of foamed PVC-U compared with its solid equivalent is its low density. Due to this, foamed PVC-U has a higher flexural stiffness per unit mass compared with the solid PVC-U. The study on the free-foamed PVC-U using optical microscopy and image analysis has shown that the area occupied by the cells is not equally distributed throughout the thickness, thus resulting in irregular density distribution.

The results show that acrylate rubber impact modifier has the potential to improve the impact strength of foamed PVC-U. However the increase in impact strength due to the increase in impact modifier concentration is only marginal compared with the decrease of impact strength due to the increase in blowing agent concentration.

Due to the higher cost of impact modifiers compared with that of PVC, impact modifiers should only be used when they increase the PVC-U foam impact performance sufficiently, after taking account of possible deterioration in other properties such as flexural stiffness. However, it

should also be remembered that sometimes impact modifiers do not show improvement at room temperature but can increase ductility of the materials and provide toughness in more demanding situations such as low temperature, high strain rate and/or notching. To determine whether impact modifiers should be used for impact strength enhancement of either solid or foamed PVC-U, it is therefore very important to specify the required impact strength and the type of impact test needed to reflect the actual end-use performance requirement.

Based upon these facts and the overall findings in this study, the following are the recommendations for the use of impact modifiers to improve the impact strength in solid and foamed PVC-U

- (1) To obtain the best impact strength enhancement at a low cost, the most efficient impact modifiers should be used at the optimum levels. Since the impact reinforcement mechanism is similar for both the solid and foamed PVC-U, the impact modifier which is the most effective for impact strength enhancement of the solid PVC-U is expected to have the same effect on the foamed PVC-U.
- (2) Since the increase of impact strength due to the impact modifiers in the free-foamed profiles is relatively marginal, the use of impact modifiers in this case is not profitable. This recommendation is however valid only for profiles with densities around  $0.6 \text{ g/cm}^3$  and further study is required to examine the effect of impact modifier content on impact strength at other densities.

## **TOUGHENING OF POLYSTYRENE**

Blends of Polystyrene (PS) with Polypropylene (PP) are developed with the objective to overcome the inherent brittleness of PS and to enhance the chemical resistance of PS. However, blends of PS with PP are immiscible and incompatible. The present study also investigates the use of SEBS to improve the miscibility and compatibility of the PS/PP blends. Using a Brabender PL2000 twin-screw extruder, blends of PS/PP in various compositions ranging from 100-60 wt % PS with and without SEBS were prepared and injection molded. The impact

strength of the uncompatibilized PS/PP blends increases with PP content but the tensile strength and flexural modulus decrease. The chemical resistance to acetone and tetrahydrofuran increases with increasing PP content. Although the impact strength increases with increasing PP content, the values are lower than expected ideal additive behaviour. This is related to the poor interfacial interaction due to incompatibility between PS and PP. The problem has been overcome with the use of SEBS. The impact strength of the PS/PP blends increases with SEBS content at the expense of tensile strength and flexural modulus. Interestingly, the degree of changes in the mechanical properties due to SEBS varies with the amount of PP in the blend. SEBS is more effective at lower PP content in enhancing the impact strength. The most optimum blend based on striking a balance between stiffness and impact strength is 90/10/25 PS/PP/SEBS. The chemical resistance of PS/PP blends increases with increasing SEBS content at lower PP content. However at major PP content, the chemical resistance decreases with increasing SEBS content. The SEM also confirms that as the SEBS content increases there is greater interaction between PS, PP and SEBS, which result in greater miscibility between the three phases.

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